Transformation products in environmental risk assessment joint and secondary persistence as new indicators for the overall hazard of chemical pollutants

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Transformation Products in Environmental Risk Assessment: Joint and Secondary Persistence as New Indicators for the Overall Hazard of Chemical Pollutants

A dissertation submitted to the Swiss Federal Institute of Technology Zürich for the degree of Doctor of Natural Sciences

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Kathrin Fenner
Abstract

For the assessment of the environmental hazard of new and existing chemicals, exposure-based hazard indicators are frequently used as screening tools. One of them is persistence, which indicates the time during which the environment is exposed to a chemical. In this work, a methodology is developed that assesses the overall environmental hazard of a pollutant and its transformation products formed in the environment. This is achieved by including the transformation products in the definition and calculation of persistence. For this purpose, the framework of multimedia models, which are the standard tools used to assess the persistence of environmental chemicals, has been expanded to account for the formation of transformation products. For each transformation product, formation terms are added to the environmental fate matrix that are proportional to the degradation rate of the precursor. Media-specific fractions of formation are used as proportionality factors between 0 and 1, indicating how much of a given transformation product is being formed. As a result, time-dependent or steady-state exposure patterns for the parent compound and each individual transformation product are obtained. To condense this exposure information, three persistence definitions were introduced. These are the Primary Persistence (PP), i.e. the persistence of the parent compound or any other single chemical, the Secondary Persistence (SP), i.e. the persistence of each transformation product as it is formed out of the parent compound, and the Joint Persistence (JP), i.e. the persistence of the entire substance family of parent compound and transformation products. Nonylphenol ethoxylates (NPnEO), perchloroethylene (PCE) and atrazine were chosen as three case studies to illustrate the definitions of PP, SP and JP. SP values might be useful tools for priority setting among transformation products of a parent compound and to trigger research into possible effects of those with high SP values. The JP was found to be a good indicator of the overall exposure of the environment due to the release of the parent compound and subsequent formation of transformation products. Therefore, the JP is suggested as a more comprehensive exposure indicator that should be used instead of the PP wherever possible.

The transformation products of NPnEO were shown to have a large impact on the persistence (JP/PP=10.2), while the transformation products of PCE (JP/PP=2.72) and atrazine (JP/PP=1.31) increase the persistence to lesser extents. Risk management decisions based on JP instead of PP can be more stringent. In the examples here, it was shown that rankings based on JP can be different from rankings based on PP, and that JP values can surpass persistence criteria, while the PP values do not.

To test the reliability of the persistence values for screening or ranking, probabilistic uncertainty analyses were conducted. They showed that the persistence values are subject to considerable uncertainty (90% confidence intervals of up to 2 orders of magnitude),
which stems mainly from uncertainty in the degradation rates (>70% contribution to variance).

To reduce calculation and data collection efforts, those transformation products need to be identified that contribute most to the JP. This was achieved by successive removal of generations of transformation products and calculation of the JP values of the remaining set of compounds. Thus, the first generation of transformation products was identified as the most important contributor to the JP in all three case studies. An important reason for this observation is the fact that the amount of chemical mass lost from the system boundaries through direct mineralization, reaction to minor transformation products or formation of bound residues increases towards higher generations. Based on these findings, a procedure was developed that allows for the identification of the most influential transformation products that account for 80–90% of the JP, while using only a reduced set of substance data and without running the multimedia model.

Instead of calculating persistence values, the exposure calculations can also be conducted such that predicted environmental concentrations (PEC) are obtained. If they are combined with effect data for each compound, i.e. predicted no-effect concentrations (PNEC), a mixture risk quotient can be calculated for the parent compound and the transformation products formed. This was done for the example of NPnEO usage in Switzerland. While the PEC values of the individual components in water were found not to exceed the corresponding PNEC values, the risk quotient of the mixture was greater than 1. Thus, within all limitations of the model used, a risk to Swiss waters stemming from the mixture of NPnEO and its transformation products was identified.

In conclusion, it was shown that, for some chemicals, the inclusion of transformation products can enhance the persistence by factors of up to 10 and more. In these cases, the hazard posed by a chemical needs to be reevaluated. It is therefore argued that transformation products should increasingly be taken into account in the assessment of chemicals. To this end, two methodologies are proposed in this work for including them in the calculation of persistence and risk quotients. Further research should go towards applying the methods to other, characteristically different case studies and towards enhancing the capability to predict transformation schemes.
Zusammenfassung


Zu diesem Zweck werden Mehrkompartimentmodelle – mathematische Modelle, die standardmäßig zur Berechnung der Persistenz eingesetzt werden – so erweitert, dass sie die Bildung von Umwandlungsprodukten miterfassen können. Dazu werden der Koeffizientenmatrix, die Abbau und Verteilung der Stoffe beschreibt, Bildungsterme für jedes Umwandlungsprodukt hinzugefügt. Diese sind proportional zur Abbaurate der Vorläufersubstanz, wobei die Proportionalitätsfaktoren angeben, wie gross der prozentual gebildete Anteil eines bestimmten Umwandlungsproduktes ist. Als Modellresultate können zeitabhängige Konzentrationsfunktionen oder stationäre Konzentrationen berechnet werden. Diese können mit Hilfe dreier Persistenzdefinitionen charakterisiert werden. Dies sind die Primärpersistenz (PP), die die Persistenz der Ausgangsverbindung oder eines anderen einzelnen Stoffes wiedergibt; die Sekundärpersistenz (SP), die eine Beschreibung des zeitlichen Verlaufs der Bildung jedes einzelnen Umwandlungsproduktes beinhaltet; und die Gesamtpersistenz (Joint Persistence, JP), die die Persistenz der gesamten Substanzfamilie, d.h. der Ausgangsverbindung und der daraus gebildeten Umwandlungsprodukte, wiedergibt.


Zur Beurteilung der Zuverlässigkeit der Persistenzwerte für die Bewertung von Stoffen wurde eine probabilistische Unsicherheitsanalyse durchgeführt. Anhand dieser konnte gezeigt werden, dass die Unsicherheit in den berechneten Persistenzwerten erheblich ist (bis zu zwei Größenordnungen für das 90% Vertrauensintervall) und dass diese Varianz zu mehr als 70% von Unsicherheiten in den Abbauraten der Stoffe herrührt.


Insgesamt wurde gezeigt, dass der Miteinbezug von Umwandlungsprodukten für bestimmte Stoffe zu einer Persistenz führen kann, die um einen Faktor 10 oder mehr höher liegt als die PP. In solchen Fällen sollte die Gefahr, die von einer Chemikalie ausgeht, neu bewertet werden. Künftige Arbeiten auf diesem Gebiet sollten sich damit beschäftigen, die zwei vorgestellten Methoden zum Miteinbezug von Umwandlungsprodukten in die Berechnung von Persistenz und Risikoquotienten zu überprüfen und weiterzuentwickeln, indem sie auf andere Fallstudien angewandt werden. Desweiteren sollten die Möglichkeiten verbessert werden, um die Umwandlungsprodukte und -schemata vorauszusagen.
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Chapter 1

Introduction

1.1 Risks from chemical products

Today, humans and the environment are exposed to an ever increasing number of man-made chemicals. These substances are used in industry, agriculture, trade and households, and reach the environment through different pathways such as outdoor applications in the case of agrochemicals, water emissions from sewage treatment plants, through air emissions from energy production and traffic, or as fugitive emissions from materials used in consumer products. Some of these chemicals can threaten human and ecosystem health, including the health of specific animals and plants living therein. During the last decades, the recognition has grown that these chemicals act through a myriad of harmful mechanisms that are difficult to understand and even harder to predict. These effects range from specific toxicity towards selected organisms, to reproductive and mutagenic effects that can affect entire food chains, on to global scale effects such as the ozone depleting potential of chlorofluorocarbons (CFC) (Ballschmiter, 1979; Ballschmiter, 1992).

As the awareness of these unwanted side-effects of chemicals grows, the producers of chemicals and the competent authorities responsible for the market admission of chemicals are increasingly challenged by their stakeholders (customers, public, NGOs, governments, international organizations) to assess the risk of chemicals, both those that are already in use and those that are being newly developed. As the number of chemicals currently in use exceeds 100'000 (EEA, 1998), this is a very demanding task to meet. There exists a serious lack of information on and monitoring of these chemicals. Even regarding the 2'000–3'000 large volume chemicals used in the EU, there are only for 25% of them enough toxicity and eco-toxicity
data publicly available to conduct a minimal risk assessment according to OECD guidelines (EEA, 1998). The reasons for this unsatisfactory situation are, first, that current risk assessment procedures are very costly and time-consuming and, second, that the process of priority setting, i.e. choosing those chemicals that should be given high priority for risk assessment, is not given enough weight, partly due to the lack of suitable indicators for prioritization (Ahlers, 1999).

Recently, the EU commission under the guidance of environment minister Margot Wallström therefore adopted a White Paper on the strategy for a future chemicals policy (COM, 2001). Its aim is to improve the information on chemicals marketed today by harmonizing the risk assessment procedure for new and existing substances and by choosing tailor-made assessment strategies for each substance according to its damaging properties, its use patterns and its exposure (Ahlers et al., 2001). In order to make this venture a success, improved assessment tools which help prioritize chemicals by providing relevant and concise information on the chemicals' fate and behavior at a screening level stage are urgently needed.

Currently, two subgroups of chemicals are given primary attention in worldwide initiatives because of their high potential for causing environmental and health damage. One of these two initiatives focuses on persistent organic pollutants (POPs): a group of man-made chemicals that are known to persist in the environment for a long time, to bioaccumulate in animals, including humans, and that are often also classified as endocrine disrupting chemicals. The POP initiative is headed by the United Nations Environment Program (UNEP) and aims to pass an international agreement on the handling of POPs, the POP convention. So far, 12 substances, including DDT, have been identified as POPs, but the exact form of the substance indicators that should be used to identify further candidate POPs is still under discussion (Klöpffer and Scheringer, 2000). The other subgroup of chemicals that is given special attention are persistent, bioaccumulative and toxic chemicals (PBT). For PBT chemicals, different identification procedures have been suggested by various international organizations and from within the scientific community (EPCRA, 1999; Ranke and Jastorff, 2000; Renner, 2001; Snyder et al., 2000). In the POP as well as in the PBT initiative, persistence is one of the central selection criteria to identify chemicals with a high potential to cause harm.
1.2 The relevance of transformation products

Several instances are known where serious environmental toxicology or chemistry problems were shown to be directly related not (or not only) to the parent compound, but to one or several of its transformation products. This is due to the often overlooked fact that degradation of chemicals does not necessarily mean that a chemical is directly mineralized, but that it might be transformed to structurally related transformation products, occasionally causing their own share of deleterious effects (Ballschmiter, 1991; Stephenson, 1977).

Historically, this phenomenon first caught the attention of the scientific community around 1970 when it became clear that the metabolites of some widely used chlorinated hydrocarbon insecticides such as DDT (2,2-bis(chlorophenyl)-1,1,1-trichloroethane) or aldrin were present in the environment in large amounts and that they were responsible for most of the concerns formerly attributed to the parent compounds (Coats, 1993). During that period, Korte et al. (1970) were among the first to extensively research the metabolism of chlorinated hydrocarbon insecticides in living organisms and their transformation through irradiation with UV-light. Among the five factors necessary for assessing the environmental importance of synthetic chemicals, they mention the metabolism under environmental conditions as one central criterion, the other four being amounts produced, persistence, tendency for global distribution and biological effects.

One of the most prominent examples of a recalcitrant transformation product is DDE (2,2-bis(chlorophenyl)-1,1-dichloroethylene), a metabolite of DDT, that is detected beside DDT in the tissues of almost every person on earth. It is found in particularly high concentrations in marine animals and indigenous people living in the Arctic. DDE is recalcitrant to degradation, easily fat soluble and therefore bioaccumulative, shows toxic effects following chronic exposure and affects the eggshell thickness of birds of prey (Ratcliff, 1967). It is therefore regulated under the POP convention together with its parent compound DDT (Hileman, 1998). In addition to DDE and some other fat-soluble metabolites of DDT (DDD (2,2-bis(chlorophenyl)-1,1-dichloroethane) and DDMU(2,2-bis(chlorophenyl)-1-chloroethylene)), more recently the polar, less toxic, but very persistent degradation product DDA (2,2-bis(chlorophenyl)acetic acid) has been found in large amounts at sites contaminated with DDT (Heberer and Dünnbier, 1999).

Another typical concern regarding transformation products besides the possibility of higher persistence (e.g., Ballschmiter, 1996; Ejlertsson et al., 1999; Lerch et al.,
higher bioaccumulation potential (e.g., Zhu et al., 1995) and higher or different toxicity than the parent compound (e.g., La Clair et al., 1998), is that transformation products can be more mobile (e.g., Key et al., 1997; Kolpin et al., 2001; Nyman et al., 1997). This is caused by the fact that primary metabolites are frequently formed by biological and chemical oxidation or through hydrolysis in order to make them more water-soluble and therefore better excretable from organisms. However, due to the enhanced water-solubility, these compounds also have a higher leaching tendency and therefore give rise to concerns about groundwater pollution as well as about effects on non-target organisms (Coats, 1993; Heberer and Dünnbier, 1999).

All these well-known, potentially negative effects of transformation products are only relevant if the transformation products are present in the environment in concentrations high enough to produce toxic effects. More recent concerns regarding transformation products, however, evolve around phenomena that manifest themselves already at concentrations that are 3–6 orders of magnitude lower than effect levels of classical acute and chronic toxic effects. Low concentrations are typical for transformation products because they are often only formed in small amounts. Also the location and time-scale of their formation is often more spread out compared to the source of the parent compound. Specific concerns in the low dose regime are endocrine disruption, a hormonal response which, for some chemical-receptor systems, might be most pronounced at low doses (Renner, 1998; vom Saal et al., 1998), chemical sensitization in general and, more specifically, sensitization for cancer (Ashford and Miller, 1998).

In line with these findings, the principles for risk assessment within the EU, as given in Directive 93/67/EEC (EEC, 1993) for new chemicals and in Regulation 1488/94/EEC (EEC, 1994) for existing chemicals, acknowledge the fact that transformation products can contribute to the overall risk of a chemical compound, but leave it open to the competent authorities to decide in which cases information on the transformation products needs to be provided by the manufacturers. The Directive 91/414/EEC (EEC, 1991) on the placing of plant protection products on the market is more stringent in that it clearly states that authorization of a new pesticide shall only be granted if the transformation products have been identified and have been shown to have no harmful effects on humans, animal health, the groundwater or the environment in general. While, for pesticides, concepts of how to identify relevant transformation products and how to test their individual risk exist, no clear instructions for the technical implementation of the inclusion of transformation products
Introduction

into risk assessment are given for other new and existing chemicals. Especially with regard to low-dose effects, the development of management and assessment procedures for them is still in its infancy.

1.3 Objectives

The aim of this work is to develop a possible methodology to include transformation products into chemical risk assessment. For this purpose, the methodology of this work was developed along the lines of current procedures for the risk assessment of chemicals, which were expanded, where necessary, with tools suited for the handling of transformation products. Special attention was given to keeping these tools as manageable as possible and to their aptness to be used to assess a large number of chemicals on a screening level. Figure 1.1 shows a simplified illustration of the process which has to be run through in order to arrive at a risk management decision regarding a specific chemical compound. The starting point for this process is a set of tests of some of the basic chemical and toxicological properties of the compound. The elliptical boxes in Figure 1.1 represent the four main steps of the process and the square boxes indicate the contribution of this work in extending those particular steps to include the assessment of transformation products.

Figure 1.1: Illustration of the process necessary to evaluate the risk of a chemical compound. The elliptical boxes represent the four main steps of the process, while the rectangles contain the specific contribution of this work in extending the scope of the process to include transformation products.

In the following description, the single steps are explained shortly and the contribution of this work for the inclusion of transformation products into each step will be outlined.
1. Tests for basic properties:

The starting point for chemical risk assessment is a number of mandatory tests such as toxicity assays and the determination of a set of basic physico-chemical properties.

In this work it is assumed that all possible transformation products of a given chemical (parent compound) have been identified and that all basic properties have been measured for them. Further, knowledge about the sequence of the transformation products, i.e. the transformation scheme, is presumed as well. Although the question of how to identify possible transformation products and which mandatory tests to assign to them is thus not within the scope of this study, it is hoped that this study will provide the necessary insight into the impact which the inclusion of transformation products within risk assessment can have and will thereby trigger research in the experimental field. To support this endeavors, a procedure is developed in this work to identify the most important transformation products.

2. Exposure and effect modelling:

The test results are used to model the fate and behavior of the chemicals in the environment.

In this work a mathematical method for the modelling of the dynamic formation and fate of transformation products is developed and integrated into an existing exposure model.

3. Quantification of hazard and risk indicators:

The resulting exposure pattern can then be assessed by either purely exposure-based hazard indicators such as persistence or by risk indicators that combine effect and exposure assessment through integrating knowledge about the toxic effects of the chemicals.

In this work, based on the exposure patterns for parent compounds and transformation products, definitions for the persistence of single transformation products as well as for the persistence of a parent compound and its transformation products in combination are introduced. Additionally, starting from the same exposure pattern, a proposal is also made on how to combine effect and exposure information to calculate the actual risk of the mixture of parent compound and transformation products.
4. Risk management decisions:

In the forth step of the chemical risk assessment procedure, risk management decisions are taken based on the actual values of the hazard and risk indicators. Possible outcomes are that the chemical is deemed harmless, that further tests are needed to decide or that the need for regulation of the chemical is evident. In this work it is discussed how the consideration of transformation products can change risk management decisions that were based on the parent compound alone.

In order to achieve the integration of transformation products into this process as proposed, the following questions need to be answered:

- How do environmental fate models need to be extended to account for the dynamic formation and fate of transformation products?
- How can new persistence measures be defined to describe the temporal course of exposure to transformation products?
- How can risk indicators be adapted to assess the additional risk introduced by transformation products?
- How big is the additional effort to determine these new substance indicators?
- How do the new indicators compare with the indicators that are conventionally determined for the parent compounds?
- Which risk management decisions are affected by the knowledge gained from considering transformation products?

1.4 Structure

After a short introduction to risk assessment and the specific problems related to transformation products in Chapter 1, Chapter 2 elaborates on the theoretical background of this work. It provides a more detailed discussion of the current risk assessment practices in the EU, which is based on risk indicators that combine effect and exposure assessment. Next, persistence and spatial range are introduced as two alternative, exposure-based hazard indicators. Further, definitions of transformation products and transformation processes as they are understood in this work
are given. An overview of legislative texts, the scientific literature and industry
guidelines that discuss approaches to include transformation products into chemical
risk assessment concludes this theoretical section.

_Chapters 3–6 focus on persistence as one exposure-based hazard indicator that can
be used for screening purposes and on the development of appropriate indicators
for the persistence of the parent compound as well as of all of its transformation
products._

Chapter 3 revisits the discussion about different possible persistence definitions and
compares those currently in use and new suggestions with regard to their ability
to best represent the time the environment is exposed to a single chemical. This
persistence of a single chemical is termed Primary Persistence (PP) in this work.
Also, the multimedia model that is used to calculate exposure and persistence is
presented.

In Chapter 4, two new persistence measures describing the additional exposure of
the environment caused by the presence of transformation products are introduced.
They are called Joint Persistence (JP), representing the persistence of the parent
compound in combination with all transformation products, and Secondary Persis-
tence (SP), representing the persistence of each transformation product alone. These
definitions are first applied to the analytically deduced exposure patterns for a parent
compound and its transformation products in a single-medium environment. Next,
it is demonstrated how the mathematical formulation of the multimedia model can
be expanded to include terms that describe the dynamic formation of transformation
products and their distribution between environmental compartments. The defini-
tions of JP and SP are then applied to the resulting multimedia exposure patterns
and this application is further illustrated with two distinctively different combina-
tions of parent compound and transformation products. Lastly, the suitability of
these definitions as measures for providing information on transformation products
for regulatory purposes is discussed.

Chapter 5 introduces three substance families, i.e. parent compounds and their
transformation products, that are used as case studies for the calculation of Pri-
mary, Secondary and Joint Persistence. They represent three different release sce-
narios and three different situations regarding the importance of the transformation
products and their overall impact on the persistence. The substance families pre-
seated are nonylphenol ethoxylates, a group of surfactants; atrazine, a formerly
widely used herbicide; and perchloroethylene, an industrial dry cleaning agent, and
their respective transformation products. To learn more about the reliability of the
Joint Persistence, Chapter 6 encompasses a probabilistic uncertainty analysis of the three case studies using Monte Carlo simulation. The results are used to identify the main contributors to uncertainty and, therefore, the most urgent research needs regarding transformation products. The importance of the different generations of transformation products is also assessed.

Chapter 7 stands apart from Chapters 3–6 as it discusses the inclusion of transformation products into current risk assessment approaches, which are based on risk indicators. For that purpose, the same modelling approach as for the persistence calculations is used, but the resulting exposure patterns are compared to toxicity thresholds. In that context, the concept of mixture toxicity is applied to the dynamically formed mixture of parent compound and transformation products, and its risk is described in terms of a mixture risk quotient. To illustrate this concept, it is applied to the usage of nonylphenol ethoxylates in Switzerland.

Chapter 8 exemplifies the possible applications of the concept of Joint Persistence and mixture risk quotient in three different risk management contexts. It illustrates how the consideration of transformation products can change decisions and thereby stresses the need to include them into risk assessment. Following that line of thought, a procedure is suggested to simplify the calculation of JP by identifying the most influential transformation products in advance.

In Chapter 9 the most important results are summarized and ideas for further research are discussed.
Chapter 2

Chemical risk assessment and transformation products

The procedure for chemical risk assessment is stated in the EU legislation. Because Swiss legislation is becoming increasingly harmonized with EU legislation and because most chemical companies operate in a multinational context, the discussion of the legal background of chemical risk assessment in this chapter will focus on EU legislation. In addition to an overview on the current risk assessment practice, the concept of exposure-based hazard assessment will be introduced as a new paradigm in the assessment of chemicals, and suggestions for its integration into the existing concept of risk assessment will be made. In the second part, the definition of transformation products as used in this work and how they are formed in the environment will be discussed in more detail. The concept of chemical risk assessment and transformation products will be brought together in the third part, where current research efforts to introduce transformation products into chemical risk assessment are presented and ensuing research needs are identified. From the preceding, the objectives of this work are deduced in more detail.

2.1 Chemical risk assessment: Current methods and new paradigms

Presently, around 100'000 industrial chemicals are marketed in the EU. In addition, 200-300 new substances are notified yearly. Possible hazards of these substances need to be assessed in time to protect the health of humans and the environment. Chemical risk assessment, comprising the elements of hazard identification, effect
assessment, exposure assessment, and risk characterization, structurally proposed for the first time by the US National Academy of Sciences in 1983, is now recognized as an essential tool to do so. However, risk assessment is a dynamic, continuously evolving process, which has changed considerably in the last two decades*. Some of the methodological aspects of chemical risk assessment that are currently under discussion will be further elaborated in this work.

In 1979, Directive 79/831/EEC (EEC, 1979) established a harmonized notification scheme for new substances as the Sixth Amendment to Directive 67/548/EEC (EEC, 1967). With the Seventh Amendment in 1992 (Directive 92/32/EEC (EEC, 1992)), risk assessment became an inherent part of the application and admission procedure of new chemicals. The seventh amendment requires the manufacturer of a new substance to notify it to the competent authority of the EU Member State in which it is manufactured or imported into before it is placed on the market for the first time. Having received the notification, the competent authority is required to carry out an assessment of the risks of the substance to man and environment.

Substances already on the market before the validity key date of EEC (1979) (18 September 1981) were defined as existing substances and systematically listed in the "European Inventory of Existing commercial Chemical Substances" (EINECS). Council regulation 793/93/EEC (EEC, 1993) established the regulatory framework for the uniform evaluation and control of the risks of existing substances. As EINECS includes more than 100,000 registered substances, priority lists nominating substances with paramount assessment needs had to be composed. In Germany, the Advisory Committee on Existing Chemicals of Environmental Relevance (BUA) of the German Chemical Society (GDCh) compiled a priority list of 300 substances, and, up to now, has accomplished extensive risk assessments for 280 of them in an exemplary effort. From 1993 on, this effort was continued by the EU, which, however, has only assessed an additional 21 substances since then.


*For an update of the US National Academy of Sciences report on risk assessment, which puts more emphasis on the need to integrate risk assessment and risk management, see NRC (1994).
Chapter 2.1.1 outlines the most important features of chemical risk assessment as described in the TGD (1996) and the key limitations of this type of risk assessment, such as low operability and some fundamental problems of effect-based risk assessment, are discussed.

In response to these shortcomings of current risk assessment practice, Chapter 2.1.2 introduces hazard-based assessment as a new paradigm in the assessment of chemicals. Specifically, the exposure-based hazard indicators persistence and spatial range are defined and their advantages and limitations for risk assessment purposes are discussed.

Exposure-based hazard indicators are based on screening information and describe the characteristic features of the environmental behavior of a substance. They might be used as exclusion or priority-setting criteria in the early stages of chemical risk assessment without referring to effects and, thereby, make the assessment more practicable and efficient (Mathes and Winter, 1993).

Finally, in Chapter 2.1.3, suggestions are made for the integration of both hazard- and risk-based concepts into a new overall framework for the assessment of chemicals. For agrochemicals, the risk assessment requirements are different because these substances are introduced into the environment in large amounts, come into direct contact with human food products and display specific modes of action. The text regulating the admission and marketing of agrochemicals is Directive 91/414/EEC (EEC, 1991), which is discussed in more detail in Chapter 2.3.

2.1.1 Risk assessment according to the TGD

Effect-based risk assessment according to the TGD (1996) distinguishes four stages:

i. Hazard identification

A base set of tests is carried out to identify the substances’ most predominant environmental effects. These include:

(a) Three acute toxicity tests for three trophic levels
(b) Test for bacterial inhibition (in order to assess any influence on the biological stage in sewage treatment plants)
(c) Test for degradation
(d) Screening test for adsorption/desorption
ii. Effect assessment

The relationship between dose (level of exposure) and the severity of an effect is established. Predicted No-Effect Concentrations (PNEC) are established by applying appropriate extrapolation factors (EF) to acute (L(E)C₅₀) or chronic (NOEC) toxicity data. The EF builds in a margin of safety that accounts for inter- and intraspecies variability, acute to chronic extrapolation and extrapolation from low observed effects to no observed effects.

iii. Exposure assessment

In order to estimate the concentration levels/doses to which the environment is exposed, the substances' emissions, transport pathways, and transformation and degradation patterns are determined. Ideally, exposure assessment is based on actual measurements. In the case of new substances though, predictive fate models need to be used to establish predicted environmental concentrations (PEC). In Appendix A.1 a short introduction to fate models for PEC predictions is given and some publicly available modelling systems are briefly described.

iv. Risk characterization

The incidence and severity of an adverse effect in an environmental compartment is determined by comparing the PEC from the exposure assessment with the PNEC from the effect assessment. The ratio PEC/PNEC is called risk quotient and, depending on its value, a set of risk management decisions are triggered. Thereby, one of the following four conclusions is drawn:

(a) No immediate concern: No need to consider the substance again until next tonnage trigger or until other data becomes available.

(b) Low concern: Define further information needs, though such information need not be requested until the next tonnage threshold is reached.

(c) Medium concern: Define further information needs and seek them immediately.

(d) High concern: Immediately make recommendations for risk reduction.

The decision between (b), (c) and (d) could be a function of the actual value of the risk quotient, which would then be allocated to one of three ranges defined by an upper and lower risk quotient value as it is suggested in the
These values, however, are not legally binding, but are left open to expert judgement. The risk reduction measures can cover a wide range of actions from modification of the classification to prohibition of the marketing and use of the substance (Furlong, 1995).

![Diagram]

**Figure 2.1: Environmental risk assessment of chemicals according to TGD (1996)**

The whole risk assessment process is illustrated in Figure 2.1, which also indicates two fundamental principles of risk assessment: First, risk is only present if both the substance exhibits a potential inherent adverse effect and a relevant exposure is given; second, risk assessment is an iterative process. This means that the conclusions are to be revised when relevant new information becomes available or when the substance attains higher production tonnages.
Shortcomings of environmental risk assessment according to TGD

The major problem associated with the risk assessment procedure according to the TGD is its low operability. From the first EU priority list (published in 1994 and comprising 110 existing substances) up to now, only 21 substances have been assessed and obtained final agreement. Similarly, an EPA survey of approximately 3'000 HPV chemicals regarding their meeting SIDS requirements (minimal Screening Information Data Set required by the OECD) found that for 43% of the substances no SIDS data was available at all and that for only 7% of the substances the required data set was complete (ENDS, 1998a).

This unsatisfactory situation is due to the fact that current risk assessment practice is a high-input process that needs large amounts of data, time and resources before the risk posed by a potentially damaging substance can be limited. In addition, the number of substances to be assessed is enormous and, so far, no clear-cut methodology for priority setting among existing substances has been agreed upon (Ahlers, 1999).

Besides the practical problem of low operability, more fundamental problems concerning the effect assessment have been pointed out by Berg and Scheringer (1994). They call attention to the fact that, if risk reduction should be successful, one has to know how risk is related to a certain action. In environmental risk assessment, this logical connection is impeded by two fundamental characteristics of environmental systems. First, a complete description of the environment is not possible due to too large a number of interacting components and relationships between them. The environment being a dynamic system, time evolution therefore becomes unpredictable. Also, system boundaries cannot be defined clearly. A system with these properties is overcomplex. The overcomplexity entails that the reaction of the system to human interventions cannot be predicted in terms of cause-effect relationships as it is attempted in environmental risk assessment.

The second fundamental problem of environmental risk assessment is its normative indeterminacy, which stands for the fact that no unique "sound" or "harmed" states of the environment as reference points for assessment are discernible. Therefore the severity of damage is not measurable in absolute terms and no clear distinction between harmless and harmful environmental changes can be made1.

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1Evidently, events can be imagined that will lead to a clearly measurable deterioration of the ecosystem condition, such as the release of large amounts of chemicals with high aquatic toxicity into a river system. Normative indeterminacy rather bears on more subtle changes, such as chronic or low-dose effects, and on the fact that it is not possible to define an absolute measure of harm.
Given these two fundamental obstacles to effect assessment, the possibilities of correctly forecasting the effects of xenobiotics must be regarded as, at best, weak. Instead, current effect assessment only points to the substances' known intrinsic hazards, describing them quite accurately, but neglecting the fact that, through the exposure of the environment to the substance, the potential for other unknown damaging effects, so-called threats, is imminent. For the same reasons, uncertainties in PNEC calculations, especially regarding the determination of the appropriate extrapolation factors, are large. They can lead to different PNEC values for the same substance and target, derived according to different methodologies, differing by two to three orders of magnitude (Fenner et al., 2001).

Recently, the precautionary principle has found admission into the regulatory framework of many European countries as a new paradigm for the management of chemicals. It states that "where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation". It thus permits a lower level of proof of harm to be used in policy making whenever the consequences of waiting for higher levels of proof may be very costly and/or irreversible (EEA, 1998). Several features of current risk assessment practice, as described above, clearly contradict the postulations of the precautionary principle. First, the process of risk assessment is very slow with the particular problem of industry delivering information very reluctantly "drop by little drop". Every time new information is made available though, a comprehensive revision of the risk assessment needs to be carried out. Thus the current risk assessment guidelines facilitate the "waiting for prove" attitude and allow the taking of action to be postponed repeatedly. Second, current risk assessment guidelines only offer instruments to assess known intrinsic effects but offer no methodology to assess unknown threats, and thus render the application of the precautionary principle in the assessment of chemicals difficult (Ballschmiter, 1985).

From the preceding, it is postulated that there is an evident need for a more effective risk assessment procedure that is oriented towards the precautionary principle. This can be achieved by defining a number of indicators that allow the setting of priorities among existing chemicals. The prioritized substances should then become subject to a more rigorous risk management procedure (see Chapter 2.1.3). Indicators suitable for priority setting should fulfill the following requirements:

to quantify the consequences of such an action.
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- Simple, generic indicators which are based on a minimal data set (e.g. available from hazard identification) and which condense this information to be easily interpretable.

- Indicators that point towards the potential for known or unknown threat and that include some clearly unwanted properties like persistence and mobility.

In the following, persistence ($\tau$ or $P$) and spatial range ($R$ or $SR$) are introduced as two exposure-based hazard indicators which have been postulated to perform well in fulfilling the requirements mentioned above.

2.1.2 Exposure-based hazard indicators

Persistence describes the temporal extent of the exposure of the environment to a chemical substance. It was postulated as early as the beginning of the 1970s as a central criterion for the assessment of chemicals (Stephenson, 1977; Frische et al., 1982; Ballschmiter, 1985; Schmidt-Bleek and Hamann, 1986). The rationale for this included, first, that persistence is a necessary condition for the accumulation of substances in the environmental media and, second, that persistence can be used as a surrogate for the highly uncertain measure of ecotoxicity.

These early claims were not very well adopted by the scientific community or legislatory bodies. This is supposedly due to their reluctancy to accept their own ignorance concerning basic ecological functions (overcomplexity) and the influence of trace amounts of chemicals on those functions (Klöpfer, 1994). Also, many persistent chemicals exhibited a low acute toxicity and it was only later recognized that these chemicals could have other deleterious effects (e.g. ozone depletion), which were particularly aggravated by their being widespread (e.g. CFCs).

Mobility was seen as another important criterion to assess the distribution and tendency of chemicals to accumulate. However, it was not suggested as assessment parameter since the perception was that it could lead both to beneficial effects (through local dilution) and to adverse effects (through spreading into other media and to distant locations).

Now, after a period of about 30 years of chemical risk assessment which has heavily focused on effect assessment and on disciplinary questions about mainly toxicological issues and single, physico-chemical properties, persistence is being revived as a criterion for chemical assessment, especially within the context of the precautionary principle. Most recently, Sweden has made suggestions for new guidelines on a
preventive chemical policy in the EU. They propose to renounce from using toxicity tests as main criteria in risk assessment and to use persistence and bioaccumulation instead as phase-out criteria for substances (Kardell, 2000).

Within this second wake of exposure-based assessment, the quantity of spatial range \( R \) was introduced as a counterpart of persistence \( \tau \), covering the spatial dimension of a chemical's distribution and fate. The concept of spatial range was first discussed by Scheringer et al. (1994) and Scheringer (1996a), who also introduced a simple global circulation model to calculate \( R \) and \( \tau \). Other definitions of spatial range then followed by Bennett et al. (1998), Van Pul et al. (1998), and Beyer et al. (2000). The relationships between different definitions of spatial range (also called characteristic travel distance, CTD) and between spatial range and persistence are discussed in detail in Bennett et al. (2001), Beyer et al. (2001) and Scheringer et al. (2001).

The calculation of both \( R \) and \( \tau \), as defined by Scheringer (1996a; 1997), is based on chemical exposure patterns. Their definition therefore does not depend on a specific distribution model, but they can also be derived from experimentally obtained exposure patterns. According to this concept, the persistence \( \tau \) is calculated assuming a single pulse input into the environment and characterizes the time span within which the chemical decays to a certain fraction of the initial concentration. Technically, it is calculated as the time integral of the chemical's total amount in the environment (also called exposure) divided by the initial amount of it released into the environment \( M_0 \) (see Equation 2.1). This definition corresponds to the equivalence width of the function \( M(t) \) (see Figure 2.2).

\[
\tau := \frac{\int_0^\infty M(t) \, dt}{M_0} \tag{2.1}
\]

The spatial range \( R \) as introduced in Scheringer (1996a; 1997) is defined as the 95% quantile range for a one-sided or the 95% interquantile range for a double-sided exposure distribution (see Figure 2.3).

The main features of \( \tau \) and \( R \) which make them ideal candidates for the indicators postulated in Chapter 2.1.1 are:

- \( R \) and \( \tau \) are mass independent, i.e., they are intensive, substance-specific properties that are independent of the amount released.

- Only few substance properties are needed for their calculation, i.e., partition coefficients and degradation rates for each environmental compartment.
• The condensation of the substance properties into two indicators makes different substances better comparable among each other and against threshold values (and thereby makes priority setting possible).

• $R$ and $\tau$ are preventive criteria because they assess exposure independent of any possible effects from exposure.

• $R$ and $\tau$ allow statements about the issues of spatial (interregional) and temporal (intergenerational) justice, i.e. they help to identify gaps between those who benefit from the use/production of a chemical and those who bear the environmental or health damage.

\[ \tau = \frac{1}{M_0} \int_0^\infty M(t) \, dt \]

**Figure 2.2:** $\tau$ as equivalence width of the function $M(t)$. The area of the rectangle $\tau \cdot M_0$ equals the time integral over $M(t)$.

\[ R = \Delta_{0.95} \]

**Figure 2.3:** $R$ as interquantile range $\Delta_{0.95}$ of the exposure distribution. Each of the unshaded ends contains 2.5% of the mass of the distribution.

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Possible applications of $R$ and $\tau$ are manifold. In risk management, they can be utilized directly as tools for decision making, see, e.g., their use as selection criteria in the POP negotiations (Klöpffer and Scheringer, 2000) or for the assessment of alternative substances in the context of risk-benefit analysis (Mathes and Winter, 1993). Further, persistence is one of the three criteria for the identification of PBT chemicals, which leads to an accelerated and adapted risk assessment procedure for those identified. In the early stages of the development of new chemicals, $R$ and $\tau$ could be used as screening criteria to select substances with short spatial and temporal ranges as candidates that are worth being further pursued. Last, $R$ and $\tau$ could be of use for the implementation of a preliminary screening step in the risk assessment procedure. This possibility is further explored in Chapter 2.1.3.

2.1.3 Hazard indicators as screening tools in risk assessment

In Scheringer et al. (2001) a suggestion is made as to how hazard indicators could be integrated into chemical assessment in order to serve as screening tools before admitting substances to a detailed risk assessment according to the TGD (1996). The scheme for the suggested decision process is illustrated in Figure 2.4. According to this scheme, a chemical substance must first go through hazard assessment, on the basis of which it is decided whether it is to be further admitted to conventional risk assessment including effect assessment, exposure assessment, and risk characterization. Hazard assessment is based on indicators that represent the potential of a substance to cause harm. In contrast, risk assessment according to the TGD aims to identify actual risk situations, in which damage is expected to occur, by comparing exposure to effect concentrations.

Two types of hazard indicators are distinguished: The exposure-based quantities persistence $P$ and spatial range $SR$, and the effect-based quantities bioaccumulation potential $B$ and toxicity $T$. Bioaccumulation potential is often expressed in terms of the log $K_{ow}$ of a substance as it is linearly related to the bioconcentration factor (log $BCF$). The main purpose of the hazard indicators is that they are comparably easy to calculate, e.g. with a spreadsheet program, and are based on a limited set of substance data, preferably not exceeding the data collected during hazard identification.

Regarding the procedure on how to use the hazard indicators to identify substances of high concern, two variants might be considered (see Figure 2.4). The first variant (a) is based purely on the concept of exposure reduction and therefore considers $P$
and SR to be sufficient as prioritization criteria (EEA, 1998; Kardell, 2000; Mathes and Winter, 1993; Scheringer et al., 1998). In addition, both these criteria are intensive properties and are therefore not a function of the amount of substance produced or released. The second variant (b) includes bioaccumulation potential and toxicity as two additional compulsory indicators in order to call for prioritization of a substance (Ahlers et al., 2001; EPCRA, 1999). Thereby toxicity is an extensive property, i.e. it is a function of the amount of substance present.

Variant (a) is generally considered a more preventive approach in that it relies purely on exposure potential, i.e. the potential of a substance to cause harm through its widespread and long-term presence, while it factors out the question of whether or not an actual damaging effect is known. Variant (b), on the other hand, is regarded as a less preventive approach as only the simultaneous presence of exposure potential
and observed toxic effects leads to the sorting out of a substance as priority chemical\textsuperscript{1}. It seems that the new approach to risk assessment suggested in Scheringer et al. (2001) is a great basis for discussing better ways for managing chemicals effectively and efficiently. However, it is also obvious that finding the exact form of the decision procedure and defining values for cut-off criteria is still a long way off and will need to be discussed intensively among different interest groups.

In the context of this necessary discussion, this work seeks to contribute to the investigation and development of the exposure-based indicator persistence, as one of the most promising tools in new chemical management. Particulary, the considering of transformation products in the calculation of persistence and in chemical risk assessment in general is brought into the discussion as one of the most important omissions of current risk assessment practices.

2.2 Transformation processes and transformation products

Chemicals in the environment are subject to a variety of transformation processes, ranging from simple isomerization to complete mineralization. Here, different types of transformation reactions and resulting transformation products are discussed and the nomenclature used in this work is introduced. Specific transformation products are defined as the only type of transformation products that are included in the methodology developed in this work to assess the potential risk of the combination of parent compounds and transformation products. The importance of this distinction lies in the necessity to treat all chemicals and their cascade of transformation products with a consistent methodology. Only then do the results from different chemical case studies become comparable.

2.2.1 Transformation processes

Transformation reactions of organic chemicals are reactions which alter their molecular structure. In the environment they can be subdivided into abiotic and biotic transformation processes. Although it is not the focus of this work, it is interesting to note that the need for such prioritization has been claimed repeatedly by different interest groups, but that strongly differing opinions regarding the actions set forth for the selected priority chemicals (chemicals of high concern) and the unselected chemicals (chemicals of low concern) exist (CEFIC, 2001; EEA, 1998; ENDS, 1998b; Kardell, 2000; Mathes and Winter, 1993; Scheringer et al., 1998).
transformation processes. Biotic reactions, i.e. transformation reactions mediated by microorganisms, are usually the only processes by which xenobiotic compounds (i.e. newly invented chemicals whose structures differ from those usually processed by organisms) may be mineralized, while abiotic processes usually yield other organic compounds.

Abiotic reactions can be further subdivided into chemical reactions, which take place in the dark without the mediation of organisms, and into photochemical reactions. In the environment the two most important chemical reactions are hydrolysis, or more generally, substitution and bond cleavage reactions mediated by nucleophilic species, and oxidation and reduction reactions. Both types of reactions mainly take place in the soil and water compartment, but volatile compounds can also be hydrolyzed by water present in the atmosphere. Photochemical reactions comprise direct photolysis, in which chemical species become excited through the absorption of sunlight and subsequently become transformed in a variety of processes, and indirect photolysis, which stands for the reaction of the organic compound with highly reactive species formed by sunlight like OH and NO\textsubscript{x} radicals. Photochemical reactions take place mainly in the air and water compartment, but also at the surface of the soil compartment.

Biotic reactions are mediated by organisms present in the water and soils of natural environments. These organisms facilitate kinetically hindered reactions by catalyzing them with the help of enzymes (e.g. biotic hydrolysis) or by investing energy to produce a more reactive species to react with the organic compound. This is the case in biotic oxidation reactions, where an electrophilic form of O\textsubscript{2} is supplied by the organisms, and in biotic reduction reactions, which are initiated by a nucleophilic form of H or a direct electron transfer. For the case of xenobiotic compounds, most microorganisms possess some unspecific enzymes which attack unknown compounds. As mentioned before, this first step in the degradation process of xenobiotics often is an oxidation reaction, which makes the compound more polar. It might then fit into the metabolic pathway or become water-soluble and be returned to the environment. Sometimes, though, these first transformation reactions can also lead to dead-end metabolites which cannot be further transformed and which therefore persist in the environment.
2.2.2 Transformation products

Depending on the transformation process, different types of transformation products need to be distinguished. Abiotic transformation processes yield mainly other organic molecules, which are structurally related to their parent compounds. We call those specific transformation products. Biotic transformation processes normally consist of a series of reactions, the first of which result in transformation products similar to or identical with the specific transformation products of abiotic reactions. Often unspecific enzymes break these compounds further down to smaller entities until they are identical with or resemble naturally occurring compounds so much that they can be transformed by specific enzyme-compound interactions. These intermediate products will be called non-specific transformation products because they have lost their unambiguous structural relation with their parent compounds and could therefore stem from different parent compounds. In most microbial degradation processes, these non-specific compounds are further broken down until they are completely mineralized, yielding mineralization products like CO₂, H₂O, HCl, and O₃.

Besides microorganisms, higher organisms are also able to transform certain xenobiotics. Their main aim is to make the compounds more polar in order to rid themselves of them by urinary excretion. These products of metabolic reactions in higher organisms are not included in the selection of transformation products considered in this work. The reason for this exclusion is that the model system used to represent the environment only comprises the compartments soil, water and air as well as some possible sub-compartments like airborne particles and sediments, but no higher organisms are included.

Here, only specific transformation products are taken into account. Non-specific transformation products are excluded from the assessment process, because it is assumed that they are readily degraded through specific microbial metabolic pathways. Regarding possible harmful effects, our focus is mainly on direct toxic effects of the chemicals on organisms in the ecosystem. General influences of organic materials on ecosystems like, e.g., on the nutrients' balance or on the global CO₂ budget are factored out. For this reason, mineralization products like CO₂ and O₃ are not included into the assessment, although they are known to have local and global scale effects on ecosystems. But, besides the fact that the amount of these products produced from the breakdown of synthetic chemicals is small compared to the amounts directly emitted from energy production systems, these problems are believed to be
an issue of life-cycle assessment rather than of environmental fate and risk analysis. All in all, only specific transformation products which bear a clear structural similarity with the parent compound are included in the assessment. For these transformation products, transformation schemes are set up that describe their formation from precursors and their successive decay to other transformation products.

2.3 Transformation products in chemical risk assessment

2.3.1 Transformation products in standard assessment

In this chapter, the status of transformation products in the assessment of chemicals legally required in the EU is reviewed. The assessment procedure is discussed separately for transformation products of pesticides and those of non-pesticides because pesticides, due to their specific use patterns, are subject to separate regulation.

Transformation products of non-pesticides

Transformation products are not formally defined in the Dangerous Substance Directive (EEC, 1993), and the only mandatory requirement regarding transformation products concerns the monitoring of transformation products in the environment:

"Apart from methods of detection and determination, information shall be given on analytical methods which are known to the notifier and allow detection of a substance and its transformation products after discharge in the environment". (art. 1.4, Annex VII.A. Directive 67/548/EEC)

However, the competent authority has the power to request more information, as stated in Article 16 of the Dangerous Substance Directive:

"If it can be shown to be necessary for the evaluation of risks which may be caused by the substance, the competent authorities may ask for further information, verification and/or confirmatory tests concerning the substances or their transformation products". (art. 16, Directive 67/548/EEC)

\(^8\)Chapter 2.3.1 has been elaborated in close collaboration with R. Quartier and is therefore in parts similar to Chapter 2 of his thesis (Quartier, 2000).
Chemical risk assessment and transformation products

Article 16 clearly implies that transformation products can contribute to the overall risk caused by a substance. Concretely, Article 16 empowers the authority to request further information concerning transformation products. However, the authority must show that this additional information is necessary for the proper evaluation of the risks. But how can this be shown? What are the criteria that transformation products must meet in order to be integrated into the risk assessment procedure? An answer to these questions can be found in the TGD (1996) (p. 253):

"Consideration should be given to whether the substance being assessed can be degraded biotically or abiotically, to give stable and/or toxic degradation products. Where such degradation can occur, the assessment should give due consideration to the effects which might arise. For new substances, it is unlikely that information will be available on such degradation products and thus only a qualitative assessment can be made. For HPV substances, however, known significant degradation products should also be subject to risk assessment. Where no information is available, a qualitative description of the degradation pathways can be made."

Thus, the authority can request more information on transformation products if it can show that the said transformation products are stable and/or toxic. However, it is explicitly admitted in the text quoted above that, in most cases, information on toxic and/or stable transformation products is not made available. Consequently, the authority will not have the necessary information to justify its request for additional information on transformation products. As a matter of fact, it is not in the interest of the notifier to provide information on transformation products, since this information could be used to justify costly additional testing or even restrictions of the use of the notified substance. This may partly explain the lack of data on transformation products.

Besides stable or toxic transformation products, transformation products of readily hydrolyzable precursors are also mentioned in the TGD (1993) (p. 277). It states that if hydrolysis of the precursor is very fast, the transformation product rather than the precursor becomes the relevant compound in the case of discharge into water.

In general, EU chemicals legislation and OECD guidelines agree to a great extent. However, it is interesting to note the registration procedure for new substances practiced in Japan as exemplified by Henkel for the registration of a new ethylene glycol
derivative for the production of polyurethanes (Höfer et al., 1999). According to the MITI legislation (Japanese Ministry of Trade and Industry, responsible for the registration of new chemicals), new substances that are shown to be easily biodegradable will be admitted to registration without further toxicity testing. However, these seemingly lax standards are aggravated by the fact that they are not only asking for the proof of primary biodegradation, but also for the proof of complete biodegradation, which is much more difficult to establish. The notifier thus needs to examine whether or not radio-labelled carbon not recovered in the respiratory tests is incorporated into refractory transformation products, and if so, those transformation products need to be isolated and identified. This requirement is identical to asking for the identification of the complete transformation scheme of a non-pesticide. In practice, Japanese registration procedures become thus much more stringent than EU procedures.

Transformation products of pesticides

Pesticides have three specific features that strongly differentiate them from non-pesticide chemicals.

1. Pesticides are meant to be released. Their occurrence in the environment is not an unwanted effect as for non-pesticide chemicals.

2. Pesticides are bioactive compounds released in the environment at concentrations high enough to cause acute effects on target pests. In the case of non-pesticide chemicals the assumption is that they are released at concentrations far below their threshold for acute effects.

3. Pesticides are used on plants that are meant to be consumed, and the consumer may be exposed through diet to residues of pesticides. This particular consumer health aspect is not relevant for most non-pesticide chemicals.

Accordingly, pesticides are regulated by a specific legislation. The central regulatory text on agricultural pesticides in the European Union is Directive 91/414 on the placing of plant protection products on the market (EEC, 1991). Directive 91/414 regulates both the data collection (Annex II) and the risk assessment (Annex VI) of pesticides. For pesticides not only the risk of the pesticide itself but of all residues has to be assessed. Residues are defined in Directive 91/414 as

"one or more substances present in or on plants or products of plant origin, edible animal products or elsewhere in the environment and resulting
from the use of a plant protection product, including their metabolites and products resulting from their degradation or reaction". (art. 2.2., Directive 91/414)

This definition is rather general, including all the substances that result from the use of the pesticides: the parent compound, the products of metabolic reactions of the pesticide in plants or animals, as well as the environmental transformation products as they are understood in the context of this work. The decisive importance of residues in the registration of pesticides clearly appears in Article 5B: Authorization of new pesticides shall be granted only if

"their residues, consequent on application consistent with good plant protection practice, do not have any harmful effects on human or animal health or on groundwater or any unacceptable influence on the environment, and the said residues, in so far as they are of toxicological or environmental significance, can be measured by methods in general use". (art. 5b, Directive 91/414)

This statement clearly implies that a substance will not be registered until it can be demonstrated that there is no risk forthcoming either from the active ingredient (a.i.) itself or from any of its relevant metabolites. This brings up two questions: First, how is the risk for the a.i. and the relevant metabolites assessed, and second, how are relevant metabolites defined?

To assess the risk to the environment, the a.i. and its relevant transformation products are tested extensively for their eco-toxicological effects and their physico-chemical properties. To demonstrate that there is no unacceptable impact on the environment, these properties are compared to a set of property-based and risk-based triggers. Unless it can be shown that none of them is exceeded, registration is not possible. The triggers with their upper limits are:

Property-based triggers\(^4\):

- DT50 > 3 months or DT90 > 1 year (measured in field)

\(^4\)DT50 stands for the degradation half-life, DT90 for the time until 90% of the a.i. is degraded. BCF is the bioconcentration factor. Non-extractables, also termed bound residues, are defined as the fraction of the compound released that is not recovered in respiratory tests nor can it be extracted as such or in the form of transformation products from the organic matrix. This fraction is bound strongly to organic matter through hydrogen, charge-transfer or even covalent bounds.
More than 70% non-extractables after 100 days with a mineralization rate of < 5% in 100 days.

Groundwater concentrations exceeding 0.1 µg/l

$BCF > 1000$ or $> 100$ (if not biodegradable)

Risk-based triggers:

- Several TER (toxicity to exposure ratio) limits for different species (mammals, birds, three trophic levels of aquatic organisms, soil microorganisms, beneficial arthropods)
- More than 30% of the beneficial arthropods affected at maximum rate of application
- Soil micro-organisms affected by > 20% after 100 days

So far, no clear methodology to identify the relevant metabolites has been available. Therefore, the EU commissioned the College voor the toelating van bestrijdingsmiddelen (CTB) to write a guidance document on relevant transformation products. This document is still at the consultation stage. In the draft version it is suggested that, in order to identify relevant metabolites, a decision scheme has to be run through (see Figures 2.5 and 2.6).

First, the a.i., besides extensive testing of its eco-toxicity, should be subject to a series of degradation studies in soil (laboratory studies under various conditions, field studies) and in aqueous systems (studies in natural waters/sediments and pond studies). From these studies a scheme of the proposed degradation pathways, including final endpoint CO$_2$ and bound residues, has to be deduced. Metabolites amounting to more than 10% of the applied mass of the a.i. at any time and in any compartment during the study are considered major metabolites. Of these major metabolites, those selected as potentially relevant ones

(a) are not inorganic or CO$_2$, or

(b) contain 4 or more C atoms or atoms other than C, H, N, and O, or

(c) are aldehydes or epoxides.

In soil and groundwater, the potentially relevant metabolites are assessed for their persistence and groundwater contamination potential (see Figure 2.5). To this end, data on degradation and sorption are required. These data are used to estimate
**Figure 2.5:** Decision scheme for relevant metabolites in soil and groundwater. DT50 stands for the degradation half-life in the respective media and $K_{oc(m)}$ stands for the organic-carbon(matter) water partition coefficient.

**Figure 2.6:** Decision scheme for relevant metabolites in surface water and/or sediment.
the degradation rate and concentration in the upper groundwater using appropriate models. If groundwater turns out to be endangered according to the upper limit of >0.1 μg/l, the metabolite is considered relevant and it becomes subject to a standard risk assessment as for the a.i.. For the PEC calculations, data on the percentage of metabolite formed in the soil metabolism study and molar fractions of the metabolites compared to the active substance are taken into account.

In some argued cases, one more additional testing step can be passed through before the metabolite is definitely deemed relevant. This step includes special testing for pesticidal activity, as well as toxicological tests on mammals and eco-toxicological tests for soil and aquatic organisms. These data are then first screened in a hazard-based approach (proof of low toxicity) and, if satisfactory, are sufficient to exclude the substance from the list of relevant metabolites.

In surface water, a metabolite that does not meet criteria (a), (b) and (c) for non-relevance has to be tested for its toxicity to water and/or sediment organisms, depending on where the metabolite resides (see Figure 2.6). If toxicity is confirmed, it will be subject to an aquatic risk assessment as for the a.i..

Conclusions
In the pesticides legislation, it is recognized that transformation products can significantly contribute to the impact of a pesticide, and the relevant transformation products must be assessed at the same level as their parent compounds. In the legislation on non-pesticide chemicals, however, almost no information is required on transformation products. Thus, one can conclude that relevant transformation products of pesticides are perceived as a serious threat, whereas transformation products of non-pesticides are perceived as relatively harmless, and therefore negligible, in the assessment procedure. In support of this point of view, it is often argued that, while the transformation products of pesticides might occur in relatively high concentrations and might inherit some of the bioactivity of the a.i., there is no reason to suspect the transformation products of non-pesticides to exhibit some kind of bioactivity, even less so since they are typically still more diluted than their precursors.

This point of view, however, seems to be largely overhauled since many examples of non-pesticide chemicals are known whose transformation products have caused considerable environmental and health damage due to their persistence, bioaccumulation potential, mobility, toxicity and other specific effects (see Chapter 1.2 for examples). Therefore, the focus of this work is on developing a methodology that is
similarly well applicable to assess the risk due to transformation products of both pesticide and non-pesticide chemicals. Referring back to the definition of specific transformation products in Chapter 2.2, it was left open as to how the transition from specific, i.e. transformation products that bear a structural similarity with their parent compound and for which only unspecific enzymes are available, to non-specific transformation products, i.e. transformation products that bear no clear structural similarity with their parent compound anymore and that can be degraded by specific enzyme-compound interactions, should be delimited. This question can hardly be answered in a general way because there exists a large number of specific enzymes whose availability depends strongly on the prevailing environmental conditions, the kind of microorganisms present and on whether adaption to a certain compound has occurred. It is therefore suggested that the criteria used in the guidance document on relevant transformation products of the CTB should be used in this work to delimit specific transformation products. The rationale behind this suggestion is that, given the functionality of a selection of nearly ubiquitously present enzyme systems, it is very likely that they will be able to efficiently degrade compounds that comply with those selection criteria, i.e. not more than 3 C atoms, no epoxides or aldehydes, no atoms other than C, H, N and O.

2.3.2 New approaches to assessing transformation products

The fact that common practice of risk assessment does not cover transformation products of industrial, non-pesticide chemicals in an adequate way is partly due to the assumptions regarding use and exposure patterns of non-pesticide chemicals as explained in Chapter 2.3.1, but also partly due to a number of methodological problems and an increase in the time and effort required for the assessment. Some of the methodological problems are as follows: the relevant transformation products have to be identified and characterized, the transformation kinetics has to be explored, and the group of chemicals forms a complex mixture, for the assessment of which new hazard and risk indicators have to be defined. Accordingly, there are only a limited number of scientific studies dealing with the risk assessment of transformation products of industrial chemicals (Behrendt et al., 1999; Belfroid et al., 1998; Quartier and Müller-Herold, 2000; Spaepen et al., 1997; Vogt, 1990; Yaffe et al., 2001). Some of them also present new approaches to the assessment of transformation products of pesticides. In the following, we will
therefore deviate from the strict separation of pesticides and non-pesticide chemicals. This is, moreover, in proper agreement with more recent tendencies in environmental hazard and risk assessment to accommodate both general chemicals and pesticides in a common concept and risk assessment framework (OECD, 1995).

The simplest approach to integrating transformation products into chemical risk assessment is to multiply the PEC calculated for the parent compound with a fraction indicating which percentage of the parent compound is actually transformed into a specific transformation product. This approach was chosen, e.g., in the draft guidelines for the risk assessment of relevant metabolites of pesticides (see Chapter 2.3.1), or in a study suggesting uniform procedures to estimate the predicted environmental concentrations of the residues of veterinary medicines (Spaepen et al., 1997).

Another, more comprehensive approach is presented by Belfroid et al. (1998). This study evaluates the data availability (physico-chemical and eco-toxicological properties) for 78 transformation products of 20 pesticides and uses these data for a qualitative prediction of their relative risk in the aquatic environment as compared to the risk of their parent compounds. Properties compared are persistence and accumulation in soil, persistence and concentrations in water, $BCF$ and/or expected bioavailability as well as toxicity. They find that about 50% of the transformation products pose a higher risk than their parent compounds. This study does not include any information on how fast or to what extent the transformation products are formed.

Three studies that do take the dynamic formation of transformation products into account are by Vogt (1990), Yaffe et al. (2001) and Behrendt et al. (1999). Vogt (1990) developed a method based on vector computing to calculate large-scale, multi-component transport and reaction mechanisms in aquifers. His algorithms take transformation, transport and sorption of various chemical components and species as well as equilibrium reactions between different species into account and calculate concentration-time profiles of the single species. No suggestions are made, however, as to how to use these results in a risk assessment context.

A very recent study by Yaffe et al. (2001) investigates the human health risk posed by the formation of nitro-PAHs from PAHs (polycyclic aromatic hydrocarbons) in the atmosphere. The fate of both PAHs and nitro-PAHs is calculated with a multimedia fate model. It is assumed that nitro-PAHs are formed irreversibly from PAHs in the atmosphere only and that therefore the dynamic partitioning of PAHs and their nitro-PAHs daughter products can be evaluated sequentially. The multimedia environmental concentrations of selected PAHs and nitro-PAHs were calculated and
were then used to estimate media-specific mutagenic densities for each chemical, i.e. their mutagenic activity multiplied with their concentration in the respective medium. These mutagenic densities were considerably enhanced for nitro-PAHs as compared to the parent compound PAHs. Especially in the compartments water and biota they were up to a factor of 10⁴ larger. A subsequent multiple pathway uptake and cancer risk analysis for two known carcinogenic nitro-PAHs showed a slightly enhanced cancer risk in comparison to the parent compound. However, if the carcinogenic potential of all transformation products was known, the difference would be expected to be even higher. This study comes closest to the present work’s intentions, as it includes the modelling of the dynamic formation of transformation products in a multimedia model and a subsequent risk assessment that assesses the effect of transformation products. It does not, however, account for the possible formation of transformation products in compartments other then air, nor does it try to assess the combined exposure or risk resulting from all compounds being present at the same time.

Behrendt et al. (1999) use knowledge-based computer models to predict the degradation pathways of different triazine herbicides in soil. They combine the predicted pathways with QSPRs (quantitative structure-property relationships) for prediction of some basic toxicological and physico-chemical properties of the substance and an analytical soil transport model for exposure calculations. From this combination, they derive comprehensive hazard profiles of the triazine herbicides and their transformation products. Concentration-time profiles of the transformation products are calculated and from them persistence is derived as the integral of the concentration-time profile, and used as one of the hazard indicators. The other hazard indicators are five descriptors for the accumulation behavior in soil, given different boundary conditions, and one descriptor of toxicity. The parent compound and the transformation products are ranked according to their relative hazard potential with the help of Hasse diagrams. To my knowledge, this is the only study that explicitly defines and calculates a persistence measure for transformation products.

The only methodology integrating transformation products into the calculation of spatial range SR as the second of the exposure-based indicators P and SR was suggested by Quartier (2000) and Quartier and Müller-Herold (2000). They introduce the secondary spatial range as the typical distance a transformation product can travel from the release position of its precursor while being degraded at the same time. The secondary spatial ranges are calculated as analytical solutions of a level IV model under the assumption of instantaneous equilibrium. Defining $\rho^A$ as the
characteristic (normal) SR of the precursor, \( \rho^B \) as the characteristic SR of the transformation product (assuming release of the transformation product as such) and \( \rho^{AB} \) as the secondary spatial range of B following release of A, they found that \( \rho^{AB} \) is a function of \( \rho^A \) and \( \rho^B \) (see Equation 2.2 for a highly precise fitting function).

\[
\rho_{\text{fit}}^{AB} := \frac{\rho^A + \rho^B}{2} + \frac{\rho^B}{2(1+\rho^A/\rho^B)} + \frac{\rho^A}{2(1+\rho^B/\rho^A)}
\]  

(2.2)

They were specifically able to show that

- \( \rho^{AB} \) is always smaller than the sum of \( \rho^A \) and \( \rho^B \).
- \( \rho^{AB} \) always lies between the larger of the two separate ranges and 1.48 times the same larger range. \( \max\{\rho^A, \rho^B\} < \rho^{AB} < 1.48 \cdot \max\{\rho^A, \rho^B\} \)
- \( \rho^{AB} \) does not depend on the amount of A transformed into B nor on the specific transformation rate.

Thus, they were able to calculate \( \rho^{AB} \) based on two partition coefficients and three media-specific degradation rates for A and B. They applied this methodology to three pairs of parent compounds and transformation products, namely aldrin/dieldrin, MTBE/TBA and benzene/phenol. For the example of aldrin/dieldrin they found a secondary spatial range of 2'000 km as compared to the spatial range of aldrin of only 830 km, and thus could show that in some cases transformation products travel further than their parent compound. This can be explained by the different environmental fate and behavior of the transformation products as well as by the fact that the transformation products are constantly formed out of the precursor while the precursor is spread out, i.e. the transformation products show a spatially diffuse pattern of emergence as opposed to the precursor, which is assumed to be released at one location only.

### 2.4 Research needs

Two research needs stand out when the current state of the art of integrating transformation products into chemical risk assessment is considered.

First, given a lack of opportunity to monitor the actual environmental concentrations of all potentially harmful transformation products of industrial chemicals, a model framework that includes transformation products needs to be developed. This framework should allow for the prediction of the environmental concentrations of all
relevant transformation products and therefore has to take their dynamic formation and subsequent further degradation/transformation into account. It should allow accommodation of different parallel reactions with different shares of the overall decay of the precursor, and should also be flexible enough to handle different numbers of transformation products. Moreover, it should allow for differing transformation patterns in the different environmental media.

Second, once the concentrations or concentration-time profiles of transformation products can be calculated, new indicators have to be developed that describe the behavior and fate of the transformation products and that can be integrated into the framework of chemical assessment. Given our preference for hazard assessment and exposure-based hazard indicators in particular, as explained in Chapter 2.1, the main research objective is to define persistence measures for transformation products. This is all the more important as the currently used persistence measures even tend to mask the occurrence of transformation products in that they give the impression that environmental exposure ceases after the time span indicated by the persistence measure has expired (Ballschmiter, 1985; Fenner et al., 2000).

More specifically, it is therefore put forward here that two new persistence measures should be introduced. One that describes the persistence of each single transformation product, called Secondary Persistence (in analogy to Secondary Spatial Range, see Quartier and Müller-Herold (2000)), and one that describes the overall persistence of the entire substance family, called Joint Persistence (Ballschmiter, 1991). Proposed uses of the new persistence measures are as follows:

- Use of Joint Persistence in chemical assessment to describe the total exposure of the environment caused by the release of the parent compound. Integrating transformation products might considerably impact the ranking of substances or the decision whether or not a certain persistence cut-off value is exceeded.

- Use of Secondary Persistence in prioritizing the different transformation products of a compound and to identify the relevant transformation products which are mentioned in the regulatory texts and which should be given special attention.

With somewhat lower priority, because the data requirements become even more excessive due to the need for effect data, we believe that there is also a need for the definition of risk-based indicators that include transformation products. Since, in the environment, transformation products and parent compounds exist together
in complex mixtures, the concept of mixture toxicity can be applied to assess this mixture by means of a mixture risk quotient.
Chapter 3

The concept of persistence

Persistence is a measure of the time the environment is exposed to a chemical. It has been repeatedly suggested as a hazard-based indicator for screening and prioritization purposes in chemical risk assessment. However, there is no single measure for evaluating persistence, but there exists a variety of persistence definitions. They differ with regard to the characteristics of the emission scenario on which they are based (e.g., pulse release, continuous source, switched off continuous source) and with regard to their underlying mathematical definition.

After an introduction to multimedia models and the derivation of their solutions for different emission scenarios, we therefore give in this chapter an overview over different persistence measures and discuss them with respect to their ability to best represent the duration of exposure of the environment to the chemical. It is crucial to understand how different persistence measures reflect different concentration-time profiles, especially with regard to, in a subsequent step, expanding the persistence definition to include transformation products.

3.1 Persistence as exposure-based hazard indicator

The simplest and frequently used approach to evaluate the persistence of a chemical is to equate it with the half-life of the chemical in a specific environmental medium \( t_{1/2,i} \). This is deduced from its first-order degradation rate constant in that medium \( k_i \) by the relationship given in Equation 3.1. The half-life of a chemical indicates the time required for its concentration to diminish to half of its original value in the medium of interest. This approach is justified as long as the chemical has a high
affinity for one compartment only and the half-life in that compartment is chosen as decision criterion.

\[ t_{1/2,i} = \frac{\ln 2}{\kappa_i} \]  

(3.1)

So far, expressing persistence in terms of media-specific half-lives has been the method of choice for defining persistence cut-off values in scoring and ranking systems for the risk assessment of chemicals. Five such sets of media-specific cut-off values for half-lives are compiled in Table 3.1 from four different frameworks for the priority setting of chemicals that include, besides other criteria, the identification of persistent chemicals.

In all four frameworks the substance is considered persistent if any one of the half-life cut-off values for the different media is exceeded. The first one is the approach for priority setting (Webster et al., 1998) of the Canadian Environmental Protection Agency (EPA) (Can/EPA). It combines the persistence criterion with the aspects of bioaccumulation and toxicity, and thus identifies PBT chemicals. If a chemical that is persistent is also found to be bioaccumulative (log K_{ow} > 5) and toxic, it is targeted for virtual elimination. A related framework is the one of the Canada-U.S. International Joint Commission (Can-US) (Webster et al., 1998). It only differs by its lower cut-off value of 56 d in water. Similarly, the U.S. EPA (US/EPA) has its own framework that distinguishes the categories persistent (P) and very persistent (VP) (EPCRA, 1999). The best known framework, whose final form is currently being negotiated, is the international framework for the identification of POPs that is established by the UNEP (2000) (POP-UNEP). In addition to a list of 12 chemicals that are known POPs and that have already been phased out or are now intended for rapid phase out, it also contains a set of cut-off criteria to identify further candidate POPs. These are criteria for persistence, bioaccumulation, long-range transport

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<td>( t_{1/2,\text{water}} ) (d)</td>
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<td>( t_{1/2,\text{sediment}} ) (d)</td>
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<td>( t_{1/2,\text{air}} ) (d)</td>
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potential and adverse effects towards human or ecosystem health. Only if all four of these areas of criteria are met does the substance become a candidate POP which might require international action.

Common to all of these frameworks is that their persistence cut-off values are based on media-specific half-lives, which entails two main problems. First, it is unclear how the half-lives should be determined in order to make them transparent enough to function for legally binding purposes. They are viewed as properties of the chemical and therefore standard procedures for their determination should be agreed upon in order to make them independent of variation in experimental or environmental conditions. Second, because only degradation processes are normally considered in the development of the half-life criteria, while the effects of partitioning to other media and mode of entry are ignored, these criteria might be excessively stringent in that a substance may have a long half-life in a medium into which it is never discharged and into which it is unlikely to partition appreciably (Webster et al., 1998).

In my opinion, these are strong points in support of considering not only the individual media half-life values, but rather how they combine with mode of entry and partitioning characteristics to result in an overall environmental persistence. Especially in the case of chemicals that exhibit a typical multimedia behavior, i.e. partition appreciably between all media, the overall persistence should be evaluated in order to properly represent the exposure pattern of the chemical. According to Gouin et al. (2000) approximately one third of the 233 chemicals they examined were proper multimedia chemicals in the sense that they were present in amounts bigger than 1% in each medium.

The analysis of the multimedia behavior can be achieved either through its simulation in multimedia models or through measurement of the dissipation of the chemical in the natural environment. To describe the measured or modelled chemical fate, two primary related types of persistence measures are distinguished. Those that describe time-independent, steady-state chemical exposure due to a continuous source of emission and those that describe dynamic exposure patterns that change in time after a chemical has been emitted into the environment as pulse release*.

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*The value of the overall persistence thus depends by definition on the release scenario (mode of entry) and on the characteristics of the model with which it is calculated. Therefore it is not a priori clear how the overall persistence could be used to compare substances with each other or against a cut-off criterion. To allow for such a comparison, it might be necessary to define standard release scenarios or standard methods to establish the release scenario for each individual
3.2 Multimedia models for calculating persistence

Multimedia models represent the environment by means of a set of well-mixed, interconnected boxes that stand for the different environmental media such as soil, air, water, sediment, suspended particles or biota. They are very popular to calculate the exposure pattern of chemicals released to the environment.

Most multimedia models developed today are deduced from the fugacity models first introduced by Mackay and Paterson (Mackay, 1979; Mackay and Paterson, 1981; Mackay and Paterson, 1982). They are based on the principle that the fate of a chemical and its distribution between environmental media depends on its physico-chemical properties such as partition coefficients and degradation rates. In these models, the partitioning of a chemical between environmental media is deduced from its fugacity in the different media. Fugacity, $f$, is a thermodynamic quantity which stands for the escaping tendency of a chemical from a specific medium. It is proportional to the concentration, $c$, in the same medium by a proportionality constant called fugacity capacity, $Z$, that is deduced from the partition coefficients of a chemical. In thermodynamic equilibrium the fugacity of a chemical is equal in all media.

Different levels of fugacity models are distinguished, i.e. level I to level IV, depending on the different assumptions regarding equilibrium, release mode and the presence or absence of loss processes. In level I models, the thermodynamic equilibrium partitioning of a fixed amount of a non-reactive compound is calculated using fugacity capacities deduced from partition coefficients. Level II models also assume thermodynamic equilibrium, but loss processes through degradation or advective outflow are allowed for. They are balanced by a continuous emission into the system. This results in a steady-state, equilibrium, flow situation.

In level I and level II models, the hidden assumption is that chemicals reach equilibrium instantaneously when released to the system. In reality, however, there are transfer resistances that limit transfer between media. These resistances are due to boundary layers between media, which hinder diffusion, and also due to advective processes such as particle deposition or spray drift, which transport chemicals into only one direction across media boundaries. The resistances lead to a non-equilibrium situation with different fugacities in different media. They are accounted for in level III models, which represent non-equilibrium, steady-state, flow

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substance. However, up to now, there is no agreement on an international level on how to define such standard scenarios (OECD, 2001).
The concept of persistence 43

situations. Level IV models additionally account for situations in which the inflow of the chemical varies over time. They allow to calculate time-dependent mass or concentration functions for all environmental compartments. They thus represent non-equilibrium, nonsteady-state, flow situations.

While some of the multimedia models in use are actually implemented in terms of fugacity, others are directly formulated in terms of concentrations. This is also the case for the model used in this work. One important distinction regarding multimedia models is whether a closed or open system is assumed. Open systems allow for advective transport out of and into the system and are adequate for calculating actual environmental concentrations, while in closed systems the only loss process is through degradation. Closed systems are more appropriate to calculate the persistence of a chemical.

In this work, the exposure patterns for persistence calculations are simulated with a closed box model. The model is solved for steady-state concentrations (level III) and time-dependent concentration functions (level IV). Based on these exposure patterns, persistence measures are calculated and the results obtained for steady-state and pulse release are investigated.

3.2.1 Model description

The box model used consists of the three media soil (s), water (w) and air (a) with averaged environmental properties and dimensions (see Figure 3.1). The dimensions of each compartment, i.e. the volumes $v_s$, $v_w$ and $v_a$, as well as the definition and quantification of the transfer processes between the media are the same as used by Scheringer (1996a), see also Klein (1985) and Mackay and Paterson (1991).

The processes considered in the model are abiotic and biotic first-order degradation processes, denoted by $\kappa_i$ in each medium $i$, and diffusive and advective transfer processes between the media, denoted by $u_{ik}$, where the sequence $i-k$ stands for transfer from medium $i$ to medium $k$. The intermedia transfer parameters represent processes such as volatilization, dry and wet deposition, leaching etc. Some of these processes are functions of the Henry's law constant, $K_H$, and the octanol-water

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*Many of these degradation processes such as hydrolysis or atmospheric oxidation are actually second-order reactions but are described by pseudo first-order rate constants in the model, assuming constant concentrations of one of the reactants such as $H_2O$, or OH radicals.
partition coefficient, $K_{ow}$. The derivation of the single transfer processes $u_{ik}$ and the parameters for their quantification are the same as in Scheringer (1996a) and can be looked up there. Advective transfer into and out of the model system is not considered, so that the resulting persistence values can be compared with the persistence values calculated in global scale or other closed-system models (Bennett et al., 1999; Scheringer, 1996a; van de Meent et al., 2000; Webster et al., 1998).

For a chemical species $x$ in the model system, the following rate equation for the concentration $c^x_i$, which takes into account all degradation and intermedia transfer processes, can be formulated:

$$\frac{dc^x_i(t)}{dt} = -\kappa^x_i \cdot c^x_i(t) - \sum_k u^x_{ik} \cdot c^x_i(t) + \sum_k u^x_{ki} \cdot c^x_k(t), \quad i, k = s, w, a. \quad (3.2)$$

The first term on the right-hand side of Equation 3.2 describes degradation, the second term represents transfer from the compartment $i$ to the other two compartments $k$, and the last term is the transfer from these other two compartments $k$ into
the compartment $i$. This system of three linear differential equations, one for each medium, can also be written as

$$
\dot{c}_x(t) = -S_x c_x(t).
$$

(3.3)

The $3 \times 3$ matrix $S_x$ is composed of the parameters $k_x$ and $u_{ik}$ according to Equation 3.2. The solutions of Equation 3.3 differ depending on the boundary conditions simulated. They are deduced in the following Chapter 3.2.2 for the situations of a continuous and a pulse release.

### 3.2.2 Model solutions

The system of linear differential equations (LDE) in Equation 3.3 can be solved assuming an unvarying flux (continuous source $q$) or assuming a single pulse input $c_0$ of chemical $x$ into the system. In case of a continuous source, a time-independent situation (level III), in which the system has already reached a steady state, and a time-dependent situation (level IV), in which the system is still evolving towards the steady state, can be further distinguished. For a single pulse input, the system will always be time-dependent. [In the explanation of the solution procedure, the index $x$, which stands for the chemical species $x$, will be omitted for the sake of generality.]

To solve Equation 3.3 for the case of a continuous source, the source vector $q$ is added (see Equation 3.4). The three elements of the vector $q$ represent the continuous release fluxes of the compound into each compartment (in mol/m$^3$-s).

$$
\dot{c}(t) = -S c(t) + q
$$

(3.4)

For the steady-state situation, the system can be easily solved by setting $\dot{c}(t)$ in Equation 3.4 to zero. The steady-state concentrations $c_i^{\text{stat}}$ are then obtained as elements of the vector $c^{\text{stat}}$ by inverting the matrix $S$ as

$$
c^{\text{stat}} = S^{-1} q.
$$

(3.5)

In order to obtain the time-dependent solution $c(t)$ for the system of LDE given in Equation 3.3 (homogenous, first-order LDE) and Equation 3.4 (inhomogeneous, first-order LDE), the eigenvalues $\lambda_1$, $\lambda_2$, $\lambda_3$ and eigenvectors $y_1$, $y_2$, $y_3$ of the main matrix $S$ need to be calculated. With those at hand, the solution for the time-dependent case of a constant, continuous source $q$ which is assumed to be switched
on at time $t = 0$ can be formulated as

$$c(t) = S^{-1}(1 - e^{-St})q,$$

(3.6)

where the expression $e^{-St}$ can be calculated as

$$e^{-St} = Y(t)Y^{-1}(0),$$

(3.7)

where $Y(t)$ is a fundamental matrix solution of Equation 3.3 and contains the elements $e^{-\lambda_i t} y_1$ as column vectors.

In case of a pulse input, the eigenvalues and eigenvectors can be used to give the general solution of Equation 3.3 as

$$c(t) = a_1 \cdot e^{-\lambda_1 t} \cdot y_1 + a_2 \cdot e^{-\lambda_2 t} \cdot y_2 + a_3 \cdot e^{-\lambda_3 t} \cdot y_3$$

(3.8)

The coefficients $a_i$ in Equation 3.8 are chosen such that they satisfy the initial condition

$$c_0 = a_1 \cdot y_1 + a_2 \cdot y_2 + a_3 \cdot y_3 = Y(0) \cdot a,$$

(3.9)

where $Y(0)$ is the $3 \times 3$ matrix whose columns are the eigenvectors $y_1, y_2$ and $y_3$. The vector $c_0$ contains the amount of chemical initially released into each compartment (in mol/m$^3$). The time-dependent vectors $c(t)$ resulting in Equations 3.6 and 3.8 characterize the single concentration functions $c_i(t)$ in all media $i$.

### 3.2.3 Persistence measures

Two types of persistence measures need to be distinguished. The first set of persistence measures describes the average temporal behavior of a chemical in a given system. Here, this type of persistence measure is called overall persistence and includes, e.g., the steady-state persistence ($\tau_{\text{stat}}$) that is calculated in level III systems and the equivalence width ($\tau_{\text{equiv}}$) that is calculated in level IV systems. The second type of persistence measures can be termed effective persistence ($\tau_{\text{eff}}(t)$) and describes the overall degradation rate in the system at one specific moment in time. Figure 3.2 shows the mass profiles $M(t)$ resulting for the two situations of (A) a continuous source $q$ switched on at $t = 0$ and switched off at $t = t_{\text{off}}$ after the system has reached steady state, and of (B) a pulse input at $t = 0$ with the entries of $c_0$ equal to those of $q$ (yet with different units). Also, Figure 3.2 illustrates how the different persistence measures relate to these mass profiles. In the following, the mathematical definitions of the different persistence measures are discussed.
Figure 3.2: Schemes of overall mass profiles obtained for a continuous source (A) and pulse input (B). It is indicated how overall and effective persistence measures describe the dynamic behavior of these mass profiles at different points in time.
Overall persistence

The persistence at steady state is obtained from the results of a level III multimedia model as a chemical’s residence time, i.e. the time spent in a reservoir by an individual molecule (Rodhe, 1992). It is thus calculated as the ratio of the overall mass contained in the system at steady state, $M_{\text{stat}}$ (in mol), and the sum of all loss processes ($\sum \kappa_i \cdot m_i^{\text{stat}}$), which, at steady state, are equal to the sum of all flows into the system, $Q$ (in mol/s) (Bennett et al., 1999; Mackay et al., 1992; van de Meent et al., 2000; Webster et al., 1998) (see Equation 3.10).

$$\tau_{\text{stat}} = \frac{\sum_i c_i^{\text{stat}} \cdot \kappa_i \cdot v_i}{\sum_i c_i^{\text{stat}} \cdot v_i} = \frac{\sum_i c_i^{\text{stat}} \cdot v_i}{\sum_i q_i \cdot v_i} = \frac{M_{\text{stat}}}{Q}. \quad (3.10)$$

In time-dependent level IV systems, the overall persistence is usually expressed as overall half-life (Rodhe, 1992) or equivalence width (Scheringer, 1996a). They are characteristics of the decreasing function $M(t)$ as it is obtained after a pulse emission or after a continuous release has ceased. The equivalence width $\tau_{\text{equiv}}$ is defined as the time-integral over the mass profile $M(t)$ divided by the initial mass present at $t = 0$, $M_0$ (see Equation 3.11).

$$\tau_{\text{equiv}} = \frac{\sum_i v_i \int_0^\infty c_i(t) \, dt}{\sum_i c_{0,i} \cdot v_i} = \frac{\sum_i e_i \cdot v_i}{\sum_i c_{0,i} \cdot v_i} = \frac{1}{M_0} \int_0^\infty M(t) \, dt. \quad (3.11)$$

In some cases, Equation 3.11 is used to describe the equivalence width after switching off a continuous source at steady state. The resulting persistence measure, $\tau_{\text{equiv,off}}$, is then called clearance time, i.e. the time it takes to empty a reservoir after all sources have been switched off. In order to calculate $\tau_{\text{equiv,off}}$, $c_{0,i}$ in Equation 3.11 needs to be replaced by $c_i^{\text{stat}}$.

The time integrals of the $c_i(t)$ in Equation 3.11 are called the total exposures $e_i$.

The vector $e = [e_a, e_w, e_a]^T$ is calculated according to:

$$e = S^{-1} c_0. \quad (3.12)$$

Equation 3.12 is obtained from Equation 3.3 by using a vector of initial concentrations, $c_0$, and by taking the integral over time of $c(t)$ (Scheringer, 1996a).

Comparing Equations 3.5 and 3.10 with Equations 3.11 and 3.12 shows that the same results are obtained for the residence time $\tau_{\text{stat}}$ and the equivalence width $\tau_{\text{equiv}}$ if $c_0$ and $q$ have the same entries (yet with different units). This means that each steady-state model can also be interpreted in terms of a pulse scenario or, in other words, that the steady-state concentrations and the residence time resulting from a
The concept of persistence 49

continuous input are equivalent to the exposure values and the equivalence width resulting from a pulse input. Due to this identical mathematical formalism of $\tau^{\text{stat}}$ and $\tau^{\text{equiv}}$, the numerical values obtained for both of them can be used equivalently. [Note that $\tau^{\text{equiv}}$ and $\tau^{\text{equiv,off}}$ do not give equal results even if $c_0$ for the calculation of $\tau^{\text{equiv}}$ and $q$ for the calculation of $c^{\text{stat}}$, and thus of $\tau^{\text{equiv,off}}$, are assumed to have the same relative entries.]

A second important observation is that, as both $M(t)$ and $M^{\text{stat}}$ are directly proportional to $M_0$ and $Q$ respectively, $\tau^{\text{stat}}$ and $\tau^{\text{equiv}}$ do not depend on the absolute values of $M_0$ or $Q$, but only on the relative magnitude of the single elements of $c_0$ and $q$. Persistence is thus a mass-independent, intensive property.

In the following, we solve the model on level IV because this gives a more detailed insight into the degradation dynamics: Comparing the point in time marked by the equivalence width, $\tau^{\text{equiv}}$, with the plot of the concentration function $c(t)$ or mass profile $m(t)$ lends a better understanding as to how persistence values should be interpreted.

Besides $\tau^{\text{equiv}}$ other possible measures of overall persistence exist that allow to describe the average time course of a decreasing mass profile as obtained after a pulse release. They are the time $\tau^{1/e}$, which denotes the time required for a decrease of the initial mass $M_0$ to a fraction of $1/e \cdot M_0$

$$\frac{M(\tau^{1/e})}{M_0} = \frac{1}{e} \approx 0.37,$$

or the mean time $\mu$, in which the masses are weighted with their respective times

$$\mu = \frac{\int_{0}^{\infty} M(t) \cdot t \, dt}{\int_{0}^{\infty} M(t) \, dt}.$$  

These two measures provide additional information on the nature of the mass profiles $M(t)$ and are further discussed in section 3.3.2 in comparison with the equivalence width.

Müller-Herold (1996) proposed a limiting law for the overall decay rate, i.e. the average rate with which the compound is degraded in the entire multimedia system, which is equivalent to the inverse of the overall persistence. He showed that the overall decay rate lies between the slowest media-specific decay rate and the decay rate based on equilibrium partitioning of mass in the environment. He also pointed out that the equilibrium partitioning limit is only a good approximation of the actual rate if the decay rates are orders of magnitude slower than the transfer rates, i.e. resistances for inter-compartmental transport are low.
Effective persistence

The effective persistence $\tau_{\text{eff}}(t)$ is defined as the inverse of the effective degradation rate $\kappa_{\text{eff}}(t)$. $\kappa_{\text{eff}}(t)$, in turn, is the sum of all media-specific degradation rates weighted with the relative amount of mass in those media as compared to the overall mass in the system at one specific moment in time (see Equations 3.15 and 3.16).

$$
\kappa_{\text{eff}}(t) = \frac{\sum_i c_i(t) \cdot \kappa_i \cdot v_i}{\sum_i c_i(t) \cdot v_i}
$$

(3.15)

$$
\tau_{\text{eff}}(t) = \frac{1}{\kappa_{\text{eff}}(t)}
$$

(3.16)

Effective persistence measures that need special mentioning are the effective persistence at $t = 0$, termed source-weighted persistence $\tau_{\text{sw}}$, where $c(t)$ is replaced by either $c_0$ or $q$, and the effective persistence near the steady state, whose value converges asymptotically towards $\tau_{\text{stat}}$.

Bennett et al. (1999) investigated the behavior of the effective persistence for different assumptions regarding the presence or absence of non-equilibrium effects and of transport across media boundaries in a two-compartment model. However, they only describe how the system evolves towards steady state after switching on a source, but do not include the behavior of the effective persistence after switching off the source or after a pulse input. These situations are further investigated in Chapter 3.3.

3.3 Comparison of different persistence measures in level IV

In the following, to illustrate and test the above introduced persistence measures, concentrations $c_i^e(t)$ are calculated for the two chemicals atrazine and methyl tert-butyl ether (MTBE) and for different release scenarios (release into soil, into water or into air). Atrazine is one of the most commonly used herbicides and is found in many surface and ground waters. The environmental fate of MTBE has become a subject of renewed interest because of the large quantities of this compound that are being used as an oxygenated additive in gasoline (Johnson et al., 2000). The input parameters for the two substances, namely the three degradation rates $\kappa_i$ and the two partition coefficients $K_H$ and $K_{ow}$, are given in Table 3.2.

For both substances, atrazine and MTBE, the overall mass profiles $M(t)$, on which the persistence calculations are based, are obtained as follows. The concentration
Table 3.2: First-order degradation rates, octanol-water partitioning coefficient and Henry’s law constant for atrazine and MTBE (Lerch et al., 1998; Solomon et al., 1996; Howard et al., 1991; Mackay et al., 1993; Torrents et al., 1997).

<table>
<thead>
<tr>
<th>compd</th>
<th>$\kappa_s$ (s$^{-1}$)</th>
<th>$\kappa_w$ (s$^{-1}$)</th>
<th>$\kappa_a$ (s$^{-1}$)</th>
<th>log $K_{ow}$</th>
<th>$K_H$ (Pa m$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>3.82·10$^{-7}$</td>
<td>2.67·10$^{-7}$</td>
<td>1.60·10$^{-4}$</td>
<td>2.68</td>
<td>2.51·10$^{-4}$</td>
</tr>
<tr>
<td>MTBE</td>
<td>4.46·10$^{-8}$</td>
<td>4.46·10$^{-8}$</td>
<td>7.27·10$^{-7}$</td>
<td>0.94</td>
<td>59.5</td>
</tr>
</tbody>
</table>

functions $c_i^x(t)$ for each compartment $i$, resulting from solving the LDE systems in Equations 3.3 and 3.4, are multiplied by the compartment’s volume $v_i$, thus providing the mass profiles $m_i^x(t)$ for each compartment. These are then added up for all compartments to give overall mass profiles $M^x(t)$. Thus, depending on the release scenario, three overall mass profiles $M^x(t)$ are obtained for each substance $x$.

### 3.3.1 Overall and effective persistence

The relationship between measures of overall and effective persistence is illustrated in Figure 3.3 for a scenario in which atrazine is released into air. Because of the short half-life of atrazine in air compared to its half-lives in soil and water and a fast transfer from air to soil and water, the resulting mass profiles are characteristic of a fast disappearance in the release compartment and transfer to and slow decay in the two non-release compartments (see graphs indicating the relative masses in Figure 3.3).

As a consequence, for the pulse release (scenario B), the effective persistence changes shortly after the release from a very small $\tau^{sw}$ of 0.07 d to a considerably higher persistence of around 40 d and slowly stabilizes there ($\tau_{\text{eff}}(\infty)$). The equivalence width $\tau^{\text{equiv}}$ represents an average persistence over the entire time period from release to total disappearance of the compound and therefore lies anywhere between $\tau^{sw}$ and $\tau_{\text{eff}}(\infty)$, e.g. here at 8.65 d. While $\tau^{\text{equiv}}$ usually represents the average rate of disappearance quite well, in the extreme case shown here it is heavily influenced by the fast decay in the release compartment and does not represent the successive slow decay in the water compartment very satisfactorily.

In case of a continuous source (scenario A), the compound is constantly released to air and therefore the steady-state persistence $\tau^{\text{stat}}$ that is reached after about 200 d
Figure 3.3: Illustration of how different measures of overall and effective persistence relate to mass profiles obtained for the release of atrazine to air. The scenarios of (A) switching on and off a continuous source, and of (B) a one-time pulse release are depicted in columns. The first set of graphs gives the mass profiles, the second set shows how the relative masses in the three compartments evolve, and the third set of graphs depicts the time course of $\tau_{\text{off}}$ and how it relates to the values of the different measures of overall persistence.
lies far below the persistence that is reached for the pulse release in scenario B after 200 d (i.e. $\tau_{\text{eff}}(\infty)$). However, the agreement between the results for $\tau_{\text{stat}}$ in scenario A and $\tau_{\text{equiv}}$ in scenario B confirms that their mathematical formulation are equivalent as mentioned in the previous section. After switching off the source in scenario A, the system behaves similarly as for the pulse release and the persistence jumps to a higher value of approximately 40 d because the mass in air is instantaneously reduced to near 0.

For scenario A, two measures of equivalence width have been calculated: $\tau_{\text{equiv, on}}$, which represents the average dynamic behavior while the system evolves towards steady state, and the clearance time $\tau_{\text{equiv, off}}$, which represents the time it takes to empty the reservoir after the source has been switched off in steady state. It can be shown mathematically that these two measures, $\tau_{\text{equiv, on}}$ and $\tau_{\text{equiv, off}}$, are always equal and that they can be expressed in the same way as functions of the dynamic matrix $S$ and source term $q$ only.

As mentioned in Chapter 3.2.3 already, the results confirm that not the same equivalence width is obtained for the pulse release with $c_0$ in scenario B, i.e. $\tau_{\text{equiv}}$, and for the clearance time after switching of the source $q$ in scenario A, i.e. $\tau_{\text{equiv, off}}$. This is the case even though the relative entries in $c_0$ and $q$ are the same. In practice, $\tau_{\text{equiv}}$ and $\tau_{\text{equiv, off}}$ are used interchangeably as valid persistence measures, often without the necessary awareness of their differences. In this work, we chose to always interpret persistence as $\tau_{\text{equiv}}$, i.e. as the time until environmental exposure has ceased after a one-time pulse release.

Lastly, it should be noticed that, for other chemical examples, $\tau_{\text{eff}}(t)$ for a continuous source does not necessarily evolve steadily from $\tau_{\text{sw}}$ to $\tau_{\text{stat}}$, but that its time course might also show an inflection point due to changes in the composition of the relative masses.

### 3.3.2 Different types of overall persistence measures

In order to distinguish between the ability of different measures of overall persistence, i.e. $\tau_{\text{equiv}}$, $\tau^{1/\varepsilon}$ and $\mu$, to represent the time during which the environment is exposed to a chemical after a pulse release $c_0$, three scenarios were calculated. The overall mass profiles for these three release scenarios, namely for the release of atrazine into water, the release of atrazine into air, and the release of MTBE into water, are depicted in Figure 3.4 (graphs 3.4A-C). It shows that fairly different profiles are obtained for the different situations. The values for $\tau_{\text{equiv}}$, $\tau^{1/\varepsilon}$ and $\mu$ for the three
graphs 3.4A-C are given in Table 3.3.

Figure 3.4: Overall mass profiles $M(t)$ of atrazine released into water (A), atrazine released into air (B) and MTBE released into water (C). $M(t)$ is the overall mass of the chemical in the model system at time $t$ when it is summed up over all compartments. As the calculated persistence values do not depend on the absolute amount of substance in the system, $M_0$ can be chosen arbitrarily and was set to 1 mol in the examples given. The vertical lines indicate the three different persistence measures $\tau_{\text{equiv}}$, $\tau^{1/\epsilon}$ and $\mu$.

If atrazine is released into water as depicted in graph 3.4A, the overall mass profile is dominated by the mass fraction of atrazine in the water compartment and therefore comes close to a single exponential decay. This is due to the compound’s slow degradation in and high affinity to the water compartment compared to the other compartments. The resulting overall mass profile can be satisfactorily described as $c(t) = a \cdot e^{-\kappa w t}$. In this case, the equivalence width equals the values calculated for $\mu$ and $\tau^{1/\epsilon}$ with $\tau_{\text{equiv}} = \mu = \tau^{1/\epsilon} = \frac{1}{\kappa w}$. Further, $\tau_{\text{equiv}}$ here correctly predicts that after another period of the length $\tau_{\text{equiv}}$ the function $M(t)$ will have decreased to $M_0 \cdot 1/e^2$.

However, when the overall mass profile is not dominated by one single compartment,
Table 3.3: Equivalence width, mean value and lifetime for the three scenarios A-C depicted in Figure 3.4 (in days).

<table>
<thead>
<tr>
<th>Graph</th>
<th>$\tau_{\text{equiv}}$</th>
<th>$\mu$</th>
<th>$\tau_{1/e}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4A</td>
<td>43.3</td>
<td>43.3</td>
<td>43.3</td>
</tr>
<tr>
<td>3.4B</td>
<td>8.65</td>
<td>40.5</td>
<td>0.09</td>
</tr>
<tr>
<td>3.4C</td>
<td>33.7</td>
<td>26.2</td>
<td>36.0</td>
</tr>
</tbody>
</table>

Its shape may deviate significantly from a single exponential decay. As observed in Chapter 3.3.1 already, this is the case for the release of atrazine into air and also for the release of MTBE into water (graphs 3.4B and 3.4C). The mass profile in graph 3.4B is the sum of a fast decay in air, into which the substance has been released, and of two slow decays in water and soil, into which the substance is transported subsequently. For this type of curve the equivalence width is always bigger than $\tau_{1/e}$, indicating that the mass profile shows a distinct tailing with the substance remaining in the overall system at low concentrations for longer time periods than the time $\tau_{1/e}$ would suggest. This effect is emphasized by the value obtained for $\mu$, which is several times bigger than $\tau_{1/e}$ and $\tau_{\text{equiv}}$ because the small amounts of substance left at long times are weighted with the respective times.

Graph 3.4C, in contrast, is typical for situations where the emission compartment has a slightly slower decay rate than the non-emission compartments into which the compound partitions after its release. In this case, the equivalence width is smaller than $\tau_{1/e}$, suggesting that the substance is degraded even faster than one expects from the value of $\tau_{1/e}$. Consequently, $\mu$ is smaller than the equivalence width for this type of mass profile.

### 3.4 Conclusions

In this chapter, it has been shown how the overall persistence can be calculated for a single compound on the basis of its fate and distribution in a multimedia model. Once the multimedia model is set up, the calculation procedure is relatively simple and needs, in this case, only five substance input parameters, i.e. its degradation rates in air, soil and water, as well as its partition coefficients, i.e. the Henry’s law constant ($K_H$) and the octanol-water partition coefficient $K_{ow}$. 
However, this seemingly ease of use draws attention off the fact that a lot of uncertainty is incorporated into these calculations. These include model uncertainty, i.e. the question whether all relevant mechanisms and media are covered in the model and how well those that are enclosed represent actual environmental processes, as well as parameter uncertainty and variability, i.e. uncertainty about how well the true values of the landscape and substance input parameters are represented by the input values used. The degree to which these different uncertainties influence the final results is analyzed in detail in Chapter 6.

One important property of persistence that was demonstrated in this chapter is that it is an intensive quantity and therefore does not depend on the amount of substance emitted into the environment. Therefore, the actual amounts emitted need not be known for the determination of persistence, which is another reason, in addition to its easy calculability, for its being a suitable screening tool for chemical risk assessment. What is important to know about the emission pattern though, is the relative share of the different emission pathways, i.e. the mode of entry of the substance. This strong dependence of the persistence on the input compartment can be seen when the persistence value (e.g. equivalence width) for release of atrazine to water (43.3 d) is compared with its value for release to air (8.7 d). Webster et al. (1998) showed how, in steady state, the overall persistence for release to all three compartments ($\tau^{\text{stst}}$) can be obtained as a linear combination of the persistence values obtained for release to one compartment only ($\tau_r^{\text{stst}}$) multiplied with the share of the release to that same compartment $r$ relative to the overall amount emitted ($q_r^* = \frac{Q_r}{\sum Q_r}$). (see Equation 3.17, with $M_r^{\text{stst}}$ being the overall mass in the system after release into compartment $r$).

\[
\tau^{\text{stst}} = \frac{\sum M_r^{\text{stst}}}{\sum Q_r} = \sum \left( \frac{\tau_r^{\text{stst}} \cdot Q_r}{\sum Q_r} \right) = \sum \tau_r^{\text{stst}} \cdot q_r^* \tag{3.17}
\]

Likewise, in level IV, one finds that the mass profiles can deviate strongly from the profile of a single exponential decay, especially if the chemical shows markedly different degradation rates in the various environmental compartments. In those cases it is therefore advisable to solve the level IV system and to include information gained from the course of the mass profile into the hazard assessment. Otherwise, the interpretation of the persistence value, calculated as $\tau^{\text{equiv}}$ or $\tau^{\text{stst}}$, as the rate at which a chemical continues to disappear after several lifetime periods have elapsed, might lead to significant discrepancies between the expected concentration and the concentration calculated by solving the level IV model.
The concept of persistence

The discussion of different measures of overall persistence first shows that their values might differ considerably depending on the type of steady-state or pulse release scenario they are set up to describe. While $\tau^{\text{equiv}}$ for a pulse release and $\tau^{\text{stat}}$ for a continuous source are mathematically equivalent and thus give the same results for the same relative entries of $q$ and $c_0$, their value is clearly different from the value of the clearance time, $\tau^{\text{equiv,off}}$, i.e. the time it takes to empty a reservoir that has reached steady state due to a continuous inflow of the source $q$. When using overall persistence as a criterion to compare substances, it is thus of utmost importance to verify that all values have been calculated according to the same definition of overall persistence.

Second, regarding the distinctive ability of $\tau^{1/e}$, $\mu$ and $\tau^{\text{equiv}}$ to reflect the specific features of different mass profiles after a pulse release, $\tau^{1/e}$ seems to be the least suitable as its value is based on $c(t)$ only and not on the integral under the concentration profile, i.e. the exposure. However, persistence is meant to be an exposure-based measure and should be able to depict the fact that the substance, in some compartments, might remain at relatively low concentrations for a long time. Therefore, $\mu$ and $\tau^{\text{equiv}}$ as two exposure-based quantities seem to be more suitable candidates. They show a distinctively different behavior when $c(t)$ deviates from a simple exponential decay, but with the current knowledge it is difficult to say which behavior would be more preferable. Both measures are discussed further in the next chapter with regard to their ability to account for transformation products.
Chapter 4

Persistence of transformation products

None of the persistence measures discussed in Chapter 3, covers transformation products and, even more problematic, they tend to mask the occurrence of transformation products since they give the impression that the environmental exposure ceases after the time span given by the persistence measure*. Therefore, persistence measures should be extended to describe the presence of transformation products as well (Ballschmiter, 1985; Ballschmiter, 1991). For this purpose, two new persistence concepts, Secondary and Joint Persistence, that include transformation products are introduced (Fenner et al., 2000). In Appendix B the corresponding persistence definitions are established in terms of the persistence measures equivalence width and mean time. They are discussed on the basis of their analytical solutions for a one-dimensional, single medium system. As a result of that discussion, equivalence width is singled out as the most suitable persistence measure to base the definition of the persistence of parent compound and transformation products on.

In Chapter 4.2, it is shown how the formation and fate of transformation products can be simulated in a multimedia model and how the model system needs to be modified in order to calculate concentration functions for any number of transformation products. Based on these concentration functions, the two new persistence definitions which describe the additional exposure of the environment that is caused by the presence of transformation products, are formulated for multimedia environments.

*Reproduced in part with permission from Fenner et al. (2000). Copyright 2000 American Chemical Society.
In Chapter 4.3, Secondary Persistence and Joint Persistence values are explicitly calculated for two pairs of parent compounds and transformation products; namely methyl tert-butyl ether (MTBE) and atrazine, and their respective transformation products tert-butyl alcohol (TBA) and desisopropyl atrazine (DIA). The suitability of both persistence definitions as measures for providing information on transformation products for regulatory purposes is discussed in Chapter 4.4.

4.1 Persistence concepts for transformation products

In order to discuss the inclusion of transformation products into persistence calculations, several terms must first be defined. The parent compound is the chemical that is emitted, voluntarily or accidentally, into the environment. In this work, only xenobiotic chemicals are considered. The transformation products are those substances that are formed through biotic or abiotic degradation of the parent compound. Only specific transformation products are included in the calculation of persistence (for a detailed definition see Chapters 2.2 and 2.3.1). The entirety of a parent compound and all its specific transformation products is termed substance family. Further, generations of transformation products are distinguished which are defined by the minimal number of intermediate transformation steps between a transformation product and its parent compound. Transformation products with the same minimal number of intermediate transformation reactions belong to the same generation.

Regarding the distinction of different persistence definitions for parent compound and transformation products, the persistence usually calculated to express the temporal fate of the parent compound is termed Primary Persistence (PP). With respect to the persistence definitions for transformation products, the following requirements can be formulated for them:

- Their mathematical formulation should be as analogous to the formulation for the PP as possible.
- They should be intensive properties of the chemical and not dependent on the amount of parent compound emitted.
- They should describe the fate of the single transformation products.
They should also describe the fate of the entire substance family.

In order to satisfy the last two requirements, two new persistence definitions are introduced.

1. A persistence definition that is based on the mass profiles of the single transformation products:

   The mass profiles of the single transformation products will be termed *secondary mass profiles* and the corresponding persistence will be termed *Secondary Persistence (SP)*. In the case of a substance family with n compounds including the parent compound, there exist n − 1 SP values for a given release scenario.

2. A persistence definition that is based on the sum of the mass profiles of the parent compound and of all of its transformation products:

   The mass profile of the sum of the mass profiles of the parent compound and of all of its transformation products will be termed *joint mass profile* and the corresponding persistence will be termed *Joint Persistence (JP)*. There exists one JP value for each substance family and a given release scenario.

The mathematical formulation of SP and JP can be based on either of the persistence measures, equivalence width \( \tau_{\text{equiv}} \) or mean value \( \mu \). Both of them are intensive measures. The definition of the mean or expected value (see Equation 3.14) can be applied without problems to the secondary and joint mass profiles in order to obtain formulations for the SP and JP that are equivalent to the formulation for the PP. The definition of the equivalence width (see Equation 3.11) can be applied to the joint mass profile in order to obtain an equivalent formulation as for the PP. It cannot, however, be applied to the secondary mass profile because the starting concentration of the transformation products, \( c_0^x \), is always zero. It is shown in Appendix B for a single medium environment and in Chapter 4.2.2 for a multimedia environment how this problem can be circumvented.

### 4.2 Transformation products in a multimedia environment

In order to better understand the behavior of the persistence definitions for transformation products in a multimedia environment, it is useful to first deduce the
analytical solutions for PP, SP and JP in a single medium environment. They are given in Appendix B. In particular, in Appendix B rationales for the choice of $\tau^{\text{equiv}}$ instead of $\mu$ as measure on which to base the persistence definitions for transformation products are given. Further, the relationship between the individual PP values of the parent compound and its transformation products and the JP are explored, and it is explained how the mathematical formulation for the SP definition was developed in best possible analogy to the equivalence width measure.

4.2.1 Model modifications

Given the fact that in every environmental system transformation products might be present, each species in the system, except for the parent compound, can be a transformation product $y$ ($y = B, C, ..., m$) of another species $x$ ($x = A, B, C, ..., m; x \neq y$). Therefore a formation term

$$\frac{dc_i^y(t)}{dt} = + \sum_x \kappa_i^{xy} \cdot c_i^x(t)$$

(4.1)

has to be added to the rate equation of the transformation product $y$ (see Equation 3.2 in Chapter 3.2.1) with $\kappa_i^{xy}$ being the rate constant at which precursor $x$ is transformed to $y$ in medium $i$. Thereby $\kappa_i^{xy}$ is a fraction of $\kappa_i^x$, i.e. $\kappa_i^{xy} = \theta_i^{xy} \kappa_i^x$, with $0 \leq \theta_i^{xy} \leq 1$ denoting the fraction of formation. For each pair $xy$ of precursor and transformation product, this additional rate equation can also be expressed by means of the diagonal formation matrix $K^{xy}$ which consists of the three rate constants of formation, $\kappa_i^{xy}, i = s, w, a$.

For the model system with the three media soil, water and air and the $m$ chemical species, of which one is the parent compound and the others are transformation products that are formed from the other species, the various $3 \times 3$ matrices $S^x$ and $K^{xy}$ can be used as block matrices to construct a main matrix $S$ according to Figure 4.1. This results in Equation 4.2, which now stands for a system of $3 \times m$ linear differential equations, which contain the fate (degradation and transfer) of all $m$ chemical species in the system as well as the formation of the $m - 1$ transformation products.

$$\dot{c}(t) = -S \cdot c(t).$$

(4.2)

In Equation 4.2, the concentrations $c_i^x(t)$ are being combined to the vector $c(t) = [c_A^A(t), c_B^A(t), c_C^A(t), \ldots, c_m^A(t), c_B^w(t), c_C^w(t)]$ and $S$ is built according to the following rules (also see Figure 4.1):
Figure 4.1: Construction of the matrix $S$ in Equation 4.2 for an example in which parent compound A decays in two parallel reaction channels into the transformation products B and D, which are both further transformed to C, hence $m=4$. The rate constants of the transformation processes are denoted by $k_{xy}^x$. $S_x$ is the submatrix of the species $x$ including its degradation and transfer processes. $K_{xy}$ is the transformation submatrix representing the transformation of the species $x$ to the species $y$.

- All submatrices $S_x$ and $K_{xy}$ have the dimension $p \times p$, where $p$ is the number of compartments, here $p = 3$.

- The main matrix $S$ has the dimension $mp \times mp$, where $m$ is the number of species in a parent compound-transformation product system.

- The $m$ submatrices $S_x$ always lie on the diagonal of $S$, while their sequence is the same as the sequence of the chemicals in $c(t)$.

- The $K_{xy}$-submatrices always lie at the position $xy$, where $x$ denotes the column and $y$ denotes the row.

How to obtain the steady-state and time-dependent solutions for the system of $3m$ linear differential equations has been explained in Chapter 3.2.2 already. Those solutions can be applied analogously in this case.

In steady state, the source vector $q$, consisting of $3m$ elements, contains the continuous release fluxes of the parent compound into each compartment (in mol/m$^3$-s),
while the remaining elements of $\mathbf{q}$ concerning the transformation products equal zero. The steady-state solutions are obtained by inversion of the matrix $\mathbf{S}$ and its multiplication with $\mathbf{q}$ (see Equation 3.5 in Chapter 3.2.2). The vector $\mathbf{c}_{\text{stat}}$ contains all steady-state concentrations of all $m$ compounds in all media $i$ according to the structure of $\mathbf{c}(t)$.

The exposure vector $\mathbf{e} = [e^A, e^A, e^B, ..., e^m, e^m]^T$ is calculated analogously by inversion of the matrix $\mathbf{S}$ and its multiplication with $\mathbf{c}_0$ (see Equation 3.12 in Chapter 3.2.3). In analogy to $\mathbf{q}$, the vector $\mathbf{c}_0$ contains the amount of parent compound released into each compartment (in mol/m$^3$), while all elements of $\mathbf{c}_0$ concerning the transformation products equal zero.

In order to solve the time-dependent equation 4.2, $3m$ eigenvalues $\lambda_1, ..., \lambda_{3m}$ and $3m$ eigenvectors $\mathbf{y}_1, ..., \mathbf{y}_{3m}$ of the main matrix $\mathbf{S}$ need to be found. The general solution of the system is then given by

$$\mathbf{c}(t) = a_1 \cdot e^{-\lambda_1 t} \cdot \mathbf{y}_1 + a_2 \cdot e^{-\lambda_2 t} \cdot \mathbf{y}_2 + a_3 \cdot e^{-\lambda_3 t} \cdot \mathbf{y}_3 + ... + a_{3m} \cdot e^{-\lambda_{3m} t} \cdot \mathbf{y}_{3m}$$

(4.3)

The coefficients $a_i$ in Equation 4.3 are chosen such that they satisfy the initial condition

$$\mathbf{c}_0 = a_1 \cdot \mathbf{y}_1 + a_2 \cdot \mathbf{y}_2 + a_3 \cdot \mathbf{y}_3 + ... + a_{3m} \cdot \mathbf{y}_{3m} = \mathbf{Y}(0) \cdot \mathbf{a},$$

(4.4)

where $\mathbf{Y}(0)$ is the $3m \times 3m$ matrix whose columns are the eigenvectors $\mathbf{y}_1, ..., \mathbf{y}_{3m}$. The resulting vector $\mathbf{c}(t)$ consists of all $c_i(t)$ for all species in all media and characterizes the $3m$ single concentration functions. Since we do not consider back reactions, including the transformation products into the calculations does not change the dynamics of the parent compound and therefore neither its persistence.

### 4.2.2 Definitions for Primary, Secondary and Joint Persistence

To include the temporal behavior of transformation products into the persistence definition of parent compounds, three different types of persistence, mathematically based on the equivalence width definition (see Equation 3.11), are calculated for parent compounds and transformation products as previously discussed in Chapter 4.1. First, the overall persistence (i.e. the average persistence over all compartments) of each separate compound (i.e. parent compound or transformation products) is determined as described in Chapter 3.2.3 (see Equation 3.10 for steady state and in
The overall persistence of single compounds is called Primary Persistence (PP) and, for a pulse release, is calculated according to the general formulation in Equation 3.11 for each compound \( x \):

\[
PP^x = \frac{\sum_i e_i^x \cdot v_i}{\sum_i c_{0,i} \cdot v_i} = \frac{1}{M_0} \int_0^\infty M^x(t) \, dt.
\]  

Equation 3.11 for time dependence. In addition to the PP, also the Joint Persistence (JP) and the Secondary Persistence (SP) are derived from the concentration vector \( c(t) \) that results from solving Equation 4.2: First, the JP is defined as the overall persistence of the sum of the masses of the parent compound and the transformation products. In a multimedia environment, it is calculated as the sum of the exposure of all substances in all compartments divided by the mass \( M_0 \) of the parent compound at \( t = 0 \). In Equation 4.6 this definition is shown for the case of a parent compound \( A \) with \( m - 1 \) transformation products \( y \):

\[
JP = \frac{1}{M_0} \int_0^\infty \left( M^A(t) + \sum_y M^y(t) \right) \, dt.
\]  

For a sequential reaction in a single medium system with all \( \theta^{xy} = 1 \), the JP, according to Equation 4.6, is equal to the sum of the PPs of the parent compound \( A \) and the PPs of the transformation products \( y \) as can be seen from Equation B.17 in Appendix B. However, in a multimedia system, the JP cannot be deduced from the PPs in a straightforward manner. Note that the JP can also be calculated from the level III solutions of the system because of the equivalence between Equation 4.6 and Equation 3.11.

The second type of persistence derived from the concentration vector \( c(t) \) is the SP, here defined as the overall persistence of each transformation product alone as it is formed while the parent compound is being degraded. Again, when the SP is calculated from the overall mass profile of the transformation product, the concept of equivalence width fails because the mass \( M^{y/2} \) at \( t = 0 \) equals zero. As exhibited in Appendix B.1, the SP of \( y \) as it is formed out of \( A \) is then calculated as the integral over the entire mass profile divided by \( M_{\text{max}}^y \), the maximum value of the mass profile of the transformation product (see Equation 4.7).

\[
SP^{y/A} = \frac{1}{M_{\text{max}}^y} \int_0^\infty M^y(t) \, dt.
\]  

\( M_{\text{max}}^y \) provides a point of reference for the transformation product \( y \) that is independent of the amount of \( y \) formed relative to \( M_0 \). (If \( M_0 \) was used instead of
information on the temporal extent of the function $M^y(t)$ and on the amount of transformation product $y$ that is formed out of $M_0$ would become mixed in the SP. This means that very low SPs would be obtained for long-lived transformation products that are formed in very small amounts.)

Based on Equations 4.6 and 4.7, the following relationship between the JP and the SPs can be formulated for a parent compound $A$ and its transformation products $y$:

$$JP = PP^A + \sum_y \frac{M^y_{\text{max}}}{M_0} \cdot SP^y/A.$$  \hspace{1cm} (4.8)

As $M^y_{\text{max}}/M_0$ is always smaller than 1, Equation 4.8 leads to a lower and an upper limit of the JP, which is given in Equation 4.9:

$$PP^A \leq JP \leq PP^A + \sum_y SP^y/A. \hspace{1cm} (4.9)$$

Different upper and lower limits of the JP can also be expressed in terms of PPs according to the following consideration: The transformation products $y$ are formed in all compartments that are accessible for the parent compound. Their contribution to the joint persistence (second term on the right-hand side of Equation 4.6) is determined by the transfer processes between the compartments and by the different formation and degradation rates in the three compartments. For a purely sequential transformation scheme with all $\theta_{xy} = 1$, this contribution to the JP is equal to or greater than the hypothetical contribution from the scenario where the transformation products are formed completely in those compartments where their PPs are lowest ($PP^y_{\text{min}}$ in Equation 4.10). In a similar way, the upper bound can be approximated by summing up the PP of the parent compound and the hypothetical contribution from the scenario where the transformation products are formed completely in those compartments where their PPs are highest ($PP^y_{\text{max}}$ in Equation 4.10). This leads to the following relationship for the special case of all $\theta_{xy} = 1$:

$$PP^A + \sum_y PP^y_{\text{min}} \leq JP \leq PP^A + \sum_y PP^y_{\text{max}}. \hspace{1cm} (4.10)$$

In most other cases where there are parallel reactions and where the fractions of formation for transformation of a precursor $x$ into different transformation products $y$ might not even add up to 1, which is what is allowed for in our algorithm, the lower limits in Equation 4.10 might be too high and the upper limits overestimate the actual JP considerably. In those cases, the $\theta_{xy}$s must be taken into account by multiplying $PP^y_{\text{min}}$ or $PP^y_{\text{max}}$ respectively with the product of all $\theta_{xy}$s or all
\( \theta_{\text{max}} \) of all transformation reactions that lead to a certain transformation product \( y \). The corresponding mathematical expression for the general case of \( \theta_{i}^{xy} \leq 1 \) is given in Equation 4.11, where the index \( ge \) stands for the series of subsequent transformation reactions that lead to a transformation product \( y \), and where \( \theta_{\text{min}}^{xy} \) and \( \theta_{\text{max}}^{xy} \) respectively are the fractions of formation in the compartments with the smallest and largest fraction of formation for that transformation step.

\[
\text{PP}^A + \sum_{y} \prod_{ge=B}^{y} \theta_{\text{min}}^{ge-1,ge} \text{PP}^y_{\text{min}} \leq \text{JP} \leq \text{PP}^A + \sum_{y} \prod_{ge=B}^{y} \theta_{\text{max}}^{ge-1,ge} \text{PP}^y_{\text{max}}. \quad (4.11)
\]

The advantage of these upper and lower bounds of the JP is that they can be derived from the PP values (i.e. from results obtained by assessing the transformation products as single substances in a level III model). In addition, the lower limit in Equation 4.11 is always more restrictive than the \( \text{PP}^A \) given as lower limit in Equation 4.9.

### 4.3 Two evaluative case studies

To illustrate the concepts of Secondary and Joint Persistence the two chemical examples from Chapter 3.3, atrazine and MTBE, are each expanded by one of their major transformation products, desisopropyl atrazine (DIA) and tert-butyl alcohol (TBA) respectively. DIA is a transformation product of atrazine often found, besides others, in the same places as atrazine itself (Solomon et al., 1996). TBA is one of the major degradation products of MTBE with a sufficiently large resistance to further degradation in soil and groundwater so that it may accumulate as an intermediate (Church et al., 1997; Church et al., 1999). Thus, both case studies represent parent compounds that are well-known environmental chemicals with transformation products that are present in the environment in considerable amounts (Church et al., 1997; Solomon et al., 1996; Squillace et al., 1996). The substance properties of the transformation products, namely the three degradation rates \( \kappa_i \) and the two partition coefficients \( K_H \) and \( K_{ow} \), are given in Table 4.1.

More specifically, the combinations atrazine-DIA (i) and MTBE-TBA (ii) have been chosen as case studies according to the ratio between the PP values of parent compound and transformation product, i.e. their persistence if each of them is released separately into the model system. They represent the two cases of (i) a persistent parent compound (atrazine) and a less persistent transformation product (DIA) and (ii) a persistent transformation product (MTBE) and a less persistent parent com-
Table 4.1: First-order degradation rates, octanol-water partitioning coefficient and Henry’s law constant for DIA (desisopropyl atrazine) and TBA (tert-butyl alcohol) (Lerch et al., 1998; Solomon et al., 1996; Howard et al., 1991; Mackay et al., 1993).

<table>
<thead>
<tr>
<th>compd</th>
<th>$\kappa_a$ ($s^{-1}$)</th>
<th>$\kappa_w$ ($s^{-1}$)</th>
<th>$\kappa_h$ ($s^{-1}$)</th>
<th>log $K_{ow}$</th>
<th>$K_H$ (Pa m³ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIA</td>
<td>3.50·10⁻⁶</td>
<td>2.50·10⁻⁶</td>
<td>5.38·10⁻⁵</td>
<td>1.15</td>
<td>1.18·10⁻⁴</td>
</tr>
<tr>
<td>TBA</td>
<td>4.01·10⁻⁸</td>
<td>4.46·10⁻⁸</td>
<td>3.26·10⁻⁷</td>
<td>0.35</td>
<td>1.46</td>
</tr>
</tbody>
</table>

pound (TBA). The PPs of the four compounds are listed in Table 4.2; they are contingent on the release scenario chosen. The ratio between the PPs of the parent compounds and the transformation products is around 10 for the pair atrazine-DIA and between 0.1 and 0.2 for the pair MTBE-TBA.

Table 4.2: PP values of the parent compounds atrazine and MTBE in comparison with the PP values of their transformation products DIA and TBA (in days).

<table>
<thead>
<tr>
<th>Atrazine-DIA</th>
<th>PP$_{Atrazine}$ (d)</th>
<th>PP$_{DIA}$ (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Release to soil</td>
<td>31.2</td>
<td>3.59</td>
</tr>
<tr>
<td>Release to water</td>
<td>43.3</td>
<td>4.63</td>
</tr>
<tr>
<td>Release to air</td>
<td>8.65</td>
<td>2.83</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MTBE-TBA</th>
<th>PP$_{MTBE}$ (d)</th>
<th>PP$_{TBA}$ (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Release to soil</td>
<td>21.3</td>
<td>148</td>
</tr>
<tr>
<td>Release to water</td>
<td>33.7</td>
<td>160</td>
</tr>
<tr>
<td>Release to air</td>
<td>16.6</td>
<td>64.6</td>
</tr>
</tbody>
</table>

In order to be inclusive of the most extreme case in which the maximal possible amount of transformation product is present in the environment, we assumed that the parent compounds are converted entirely into their respective transformation products in each compartment ($\theta_{az} = \theta_{aw} = \theta_{az} = 1$). Here, this assumption is used for the sake of clarity of the results and ignores the fact that in reality the parent compounds are transformed into a multitude of different transformation products whose relative share additionally depends on the degradation compartment.

For the calculation of the concentration profiles of the transformation products, Equation 4.2 was solved as shown in Equations 4.3 and 4.4 for $p = 3$ and $m = 2$. The results for Secondary and Joint Persistence (in days) as well as the estimates of
the upper and lower bounds of the JP are listed in Table 4.3 for the pairs atrazine-DIA and MTBE-TBA, respectively.

Table 4.3: SP values of the transformation products DIA and TBA and JP values of the pairs atrazine-DIA and MTBE-TBA (in days). In addition, the lower (LoLim) and upper limit (UpLim) estimates for the JP according to Equation 4.10 are given.

<table>
<thead>
<tr>
<th>Atrazine-DIA</th>
<th>$SP^{DIA/\text{Atrazine}}$ (d)</th>
<th>$JP^{\text{Atrazine-DIA}}$ (d)</th>
<th>LoLim (d)</th>
<th>UpLim (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Release to soil</td>
<td>42.2</td>
<td>34.8</td>
<td>34.0</td>
<td>35.8</td>
</tr>
<tr>
<td>Release to water</td>
<td>56.6</td>
<td>47.9</td>
<td>46.1</td>
<td>47.9</td>
</tr>
<tr>
<td>Release to air</td>
<td>5.87</td>
<td>11.8</td>
<td>11.5</td>
<td>13.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MTBE-TBA</th>
<th>$SP^{\text{TBA/MTBE}}$ (d)</th>
<th>$JP^{\text{MTBE-TBA}}$ (d)</th>
<th>LoLim (d)</th>
<th>UpLim (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Release to soil</td>
<td>134</td>
<td>87.9</td>
<td>85.9</td>
<td>181</td>
</tr>
<tr>
<td>Release to water</td>
<td>156</td>
<td>105</td>
<td>98.3</td>
<td>194</td>
</tr>
<tr>
<td>Release to air</td>
<td>123</td>
<td>81.5</td>
<td>81.2</td>
<td>177</td>
</tr>
</tbody>
</table>

In order to illustrate the persistence values in Table 4.3, the mass profiles on which the calculations of JP and SP are based are shown in Figures 4.2 and 4.3 and the corresponding persistence values are marked by vertical lines.

4.3.1 Comparison of Joint and Secondary Persistence

For the two pairs of chemicals analyzed here, the JP is maximally 5 times and the SP maximally 7 times bigger than the PP of the parent compound (Tables 4.2 and 4.3, release of MTBE to air). The highest JP values in our examples are slightly bigger than the sum of the two PPs. It can be shown though that with different substance input parameters, according to Equation 4.11, JPs can result that are several times bigger than the sum of the PPs in the same compartment.

If the SP is compared to the PP of the transformation product, one finds that the SP surpasses the PP significantly if a long-lived parent compound leads to a short-lived transformation product ($SP^{DIA} \approx 12.0 \cdot PP^{DIA}$ for the release of atrazine to water, Tables 4.2 and 4.3). In this situation, the amount of the transformation product is, after a short transient phase, directly proportional to the amount of the parent compound, which is referred to as secular equilibrium in radiochemistry (Lieser, 1997). The integration of transformation products into the risk assessment process
Figure 4.2: Combination of the overall mass profiles of the parent compound atrazine for three different release scenarios in a multimedia environment (left graphs) with the overall mass profiles of the transformation product DIA (middle graphs), resulting in three joint mass profiles (right graphs). The vertical lines indicate the position of the three persistence measures PP, SP and JP, respectively.
Figure 4.3: Combination of the overall mass profiles of the parent compound MTBE for three different release scenarios in a multimedia environment (left graphs) with the overall mass profiles of the transformation product TBA (middle graphs), resulting in three joint mass profiles (right graphs). The vertical lines indicate the position of the three persistence measures PP, SP and JP, respectively.
by conducting a single substance risk assessment for them as it is done in Belfroid et al. (1998) therefore seems questionable. The naturally occurring exposure is only represented properly if the transformation process itself is included into the calculations.

If the fractions of formation deviate from the assumed case that they all equal 1, the JP generally becomes smaller. Thereby the compartment-specific contribution of the transformation product \( y \) to the overall exposure is linearly proportional to its fraction of formation in that compartment. The value of the SP, however, does not change as long as the ratio of \( \theta_\text{sp} : \theta_\text{wp} : \theta_\text{ap} \) is kept constant and only the absolute values of \( \theta_\text{sp} \) vary. This is in agreement with the finding in Appendix B.2 that, in a single medium environment, the SP is not influenced by changing values of \( \theta_\text{sp} \). Similarly, Quartier and Müller-Herold (2000) found that the magnitude of the formation constant \( \kappa_\text{sp} \) has no influence on their calculation of secondary spatial ranges.

### 4.3.2 Comparison with measured mass profiles

The comparison of the mass profiles obtained by the model calculations presented here with mass profiles measured in field and laboratory experiments reveals congruence in some relevant aspects. A main finding of our calculations, namely that transformation products have an enhanced potential for persistence compared to their individual PP if the precursor compound is longer-lived than the individual transformation product, is confirmed by results presented in Solomon et al. (1996). There the occurrence of DIA as a transformation product of atrazine in different laboratory test systems is reported and the maximum of the experimental secondary mass profile lies at times as long as 275 days for some of the test systems. For the same series of measurements, maximal concentrations of DIA at 8% of the originally applied amount of atrazine have been found. This is consistent with our finding that even if atrazine is entirely transformed to DIA in all compartments, the maximal concentration of a short-lived transformation product such as DIA is still low (approx. 10% of the initial concentration of atrazine for release to soil and water).

Regarding the pair MTBE-TBA, several experimental studies (Church et al., 1997; Church et al., 1999; Salanitro et al., 1994) indicate that there is evidence that TBA is at least as resistant to biodegradation as MTBE. Salanitro et al. (1994) measured the primary mass profile of MTBE, the primary mass profile of TBA and the secondary mass profile of TBA for a mixed bacterial culture developed from microorganisms...
present in a chemical plant biotreater sludge. It was found that TBA alone and TBA as a transformation product of MTBE declined at a slower rate than MTBE did. This is in accordance with our findings. The maximal TBA concentration of 50\% of the amount of MTBE applied corresponds well to the maximal concentrations between 45\% and 50\% we calculated for the long-lived transformation product TBA for all three release scenarios. The agreement between calculated and experimental results is a reassuring indicator that our model system is successful in reflecting the relevant features of the mass profiles of parent compounds and their transformation products.

4.4 Conclusions

Although in these two case studies not all environmentally relevant transformation products of atrazine and MTBE are considered, the case studies demonstrate that inclusion of the transformation products leads to persistence values that are significantly different from those obtained for the parent compounds alone. Thus, we argue that transformation products should not be disregarded in the standard procedures for the assessment of chemicals.

As generally applicable measures for the persistence of transformation products, which might be used for regulatory purposes, the two quantities SP and SJP have varied advantages and shortcomings.

The SP seems to be well suited to characterize and compare individual transformation products as they occur in the transformation scheme. It indicates the temporal extent of the exposure of the environment to each single transformation product. As the SP is related to the particular transformation scheme in which the chemical occurs, it is not a property of the chemical alone, but also of its position in the transformation cascade of a particular parent compound. Thus, the SP allows one to establish an exposure-based ranking among the different transformation products of one parent compound, on which, for example, a priority list could be based that indicates transformation products in need of further, effect-based testing. Drawbacks of the SP are, first, that it gives no indication of the amount of transformation product present relative to the amount of the parent compound and, second, that, since its calculation is based on the maximum mass ($M_{\text{max}}^p$), the level IV system has to be solved explicitly in order to calculate the SP.

The JP, in comparison, contains information about how much the transformation
products contribute to the total mass in the system. It is therefore a suitable indicator of the total exposure of the environment to chemicals, caused by the release of the parent compound. A ranking of several parent compounds including transformation products according to their JP might considerably differ from a ranking based on the PP of the parent compounds alone as presented by Scheringer (1997).

As the JP can be calculated by means of matrix inversion, analogously to solving a level III system, customary spreadsheet programs for level III systems can easily be adopted to evaluate JP values.

In our concept of assigning persistence measures to transformation products, the JP is the key quantity that shows the relevance of the sum of all transformation products as compared to the parent compound alone. In addition, the SP provides auxiliary information if one is interested in a detailed assessment of the individual chemicals occurring in the transformation scheme.

In conclusion, we have shown how the fate of transformation products can be included in level III and level IV multimedia models and how the resulting additional exposure of the environment can be expressed by means of Joint and Secondary Persistence. Regarding the chemical risk assessment practice, these two quantities might be of particular importance if the transformation products have a higher toxicity than the parent compound or if their toxicity is unknown. In those cases, they might serve as useful quantities to anticipate, in accordance with the precautionary principle, possible effects.
Chapter 5

Case studies: nonylphenol polyethoxylates, perchloroethylene and atrazine

In this chapter, the concepts of Secondary and Joint Persistence are further investigated with regard to their applicability, content and significance. For that purpose, three chemicals including their transformation products were selected as case studies. These are the widely used herbicide atrazine, nonylphenol polyethoxylates (NPnEO) as a group of surfactants, and perchloroethylene, an industrial cleaning agent used in metal cleaning and dry cleaning.

The three chemicals have in common that they have been used historically in large amounts and, in the case of perchloroethylene and NPnEO, with little attention being paid to prevent their emission to the environment. For that reason, all three chemicals can be measured in the environment in considerable amounts. Also, each of them has certain transformation products that are present in the environment alongside the parent compound and that are known to possess potentially damaging properties, e.g., ecotoxicity, cancerogenic activity, estrogenic activity. As a consequence of their widespread presence and known harmful effects, they have been investigated extensively and therefore the data availability is sufficiently good – this was another reason for having chosen these three examples.

Apart from these common features, the three case studies differ in some decisive points. Regarding the emission scenario, they represent distinctively different cases. Atrazine, as an agrochemical, is produced to be applied to soil. Perchloroethylyene emissions are mainly fugitive emissions into air due to leaks in the nearly closed
cycles of the cleaning machines and spillage during decanting. NPnEO emissions are primarily emitted into receiving waters of sewage treatment plants, where some of the amount emitted by households and industry has already been partially transformed.

The case studies also differ with regard to the number of identified specific transformation products and the number of generations of transformation products. While five generations of transformation products and eleven transformation products are taken into account for atrazine, only three generations and eight transformation products, and three generations and five transformation products are considered relevant for perchloroethylene and NPnEO, respectively. Lastly, the significance and behavior of the transformation products relative to their parent compounds is different in the three case studies. This aspect will become clearer when the resulting mass distributions and persistence values are compared for the three case studies. The case studies are discussed in more detail in Chapters 5.1–5.3, while methodological aspects of substance data collection and processing are presented in Appendix C.1. In Chapter 5.4, model calculations for the three case studies are then performed and point estimates for PP, JP and SP are calculated. In Chapter 5.5, some first conclusions regarding the case studies and the applicability of the measures JP and SP are drawn.

For the discussion of the transformation schemes in the three case studies, it is important to know that the following rules were adhered to to estimate fractions of formation for the individual pathways: If no information was available for the decay of a certain precursor into its transformation products, generic fractions of formation were assumed, i.e. they were set to 1 in the case of a single transformation pathway only, to 0.5 for two parallel pathways, and to 0.33 for three parallel pathways. If more than one data point for a certain pathway was found, the average fraction of formation was calculated as arithmetic mean of all literature values. In some instances, the sum of the fractions of formation of a given precursor does not add up to 1, e.g., for NP1EO and NP1EC in water or for atrazine, DIA, DEA and HA in soil. This signifies that other compounds are being formed simultaneously which do not fall within the system boundaries of the investigations. Reasons for exclusion of compounds are as follows: (i) they do not comply with the selection criteria for specific transformation products, (ii) they are disputed or not unambiguously identified, or (iii) they are irreversibly bound to organic material (at least on the time-scale of the other degradation and transfer processes in the system).
5.1 Nonylphenol polyethoxylates (NPnEO) and their transformation products

In this case study we investigate the still widely used nonylphenol polyethoxylates (NPnEO) and their transformation products, including short-chain nonylphenol ethoxylates, nonylphenoxy carboxylic acids, and nonylphenol (NP). The entirety of all these substances, which basically are derivates of NP and which constitute the substance family of NPnEO and its transformation products, is abbreviated as NPE.

**NPE usage**

Nonylphenol ethoxylates are nonionic surfactants, consisting of an apolar alkylphenol moiety (branched or linear) and a polar ethoxy chain, whereas the chain length can vary between $n = 1-30$ (see Figure 5.1). Commercially used nonylphenol ethoxylates are mixtures of NPnEO compounds with different chain lengths. Usually, the distribution of oligomers in the original commercial mixture centers around NP9EO to NP15EO.

\[
\text{C}_9\text{H}_{19}-\overset{\text{O}}{\text{O}}-\overset{\text{CH}_2-\text{CH}_2-\text{O}}{\text{n}}-\text{H}
\]

*Figure 5.1: Molecular structure of nonylphenol polyethoxylates (NPnEO) with nonyl (\(\text{C}_9\text{H}_{19}\)) moiety, phenolic ring and \(n\) ethoxy units condensed onto it.*

NPE are HPV chemicals that have been used for more than 40 years as detergents, emulsifiers, wetting agents and dispersing agents. NPE containing products are used in many sectors, including textile processing, pulp and paper processing, oil and gas recovery, steel manufacturing and power generation (*E.C.*, 2000). The worldwide yearly production for private, agricultural and industrial usage amounts to 500'000 t (*Di Corcia et al.*, 2000).

In Switzerland NPEs were banned from use in domestic cleaning agents in 1987. However, industrial NPE usage in other products still exceeds 400 tons per year in Switzerland (*Rimml et al.*, 2000).

**NPnEO and its transformation products in the environment**

According to the oligomer distribution found in commercially available mixtures of NPnEO, the parent compound in our case study is assumed to have properties
typical of NP9EO to NP15EO. NPnEO are mainly emitted into waste waters of industrial facilities and households. Nowadays, most of these waste waters are treated in sewage treatment plants, during which treatment NPnEO are partially degraded by microorganisms to compounds with shorter ethoxy chains (NP1/2EO) and partly carboxylated ethoxy chains (NP1/2EC) and under anaerobic conditions further to nonylphenol (NP) (see Figure 5.2). These transformation products reach the environment via secondary effluent and sewage sludge. In the environment they are further degraded according to the scheme in Figure 5.2.

**Figure 5.2:** Simplified transformation scheme of NPnEO in waste water treatment plants and in natural environments (soil, water and sediment) according to Ahel et al. (1994a), Di Corcia et al. (1998), Ejlertsson et al. (1999), Kvestak and Ahel (1995), and Maguire (1999). The importance of the individual pathways in each environmental medium is expressed in terms of media-specific fractions of formation given in Table 5.1.

The degradation of long-chain ethoxylates during waste water treatment is quite efficient under aerobic conditions. The compounds with less ethoxy units, on the other hand, are more persistent. Under some conditions, smaller fractions of long-chain ethoxylates can also be carboxylated at the nonyl unit leading to doubly carboxylated metabolites with both the alkyl and the ethoxylate chain oxidized...
(CAPECs). As they are only measured occasionally (Jonkers et al., 2001), they are not included as transformation products.

Due to their higher $K_{ow}$ values as compared to the long-chain ethoxylates, the short-chain ethoxylates adsorb more strongly to particles and organic material. For the same reason, they possess a higher bioaccumulation potential and are more toxic than the long-chain ethoxylates. Besides their unspecific toxicity, the short-chain ethoxylates, acids and nonylphenol itself also display estrogenic activity, and therefore belong to the group of endocrine disrupters, which interfere with the hormone system by mimicking hormonal activity (Ahel et al., 2000; Jobling et al., 1996; Metcalfe et al., 2001).

NPnEO and its transformation products are found in virtually all water bodies and sediments in industrialized countries. In the 90ies, the highest concentrations were reported from Switzerland and the United Kingdom, in some situations reaching levels of up to 100 $\mu$g/l. Due to a number of risk reduction measures, such as restricted use in household products, the concentrations have sunken considerably since then, e.g. in Switzerland to about 5% of the concentration before the ban (Ahel et al., 2000). Today, concentrations of the lipophilic transformation products (NP, NP1EO, NP2EO) in secondary effluents of sewage treatment plants in Switzerland range between 1–5 $\mu$g/l, while concentrations for the acids (NP1EC, NP2EC) are approximately 5 times higher, ranging between 5–20 $\mu$g/l. A survey of nonylphenolic compounds in ambient waters revealed concentrations of 0.05–0.5 $\mu$g/l for the lipophilic transformation products, with NP being the most abundant component, and concentrations of 0.5–3 $\mu$g/l for the acids (Ahel et al., 2000). Regarding the higher concentrations of the acids, it is interesting to note that, although NP2EC and NP1EC are considered less toxic than the ethoxylates and NP, some experimental studies (Jobling et al., 1996) indicate that they are only slightly less estrogenic than NP and NP1EO. They might therefore contribute significantly to the endocrine-disrupting potential associated with NPnEO usage.

In most other industrialized countries, similar concentrations are measured in water. In a river in the Tokyo metropolitan area concentrations of NP between 0.05–1.08 $\mu$g/l and of NP1EO between 0.04–0.81 $\mu$g/l were measured (Isobe et al., 2001). Marcomini et al. (2000) measured NPE concentrations in the Venice lagoon in Italy and in two adjacent riverine stations and found concentrations of 1.1–38.5 $\mu$g/l for total NPnEO (n=0–20) and of 0.5–102 $\mu$g/l for the acids. They generally found the acids' concentrations to be 2–3 times higher in the river and 1–2 times lower in the rather anaerobic lagoon than the ethoxylates' concentrations.
Recent findings by Dachs et al. (1999) reveal the occurrence of NP in air too. They found NP in coastal and urban atmospheres, which NP reaches through water-to-air volatilization. Measured concentrations range between 0.13–81 ng/m³ in coastal and suburban air and may be relevant to human and ecosystem health.

Transformation scheme
The transformation scheme of NPnEO in the environment and in sewage treatment plants is given in Figure 5.2. The relative importance of the degradation pathways as shown in Figure 5.2 depends on the conditions in the environmental media. If there is enough oxygen present, as it is the case in surface water and upper soil layers, the carboxylation of NPnEO to NP1EC and NP2EC is favored. Therefore the fractions of formation $\theta_{1,s}$ and $\theta_{1,w}$ are estimated to be 0.7 (see Table 5.1). In aerobic media, NP is expected to be mineralized quickly. So the fractions of formation of NP in the aerobic soil compartment, $\theta_{3,s}$ and $\theta_{8,s}$, are set to 0 (note, however, that the mineralization of NP1EC and NP1EO proceeds through NP).

Table 5.1: Fractions of formation in the media soil, water and air. In air, no transformation reaction according to the scheme in Figure 5.2 are expected. The fractions of formation were determined from transformation schemes taken from Ahel et al. (1994a), Di Corcia et al. (1998), Ejlertsson et al. (1999), Kvestak and Ahel (1995) and Maguire (1999), and and from discussions with experts.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Fractions of formation in soil ($\theta_{r,s}$)</th>
<th>Fractions of formation in water ($\theta_{r,w}$)</th>
<th>Fractions of formation in air ($\theta_{r,a}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NPnEO$\rightarrow$NP2EC</td>
<td>0.7</td>
<td>0.7</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>NP2EC$\rightarrow$NP1EC</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>NP1EC$\rightarrow$NP</td>
<td>0</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>NPnEO$\rightarrow$NP2EO</td>
<td>0.3</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>NP2EO$\rightarrow$NP2EC</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>NP2EO$\rightarrow$NP1EO</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>NP1EO$\rightarrow$NP1EC</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>NP1EO$\rightarrow$NP</td>
<td>0</td>
<td>0.3</td>
<td>0</td>
</tr>
</tbody>
</table>

It has been shown that, under anaerobic conditions, NP is formed from NP1EO and NP1EC and that it is more persistent under these conditions (Isobe et al., 2001; Marcomini et al., 2000). Because, in the 3-box model, no anaerobic media
are represented, it is assumed that part of the water compartment includes some anaerobic sediment. Therefore the fractions of formation of NP in water, \( \theta_{3,w} \) and \( \theta_{8,w} \), are set to an arbitrary value of 0.3 to account for anaerobic formation of NP. The importance of oxidation of NP2EO to NP2EC and of NP1EO to NP1EC is not known exactly, so the fractions of formation \( \theta_{5,i} \) and \( \theta_{7,i} \) are set to 0.5 for all media \( i \) (see Table 5.1). The consequences of this simplification are tested in Chapter 6.3.1, where the JP is calculated for a 4-box model that explicitly includes an anaerobic sediment compartment.

In air, it is expected that NPnEO and its transformation products are efficiently degraded through reaction with OH-radicals and through photochemistry without building up any of the other transformation products. Therefore all fractions of formation in air, \( \theta_{r,a} \), are set to 0.

### Substance data

The Henry's law constant, \( K_H \), octanol-water partition coefficient, \( K_{ow} \), and media-specific half-lives of the six chemical species investigated here are given in Table 5.2.

**Table 5.2: Physico-chemical parameters and half-lives of NPnEO and its transformation products.** All values were calculated as geometric means when more than one data point was available. The underlying data collection can be found in Appendix C.2.1. The temperatures at which the degradation rates reported in the literature were measured vary between 284 and 310 K.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( K_H ) (Pa·m³/mol)</th>
<th>( \log K_{ow} )</th>
<th>( t_{1/2,a} ) (d)</th>
<th>( t_{1/2,w} ) (d)</th>
<th>( t_{1/2,a} ) (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPnEO</td>
<td>1.18 \cdot 10^{-26}</td>
<td>2.47</td>
<td>38.4</td>
<td>6.90</td>
<td>0.0406</td>
</tr>
<tr>
<td>NP2EC</td>
<td>3.21 \cdot 10^{-4}</td>
<td>1.34</td>
<td>21.2</td>
<td>34.3</td>
<td>0.144</td>
</tr>
<tr>
<td>NP1EC</td>
<td>0.0557</td>
<td>1.34</td>
<td>21.2</td>
<td>21.2</td>
<td>0.191</td>
</tr>
<tr>
<td>NP2EO</td>
<td>2.91 \cdot 10^{-4}</td>
<td>4.21</td>
<td>18.8</td>
<td>16.4</td>
<td>0.129</td>
</tr>
<tr>
<td>NP1EO</td>
<td>0.0506</td>
<td>4.17</td>
<td>29.8</td>
<td>25.9</td>
<td>0.166</td>
</tr>
<tr>
<td>NP</td>
<td>11.02</td>
<td>4.48</td>
<td>19.0</td>
<td>45.0</td>
<td>0.430</td>
</tr>
</tbody>
</table>

Because of a lack of experimental data, some of the \( K_H \) and \( K_{ow} \) values were estimated with the estimation software HenryWin (Meylan and Howard, 1991) and KowWin (Meylan and Howard, 1995). To specify the half-lives of NPnEO and its transformation products, data from 7 studies were collected (see Appendix C.2.1). If more than one half-life for a substance in one particular medium was found, the
geometric mean was calculated to determine an average half-life. The obtained average half-lives are in agreement with the faster degradation of long-chain NPE as compared to short-chain NPE as reported by Giger et al. (1984).

5.2 Perchloroethylene and its transformation products

The second case study focuses on perchloroethylene (PCE) and its transformation products. PCE and three of its transformation products, namely trichloroethylene (TCE), dichloroethylene (DCE) and vinylchloride (VC), are chlorinated solvents and belong to the group of volatile organic compounds (VOCs). They are used in many industrial processes because of their low flammability and low explosive potential. All of them are detected in air and groundwater and are reported world-wide (Yeh and Kastenberg, 1991).

**PCE usage**

In 1994, worldwide PCE production amounted to 245'000 t, 164'000 t of which were produced in Western Europe (ECETOC, 1999b). During the 1990s, the annual production level of PCE had fallen constantly, among other reasons because production of CFCs, for the production of which PCE was used as an intermediate, became restricted.

Nowadays, PCE is mainly used as solvent for fat, oils, greases, waxes, rubber, gum and tar. Its principal use is as solvent in the dry-cleaning industry (80%) and for vapor-phase metal degreasing in the engineering industry (18%). Other uses (2%) are as intermediate in the manufacture of trichloroacetic acid (TCA) and of fluorocarbons (CFCs, now banned, and HCFCs), as well as extracting agent in a number of chemical production steps (ECETOC, 1999b).

**PCE and its transformation products in the environment**

The majority of PCE released partitions into air, due to its high Henry’s law constant. In 1994, yearly releases in Western Europe during use were estimated to amount to approximately 70'000 t into the atmosphere and 8'000 t into the water from the secondary effluents of sewage treatment plants (ECETOC, 1999b). Due to its relatively long lifetime in air (1–5 months), PCE is found ubiquitously in the atmosphere (Wiedmann et al., 1994). In addition, due to careless handling, storage and its high chemical stability, it is also the most frequently encountered
groundwater contaminant. In a survey of ground water sources and drinking water supplies in 1985/86 in Germany, PCE was found in 49% of all drinking water supplies and in 14% of all groundwater sources. PCE is also a common contaminant of surface waters, while soil contamination with PCE is usually a rather local phenomenon. PCE contamination levels typically encountered in environmental media are compiled in Table 5.3.

Table 5.3: PCE concentrations measured in different environmental media up to the year 1994 (ECETOC, 1999b). It is generally assumed that, since then, levels have sunken further due to a decreasing production volume and increased use of closed systems in dry and metal cleaning.

<table>
<thead>
<tr>
<th>PCE in troposphere</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.014–0.069 µg/m³</td>
<td>over oceans in Southern hemisphere</td>
</tr>
<tr>
<td>0.048–0.882 µg/m³</td>
<td>over oceans and remote land in Northern hemisphere</td>
</tr>
<tr>
<td>0.14–2.1 µg/m³</td>
<td>over rural areas in Northern hemisphere</td>
</tr>
<tr>
<td>0.14–23 µg/m³</td>
<td>over urban and suburban areas in Northern hemisphere</td>
</tr>
<tr>
<td>&lt;0.001–0.115 µg/l</td>
<td>in rainwater and snow</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PCE in surface water</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001–0.0021 µg/l</td>
<td>open ocean</td>
</tr>
<tr>
<td>0.43 µg/l</td>
<td>ocean near coast</td>
</tr>
<tr>
<td>0.004–2.5 µg/l</td>
<td>in Western European rivers</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PCE in soil air</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5–30 µg/m³</td>
<td>industrial area in Germany</td>
</tr>
<tr>
<td>2.1–4.8 µg/m³</td>
<td>forest area in Germany</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PCE in sediment</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>30–6'000 µg/kg wet weight</td>
<td>Liverpool Bay, UK</td>
</tr>
<tr>
<td>18–50 µg/kg wet weight</td>
<td>River Rhine</td>
</tr>
</tbody>
</table>

The transformation of PCE released into air gives rise to mainly two groups of transformation products, besides the large amounts of phosgene (COCl₂) being formed in air (see Figure 5.3). On the one hand, there is the group of lesser chlorinated ethylenes (TCE, DCE, VC), which are formed when PCE is deposited onto soil and water surfaces and, from there, is transported into anaerobic environments, and, on the other hand, there is the group of chloroacetic acids (TCA, DCA, MCA),
which are formed when trichloroacetic acid chloride (TCAC) formed from PCE in the troposphere is hydrolyzed and deposited onto soil and water surfaces. Like PCE, the lesser chlorinated ethylenes are all major industrial chemicals belonging to the group of VOCs and are also present in the environment quite ubiquitously. All of them are well-known groundwater contaminants and while PCE, TCE, and DCE are only suspected carcinogens, VC has been unequivocally identified as such. The anaerobic biodegradation of PCE to TCE, DCE and VC therefore only adds to the concentrations already present in the environment due to their direct industrial usage. However, using a similar modelling concept as ours, it could be shown that, for emission scenarios in Los Angeles county, the exposure to these compounds is enhanced by two orders of magnitude when the linear biodecay from PCE to VC is considered in addition to the direct industrial emissions (Yeh and Kastenberg, 1991).

The three chloroacetic acids (TCA, DCA, MCA) are also widely distributed environmental pollutants and due to their phytotoxic potential are of considerable environmental concern. In fact, TCA and MCA have even been used as plant growth inhibitors until the late 1980s. Nowadays, the sources of chloroacetic acids present in the environment are less clear. The major sources currently under debate are as follows: (i) formation in the atmosphere by photochemical degradation of chlorinated solvents, and (ii) natural occurrence/formation. Mass flux calculations showed that precipitation is the major source of chloroacetic acids to water and soil (average concentrations in precipitations: MCA 1430–2770 ng/l, DCA 390–1370 ng/l, TCA 95–380 ng/l). In a study on mass fluxes and occurrence of TCA in Switzerland, waste water effluents were found to contribute an additional 27% to the total input of TCA into the environment (Berg et al., 2000).

Transformation scheme

Transformation scheme of PCE in troposphere

Tropospheric PCE is degraded to about 87% by OH- to yield COCl2 and to about 13% by Cl- to yield 80% TCAC and again 20% COCl2 (ECETOC, 1999b). Therefore the fractions of formation for COCl2 and TCAC, \( \theta_{1,a} \) and \( \theta_{2,a} \) in Table 5.4 were set to approx. 0.9 and 0.1, respectively.

The COCl2 formed in the troposphere is basically unreactive in the gaseous phase. Its reaction with OH- is endothermic, it is unreactive towards H2O vapor and its absorption cross-section near the UV and visible light is small (Helas and Wilson, 1992). But COCl2 is known to dissolve in water and hydrolyze. It is therefore most
Figure 5.3: Simplified transformation scheme of PCE in water and soil (solid arrows) and in air (dashed arrows). The transformation scheme was built from the transformation reactions discussed by Berg et al. (2000), Bradley (2000), Burston et al. (1993), Dilling et al. (1975), Fukami et al. (1995), Glaze et al. (1993), Haiber (1996), Holliger (1995), Kindler et al. (1995), Klier et al. (1999), Miyamoto and Urano (1996), Schöler (1998), Tuazon et al. (1988), Vogel et al. (1987), Wiesmann and Herbst (1999), Worsnop et al. (1992), and in BUA PCE (1994) and ECETOC (1999b). The importance of the individual pathways in each environmental medium is expressed in terms of media-specific fractions of formation given in Table 5.4.
likely to be removed from the troposphere by hydrolysis in cloudwater and subsequent deposition onto the ocean and other wet surfaces. An average tropospheric residence time for COCl\textsubscript{2} of about 70 d is assumed (Kindler et al., 1995). During that time about 91% of the COCl\textsubscript{2} is removed through hydrolysis in cloudwater and the remaining 9% reach the ocean surface by means of dry deposition and diffusion processes.

The TCAC formed in the troposphere is removed either by ways of photolysis with a lifetime of 60 d, the main product of that degradation pathway being COCl\textsubscript{2}, or by ways of hydrolysis in cloudwater to TCA with a lifetime of about 14 d (Kindler et al., 1995). This results in an overall lifetime for removal from the troposphere of around 11 d, with a 80% loss via wet removal to TCA (\(\theta_{6,a} = 0.8\)) and a 20% loss via photolysis to COCl\textsubscript{2} (\(\theta_{3,a} = 0.2\)). In contrast, values reported in literature for the overall lifetime of TCA against removal processes are somewhat higher, on the order of 20 d (Kindler et al., 1995) or smaller than 2 months (Worsnop et al., 1992). Most of the TCA formed in the troposphere is found to be attached to particles and is therefore removed from the troposphere by wet and dry particle deposition. The fraction of TCA remaining in the gaseous phase is oxidized by OH-. The products of this oxidation are not known. In the same manner, DCA and MCA, which may be transformation products of TCA formed in soil, water and sediment, are also oxidized by OH- in the troposphere. In these cases too no specific reaction products are known to have been reported.

The TCE formed in the sediment or in aquifers through anaerobic dehalogenation of PCE is often found in the troposphere because of its high volatility. There it is degraded by OH- to about 28% COCl\textsubscript{2}, with the remaining TCE being degraded by Cl- to DCA (50% of original TCE) and to 2 HC(O)Cl (16% of original TCE) (Tuazon et al., 1988). Therefore \(\theta_{4,a}\) and \(\theta_{5,a}\) in Table 5.4 were set to 0.28 and 0.50, respectively. DCE and VC formed in the sediment or in aquifers through anaerobic dehalogenation of TCE and DCE might also be found in the air compartment. DCE reacts to about 30% with OH- and to about 50% with Cl- present in the troposphere and decays nearly quantitatively to 2 equivalents of HC(O)Cl (Tuazon et al., 1988). VC is degraded quantitatively through the reaction with OH- to about equal parts to HC(O)Cl and to formaldehyde as intermediates before complete mineralization (BUA VC, 1989; Tuazon et al., 1988).
Table 5.4: Fractions of formation in the media soil, water and air. For explanation of values see text on transformation schemes in soil, water, air and sediment.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Fractions of formation in soil ($\theta_{r,s}$)</th>
<th>Fractions of formation in water ($\theta_{r,w}$)</th>
<th>Fractions of formation in air ($\theta_{r,a}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PCE→COCl₂</td>
<td>0</td>
<td>0</td>
<td>0.9</td>
</tr>
<tr>
<td>2</td>
<td>PCE→TCAC</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>TCAC→COCl₂</td>
<td>0</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>TCE→COCl₂</td>
<td>0</td>
<td>0</td>
<td>0.28</td>
</tr>
<tr>
<td>5</td>
<td>TCE→DCA</td>
<td>0.04</td>
<td>0.04</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>TCAC→TCA</td>
<td>1.0</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>7</td>
<td>PCE→TCE</td>
<td>0</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>TCE→DCE</td>
<td>0</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>DCE→VC</td>
<td>0</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>PCE→TCA</td>
<td>0.15</td>
<td>0.15</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>TCA→DCA</td>
<td>0.3</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>DCA→MCA</td>
<td>0.3</td>
<td>0.3</td>
<td>0</td>
</tr>
</tbody>
</table>

Transformation scheme of PCE in surface water and soil
The fate of PCE and its transformation products in the soil layer is quite similar to their fate in the water compartment as far as the transformation scheme is concerned. The two compartments are therefore discussed together.
PCE is resistant to aerobic biodegradation and is therefore not degraded biotically in surface waters and soil. However, it is subject to very slow abiotic degradation in both compartments with half-lives of around one year. Possible abiotic degradation processes are (a) direct photolysis, which is believed to be of minor importance (Atri, 1985; BUA PCE, 1994); (b) indirect photooxidation with free OH-radicals, which leads most likely in parts to a total mineralization and in parts to TCA and HCl (Dilling et al., 1975; Glaze et al., 1993); and (c) abiotic hydrolysis or dehalogenation, which probably also leads to TCA and HCl (Atri, 1985). From that information, fractions of formation for TCA of 0.15 for $\theta_{10,s}$ and $\theta_{10,w}$ were deduced.
Like PCE, TCE is also resistant to aerobic biodegradation, unless there are bacteria available which are capable of oxidizing it cometabolically with other compounds such as phenol, toluene, methane or propane (Wiesmann and Herbst, 1999). These conditions are quite likely to be present in the surface waters under consider-
ation (Bradley, 2000). In addition, in soil, large fractions consist of aromatic hydrocarbons and it is therefore believed that enough substrate for cometabolic oxidation is available. The cometabolic oxidation is most likely to follow a Michaelis-Menten-Kinetic, but so far has not been quantified properly (Wiesmann and Herbst, 1999). The remaining abiotic processes for degradation are again very slow and nearly negligible (Dilling et al., 1975). Possible abiotic processes for the degradation of TCE are (a) indirect photooxidation with free OH· radicals, which leads in some part to a total mineralization and in some parts to DCA and HCl (Dilling et al., 1975; Glaze et al., 1993); and (b) abiotic hydrolysis or dehalogenation, which probably also leads to DCA and HCl. The formation of DCA in soil and water was accounted for by setting $\theta_{DCA, s}$ and $\theta_{DCA, w}$ to 0.04.

In contrast to PCE and TCE, DCE can be mineralized through direct aerobic oxidation by many microbes present in most surface waters and soils (Bradley, 2000; Clement et al., 2000). Evidence for aerobic DCE biodegradation has been observed mainly in subsurface soils and stream-bed sediments so far (Clement et al., 2000). With a layer thickness of 10 cm, the model soil compartment comprises surface and subsurface soil layers and we therefore assume aerobic biodegradation to take place there. In addition, like TCE, DCE can also be degraded through cometabolic oxidation (Bradley, 2000; Clement et al., 2000). Both pathways are assumed to lead to complete mineralization of DCE.

COCl$_2$ and TCAC are both hydrolyzed very rapidly in water and in pore water of soil to CO$_2$ and HCl, or TCA and HCl respectively ($\theta_{DCA, s} = 1$ and $\theta_{DCA, w} = 1$).

TCA is not thought to be very stable in soil nor water, and decomposes in lysimeter or trickling filter experiments (Haiber, 1996; Schöler, 1998). The degradation mechanisms are not very well known yet, but the two most likely pathways are dechlorination to DCA and decarboxylation to CHCl$_3$ (Schöler, 1998). Both abiotic and microbial degradation are considered important elimination pathways leading to those products (Berg et al., 2000). In soil, it has been found that the transformation to DCA and CHCl$_3$ is not quantitative, but accounts only for about 30% of the original amount of TCA (Haiber, 1996) ($\theta_{DCA, s} = 0.3$). In water, the same behavior was assumed ($\theta_{DCA, w} = 0.3$).

No relevant literature regarding the degradation of DCA in soil and water could be found. In analogy to TCA, we assume reduction to MCA or mineralization to CO$_2$ and HCl to be the most likely degradation pathways ($\theta_{MCA, s} = 0.3$ and $\theta_{MCA, w} = 0.3$).

MCA is found mainly in the water compartment, where it is degraded either by very slow hydrolysis to glycolic acid or, more readily, through biodegradation to CO$_2$ and
HCl (Boethling and Alexander, 1979; Eriksson et al., 1995; Meylan and Howard, 1999). Different tests conducted according to OECD guidelines confirm that MCA is readily biodegradable (BUA MCA, 1993).

Transformation scheme of PCE in sediment layer
For the degradation of PCE, anaerobic biodegradation processes in subsurface environments are crucial. Because the 3-box model does not include a separate sediment compartment, parts of the water compartment were assumed to contain some sediment where anaerobic processes can take place. This assumption is supported by a recent study that showed that PCE and TCE are reductively dechlorinated in sediment columns, even under bulk aerobic conditions. As a possible explanation for this observation, anaerobic microsites have been suggested (Burston et al., 1993; Holliger, 1995). Still, the consequences of this simplification will be tested in Chapter 6.3.1, where the JP of PCE is calculated in a 4-box model that explicitly includes an anaerobic sediment compartment. Here, in the 3-box model, arbitrary values of \( \theta_{7,w} = \theta_{8,w} = \theta_{9,w} = 0.3 \) are used instead to represent the anaerobic degradation pathway of the chloroethenes in the model.

In the anaerobic region, reductive dechlorination, especially of the higher chlorinated ethenes (PCE and TCE) to their lesser chlorinated transformation products (DCE and VC), is the main transformation pathway for PCE. The reductive dechlorination can be carried out by microorganisms, collectively termed halorespirers, which are able to grow using chloroethenes as sole terminal electron acceptors (Bradley, 2000). PCE, with four chlorine atoms, is a stronger oxidant than all of the naturally occurring electron-accepting species in groundwater systems, with the notable exception of \( \text{O}_2 \). Thus, PCE readily undergoes reductive dechlorination to TCE except in aerobic environments. Reductive dechlorination of TCE to DCE occurs under \( \text{Fe(III)} \)-reducing conditions and in more strongly reducing environments. Reductive dechlorination of DCE to yield VC apparently requires at least \( \text{SO}_4 \)-reducing conditions. Because VC is the least oxidized of the chloroethenes, the reductive dechlorination of VC to the non-chlorinated product, ethene, is characteristically slow and significant only under highly reducing, methanogenic conditions (Bradley, 2000). Under comparable conditions, it is reduced to ethene about 10 times slower than the other chloroethenes (Ferguson and Pietari, 2000).

Through the reductive dechlorination of TCE, three DCE-isomers are formed, namely 1,1-DCE, 1,2-cis-DCE and 1,2-trans-DCE. In most experimental settings, 1,2-cis-DCE has been found to be the dominant transformation product with a share of
65-90% of the total DCE load formed (Bradley, 2000; BUA PCE, 1994; BUA TCE, 1993; Burston et al., 1993). In our model this distinction is neglected and mean properties are used.

*Substance data*

The Henry’s law constant $K_H$, octanol-water partition coefficient $K_{ow}$, and media-specific half-lives of the nine chemical species investigated here are given in Table 5.5. The only data points that could not be found in the scientific literature or in databases were the half-lives of DCA in soil and surface water. The biodegradation half-life of DCA was used as a surrogate, which was estimated by using the BioWin method in the EPIWIN package (Boethling et al., 1994). To specify the half-lives of PCE and its transformation products, data from 24 sources were collected (see Appendix C.2.2). For the specification of $K_H$ and $K_{ow}$ data from 11 studies were used. If more than one data point for a substance input parameter was found, the geometric mean was calculated to determine an average input value.

*Table 5.5: Physico-chemical parameters and half-lives of PCE and its transformation products. All values were calculated as geometric means when more than one data point was available. The underlying data collection can be found in Appendix C.2.2. The temperatures at which the degradation rates in soil, water and sediment reported in the literature were measured vary between 288 and 308 K. The temperature for the estimation and measurement of gas-phase degradation rates varied between 265 and 298 K.*

<table>
<thead>
<tr>
<th>Substance</th>
<th>$K_H$ (Pa·m$^3$/mol)</th>
<th>log $K_{ow}$ (-)</th>
<th>$t_{1/2,s}$ (d)</th>
<th>$t_{1/2,w}$ (d)</th>
<th>$t_{1/2,a}$ (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>1650</td>
<td>2.81</td>
<td>162</td>
<td>137</td>
<td>31.1</td>
</tr>
<tr>
<td>TCE</td>
<td>1000</td>
<td>2.74</td>
<td>1880</td>
<td>1440</td>
<td>2.76</td>
</tr>
<tr>
<td>DCE</td>
<td>689</td>
<td>1.86</td>
<td>42.0</td>
<td>42.0</td>
<td>3.14</td>
</tr>
<tr>
<td>VC</td>
<td>5370</td>
<td>1.46</td>
<td>14.7</td>
<td>14.7</td>
<td>1.22</td>
</tr>
<tr>
<td>COCl$_2$</td>
<td>905</td>
<td>-0.71</td>
<td>$1.01 \cdot 10^{-6}$</td>
<td>$1.01 \cdot 10^{-6}$</td>
<td>53.1</td>
</tr>
<tr>
<td>TCAC</td>
<td>131</td>
<td>0.90</td>
<td>$1.37 \cdot 10^{-7}$</td>
<td>$1.37 \cdot 10^{-7}$</td>
<td>11.3</td>
</tr>
<tr>
<td>TCA</td>
<td>2.03·10$^{-3}$</td>
<td>1.49</td>
<td>36.1</td>
<td>53.8</td>
<td>58.6</td>
</tr>
<tr>
<td>DCA</td>
<td>5.49·10$^{-3}$</td>
<td>0.92</td>
<td>3.50</td>
<td>3.50</td>
<td>11.0</td>
</tr>
<tr>
<td>MCA</td>
<td>6.22·10$^{-4}$</td>
<td>0.21</td>
<td>3.08</td>
<td>3.08</td>
<td>17.2</td>
</tr>
</tbody>
</table>
5.3 Atrazine and its transformation products

The third case study discusses the fate of the triazine herbicide atrazine (2-chloro-4-ethylamino-6-isopropyl-amino-s-triazine) (see Figure 5.4) and its transformation products. Atrazine is one of the most used herbicides worldwide. Because of its medium persistence in soil and water, the persistence of some of its transformation products and its relatively high mobility, atrazine itself and some of its primary transformation products are often encountered contaminants in surface waters and groundwater.

**Atrazine usage**

Atrazine is used as a selective herbicide for the control of annual broadleaf and grass weeds in corn, sorghum, sugarcane and other crops. Its use as vegetation control on banks and railways should be virtually eliminated by now. Atrazine controls its target weeds by reversible inhibition of photosynthesis.

Worldwide production in the 1980s was around 90'000 t/y and the use in the early 1990s amounted to 32'000–34'000 t/y in North America (Solomon et al., 1996) and to an average of about 1'000–2'000 t/y in European countries (per country) (Rippen, 1987). Application rates of the formulated products were reduced considerably from 3.4–5.6 kg/ha in 1990 to 2.2–2.8 kg/ha in 1993 (Solomon et al., 1996). In 1995, Ciba-Geigy, the original producer of atrazine, recommended a maximum rate of 1.5 kg active ingredient (a.i) per hectar according to the tenets of Good Farming Practice (Ciba, 1995a).

![Molecular structure of atrazine](image)

*Figure 5.4: Molecular structure of atrazine, belonging to the class of s-triazine derivatives.*

**Atrazine and its transformation products in the environment**

Atrazine, like most parent herbicides, is subject to slow, but complete mineralization in the environment. On the way to mineralization, however, a number of relatively stable and persistent transformation products can be formed (see Figure 5.5). Indeed, research has shown that transformation products of atrazine are prevalent in
surface water and groundwater, in groundwater often being more frequently detected than the parent compound itself (by a factor of up to 12) (Kolpin et al., 2001; Lerch et al., 1999). The aquatic ecological effects of atrazine and its transformation products therefore are of possible concern, especially since some of the transformation products are phytotoxic too (even though by a factor of 5–10 less than the parent compound (Solomon et al., 1996)).

Dissipation of atrazine applied to soil in pre- and post-emergence applications happens, due to its moderate solubility, through surface runoff and leaching, as well as through volatilization. Because of its low hydrolysis and aqueous photolysis rate, an extended stay in the water compartment has to be expected. While DEA is more mobile than atrazine, the hydroxylated transformation products (HA, DEHA, DIHA) are less mobile than atrazine and therefore show a reduced leaching potential. Atrazine concentrations measured in the environment are 0.56–9.0 \( \mu \text{g/l} \) in Midwestern rivers in the U.S., and 0.37–4.7 \( \mu \text{g/l} \) in Midwestern lakes and reservoirs (Solomon et al., 1996). The concentrations of the transformation products in % of the concentration of the parent compound amount to 12–28% for DEA and 4.9–15% for DIA in the rivers, and to 18–39% for DEA, 5–24% for DIA and 38% for HA in the reservoirs. These concentrations display a typical pattern for transformation products of atrazine in water, namely a DEA:DIA ratio of about 3:1, and that HA is generally the most abundant transformation product. Besides HA, other hydroxylated transformation products (DEHA, DIHA) were also measured in creeks and streams with concentrations ranging from <0.12–1.9 \( \mu \text{g/l} \) for DEHA and <0.12–0.72 \( \mu \text{g/l} \) for DIHA. HA concentrations in the same location were between 0.18–0.57 \( \mu \text{g/l} \) (Lerch et al., 1998).

Given the U.S. EPA maximum permissible contaminant level for atrazine or any of its transformation products of 3 \( \mu \text{g/l} \), this level is found to be quite frequently exceeded in natural water bodies. Similarly, the European maximum permissible level of s-triazine herbicides in drinking water of 0.1 \( \mu \text{g/l} \) was found to be exceeded in 10% of water samples taken in the UK (Comber, 1999).

Due to a volatilization loss of around 2% of the applied mass, trace concentrations of atrazine, DEA and DIA are found in the air and have been shown to be transported atmospherically over hundreds of kilometers, which resulted in their precipitation onto pristine areas. Concentrations measured in the precipitation range from 0.005–1.8 \( \mu \text{g/l} \) (Thurman and Cromwell, 2000).
Figure 5.5: Simplified transformation scheme of atrazine in water and soil (solid arrows) and in air (dashed arrows). The transformation scheme was built from the transformation reactions discussed by Acero et al. (2000), Minero et al. (1992), Pelizzetti et al. (1990), Thurman et al. (1994), Torrents et al. (1997), and Störmann and Jastorff (1993). The importance of the individual pathways in each environmental medium is expressed in terms of media-specific fractions of formation given in Table 5.6.
Transformation scheme
The degradation of atrazine in the environment occurs through biotic and abiotic processes. Because the s-triazine ring is quite resistant to biological degradation, abiotic processes are comparably important in the case of atrazine. Typical degradation processes occurring, both biotically and abiotically, are dechlorination, alkyl side chain oxidation, N-dealkylation, deamination and final ring cleavage. Different sequential combinations of these degradation processes lead to the variety of transformation products that make up the transformation scheme in Figure 5.5.

Table 5.6: Fractions of formation of the transformation products of atrazine in the media soil, water and air. The fractions of formation were determined from transformation schemes taken from Acero et al. (2000), Ciba (1995b), Comber (1999), Lerch et al. (1998), Minero et al. (1992), Pelizzetti et al. (1990), Störmann and Jastorff (1993), Thurman et al. (1994), and Torrents et al. (1997).

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Fractions of formation in soil ($\theta_{r,s}$)</th>
<th>Fractions of formation in water ($\theta_{r,w}$)</th>
<th>Fractions of formation in air ($\theta_{r,a}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Atrazine $\rightarrow$ DEA</td>
<td>0.08</td>
<td>0.10</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>Atrazine $\rightarrow$ DIA</td>
<td>0.03</td>
<td>0.05</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>Atrazine $\rightarrow$ HA</td>
<td>0.10</td>
<td>0.09</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>DEA $\rightarrow$ DEHA</td>
<td>0.16</td>
<td>0.25</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>DEA $\rightarrow$ DAA</td>
<td>0.29</td>
<td>0.47</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>DIA $\rightarrow$ DIHA</td>
<td>0.09</td>
<td>0.12</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>DIA $\rightarrow$ DAA</td>
<td>0.33</td>
<td>0.46</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>HA $\rightarrow$ DIHA</td>
<td>0.1</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>HA $\rightarrow$ DEHA</td>
<td>0.3</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>DIHA $\rightarrow$ DAHA</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>DEHA $\rightarrow$ DAHA</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>DAA $\rightarrow$ DAHA</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>13</td>
<td>DAA $\rightarrow$ atr9</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>14</td>
<td>DAHA $\rightarrow$ atr10</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>15</td>
<td>atr9 $\rightarrow$ atr10</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>16</td>
<td>atr9 $\rightarrow$ atr11</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>17</td>
<td>atr10 $\rightarrow$ CYA</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>18</td>
<td>atr11 $\rightarrow$ CYA</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
Of all abiotic degradation processes, photocatalytic degradation, mainly initiated by OH· radicals, is the most important process in soil and water. For this reason, the transformation scheme for the air compartment, where atmospheric oxidation by OH· radicals is the main degradation process, is very similar to those in soil and water. However, according to Pelizzetti et al. (1990), DEHA and DIHA are not formed in the air compartment.

The transformation products that are oxidized at the alkyl side chain are only minor transformation products and have not been reported to have been found in the environment in measurable amounts. Thus, they were not included in the transformation schemes.

The last compound considered in the transformation scheme of atrazine is cyanuric acid (CYA). It is believed to be a natural compound as can be concluded from its isolation from soil as early as 1917 (Novartis, 1995). CYA has been shown to be inert to direct and indirect photolysis (Pelizzetti et al., 1990) and is relatively stable towards biodegradation due to its aromatic structure. Once ring cleavage is achieved though, the resulting transformation product is biuret (H₂N(C(O)NHC(O)NH₂), which is readily transformed to urea, an ubiquitous natural compound. Therefore, the transformation products of CYA are not further considered in the transformation scheme.

Transformation scheme of atrazine in surface water and soil

For the abiotic degradation of atrazine, indirect photolysis is the most important pathway (half-life of 2–10 d) and direct photolysis the least important (half-life of approximately 1 y). For the biological degradation, half-lives range between 10–114 d in aerobic waters and soils. The three predominant transformation products of the first generation are DIA, DEA and HA. All three are only formed in amounts around or smaller than 10% of the original mass of the parent compound, with HA being the major transformation product in most cases, sometimes even surpassing 10%. For the transformation of atrazine into DEA, DIA and HA, different fractions of formation were obtained from Ciba (1995b), Comber (1999), Lerch et al. (1998), Thurman et al. (1994), and Torrents et al. (1997), and from own calculations based on concentration profiles in Solomon et al. (1996) and in Winkelmann and Klaine (1991). For each transformation reaction in soil and water the arithmetic mean of all fractions of formation was calculated. The values for reactions 1–3 in soil and water range between 0.03 and 0.1 and are given in Table 5.6.

One reason for the low fractions of formation of the first few generations are the large fractions of atrazine and its transformation products DEA, DIA and HA that
are bound to organic matter and plants. These fractions, called bound residues, are defined as molecules that remain associated with various fractions of soil even after intensive extraction with polar and nonpolar solvents. Bound residues are generally not bioavailable to animals living in soil, but have been shown to be bioavailable to plants (Winkelmann and Klaine, 1991). As the time-scale of their re-mobilization (approx. 10 years) is considerably different from the time-scale of the transformation half-lives of the extractable fraction, they were not further considered in our model. If the aim was to predict realistic local concentrations, the bound residues would have to be taken into account as continuous background source. Bound residues for atrazine, DEA, DIA and HA are assumed to account for 61%, 45%, 42% and 40% respectively of the amount of each compound present in the whole system (Ciba, 1995b; Novartis, 1997). The fractions of formation for DEA and DIA further reflect the finding that deethylation versus deisopropylation always proceed in ratios of ~3:1 in soil and of ~2:1 in water and air (Thurman et al., 1994).

For the transformation of DEA and DIA in water to DEHA, DIHA and DAA, fractions of formation for direct and indirect photolysis (Torrents et al., 1997) and under natural light (Comber, 1999) could be found. Again, the arithmetic mean was calculated and $\theta_{4,w} - \theta_{7,w}$ were found to range between 0.12–0.47. Since it was assumed that in water only 10% of the compounds were bound to organic matter, the fractions of formation of DEHA and DIHA from HA in water were obtained by splitting the remaining 90% HA using the ratio 2:1 for deethylation versus deisopropylation ($\theta_{8,w} = 0.3$, $\theta_{9,w} = 0.6$).

The fractions of formation for the corresponding first-to-second-generation reactions in soil were obtained by using the same ratios for parallel reactions as in water, but scaling the percentage of decay to the readily available fractions of DEA, DIA and HA, i.e. the remaining fractions that were not present in the form of bound residues (see $\theta_{4,s} - \theta_{9,s}$ in Table 5.6).

From the second generation of transformation products onwards, no information could be found either on the amounts of compounds present as bound residues or on the fractions of formation. Therefore generic fractions of formation in soil and water were assumed, i.e. equal shares were attributed to all parallel transformation reactions of a given precursor (see $\theta_{10,s} - \theta_{18,s}$ and $\theta_{10,w} - \theta_{18,w}$ in Table 5.6).

Transformation scheme of atrazine in troposphere
As mentioned before, the transformation scheme of atrazine in air resembles the scheme in soil and water with the exception that DIHA and DEHA are not being
formed (Pelizzetti et al., 1990). Regarding the fractions of formation, it can be found that reaction 3 (formation of HA) is of minor importance, accounting for only 10% of the initial degradation of atrazine (θ_{3,a}=0.1), and that the main degradation routes go through reaction pathways 1 and 2. These were split according to the ratio 2:1 for deethylation versus deisopropylation for reaction with OH\- radicals (Thurman et al., 1994) (θ_{1,a}=0.6 and θ_{2,a}=0.3).

No information could be retrieved about the fractions of formation of the remaining transformation reactions in air. Thus, generic fractions of formation were attributed to the remaining transformation pathways in air too.

**Substance data**

The Henry’s law constant, \( K_H \), organic carbon-water partition coefficient, \( K_{oc} \), and media-specific half-lives of the twelve chemical species investigated here are given in Table 5.7.

**Table 5.7:** Physico-chemical parameters and half-lives of atrazine and its transformation products. All values were calculated as geometric means when more than one data point was available. The underlying data collection can be found in Appendix C.2.3. The temperatures at which the degradation rates reported in the literature were measured vary between 284 and 308 K.

<table>
<thead>
<tr>
<th>Substance</th>
<th>( K_H ) (Pa\cdot m^3/mol)</th>
<th>( K_{oc} ) (-)</th>
<th>( t_{1/2,a} ) (d)</th>
<th>( t_{1/2,W} ) (d)</th>
<th>( t_{1/2,A} ) (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>3.61 \times 10^{-4}</td>
<td>129</td>
<td>42.1</td>
<td>34.4</td>
<td>0.186</td>
</tr>
<tr>
<td>DEA</td>
<td>1.55 \times 10^{-4}</td>
<td>56.1</td>
<td>33.3</td>
<td>4.50</td>
<td>0.434</td>
</tr>
<tr>
<td>DIA</td>
<td>1.18 \times 10^{-4}</td>
<td>61.4</td>
<td>32.2</td>
<td>3.67</td>
<td>0.894</td>
</tr>
<tr>
<td>HA</td>
<td>6.36 \times 10^{-8}</td>
<td>793</td>
<td>88.3</td>
<td>7</td>
<td>0.291</td>
</tr>
<tr>
<td>DIHA</td>
<td>3.51 \times 10^{-11}</td>
<td>600</td>
<td>7</td>
<td>7</td>
<td>0.0514</td>
</tr>
<tr>
<td>DEHA</td>
<td>4.66 \times 10^{-11}</td>
<td>927</td>
<td>7</td>
<td>7</td>
<td>0.0486</td>
</tr>
<tr>
<td>DAA</td>
<td>4.02 \times 10^{-5}</td>
<td>54.7</td>
<td>19.0</td>
<td>14</td>
<td>68.0</td>
</tr>
<tr>
<td>DAHA</td>
<td>1.21 \times 10^{-11}</td>
<td>298</td>
<td>7</td>
<td>7</td>
<td>0.187</td>
</tr>
<tr>
<td>atra9</td>
<td>1.19 \times 10^{-5}</td>
<td>20.8</td>
<td>7</td>
<td>7</td>
<td>42.4</td>
</tr>
<tr>
<td>atra10</td>
<td>9.86 \times 10^{-10}</td>
<td>47.5</td>
<td>7</td>
<td>7</td>
<td>0.349</td>
</tr>
<tr>
<td>atra11</td>
<td>9.82 \times 10^{-10}</td>
<td>124</td>
<td>7</td>
<td>7</td>
<td>26.7</td>
</tr>
<tr>
<td>CYA</td>
<td>1.38 \times 10^{-13}</td>
<td>124</td>
<td>6.90</td>
<td>7</td>
<td>51.1</td>
</tr>
</tbody>
</table>

Data for the species DEHA, DIHA, DAHA and atra9–atra11 were very scarce and were therefore mainly estimated with the help of the EPIWIN package (Meylan and
Howard, 1999). To specify the half-lives of atrazine and its transformation products, data from 32 studies were collected (see Appendix C.2.3). For the specification of $K_H$ and $K_{sc}$, data from 7 studies were used. If more than one data point for a substance input parameter was found, the geometric mean was calculated to determine an average input value.

5.4 Results for Primary, Secondary and Joint Persistence

5.4.1 Mass distributions

Regarding the mass distributions, two questions are of interest. First, how much the single compounds contribute to the total mass in the system (see left graphs in Figure 5.6) and second, how the individual compounds are distributed between the compartments air, soil and water (see right graphs in Figure 5.6). In order to obtain the mass distributions, steady state was assumed and all three case studies were solved as level III systems. Inputs were assumed to be to water for NPnEO, to air for PCE and to soil for atrazine. The resulting distributions for all three case studies are given in Figure 5.6.

The share of total mass attributable to the parent compound versus to the entirety of all transformation products differs considerably between the three case studies. While for NPnEO the parent compound accounts for only 10% of the total mass, PCE accounts for 37% within its substance family and atrazine for 77%.

In more detail, all transformation products in the NPnEO case study make large contributions to the overall mass, with two of five (NP2EC, NP1EC) accounting for higher shares than the parent compound itself. In the PCE case study, there is only one dominant transformation product, namely COCl₂, with a share of 57%. Besides COCl₂, only TCA and TCAC contribute more than 1%, while the contribution of all other transformation products is negligible. In short, only the first generation of transformation products in air contributes to the overall mass in the PCE case study.

In the atrazine case study, the parent compound itself is clearly dominant and only one transformation product, namely HA, has a share bigger than 10%, which agrees well with experimental findings (see Chapter 5.3). Except for DEA with a share of 3%, all transformation products other than HA are equally important with shares of
Figure 5.6: Contribution of parent compound and transformation products to the total mass in the system (left graphs, scaled to 1) and mass distributions of all compounds in the system between the compartments soil, water and air (right graphs). System was solved for steady-state conditions, i.e. as level III model. Emissions were to water for NPnEO, to air for PCE and to soil for atrazine.
around 1%. One reason for that similarity between second and higher generations of transformation products of atrazine might be that the half-lives in soil and water of most of these compounds had to be estimated with BioWin (Boethling et al., 1994) and ended all up being 7 days. Therefore, compounds of later generations display virtually the same persistence and partitioning behavior as their precursors, which makes them all equally important. Given the current lack of data, it might therefore not be necessary to model them all individually.

The three case studies further differ with respect to the favorite residence compartments of their compounds. These depend on the partition coefficients and the half-lives of the compounds, but also on the relative amount with which they are emitted to or formed in the three different compartments. A first approximation of the actual distribution behavior which includes the emission or formation scenario can be obtained by comparing the partition coefficients of the compound in question to the partition coefficients of a large set of compounds and their respective distribution behavior in a level II model, and thereafter predict the distribution behavior of the compound in question. Along these lines, Gouin et al. (2000) developed a two-dimensional plot of log $K_H$ versus log $K_{ow}$ which allows to estimate the distribution behavior of a chemical from these two partition coefficients. This method was applied to all compounds in all three case studies and the resulting favorite residence compartments are listed in Table 5.8.

The results from the level III system indicate that NPnEO and its transformation products are all mainly found in water. This is due to their high water solubility, and therefore low $K_H$, which originates from the polar ethoxy chain. In the case of NP, only the nonpolar part of the original NPnEO surfactant is left, leading to a considerably higher $K_H$ value, which manifests itself in the fact that NP is the only compound for which model calculations indicate a small fraction in air (1%). This mass distribution for NP is in agreement with findings by Dachs et al. (1999), who measured small amounts of NP in air, and with the mass distribution for NP as predicted according to Gouin et al. (2000) (see Table 5.8).

In contrast to the NPnEO case study, the PCE case study shows distinctly different favorite residence compartments for different compounds. The prediction of the distribution behavior of the chloroacetic acids and TCAC, based on their partition coefficients, shows a clear preference for the water compartment (with TCA also showing some preference for the soil and TCAC for the air compartment), while PCE itself and the other chloroethylenes as well as COCl$_2$ clearly prefer to partition into air. For all compounds with the exception of the lesser chlorinated ethylenes
Table 5.8: Favorite residence compartments of all compounds in the three case studies, determined for a level II model according to Gouin et al. (2000).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Favorite residence compartments</th>
<th>Compounds</th>
<th>Favorite residence compartments</th>
<th>Compounds</th>
<th>Favorite residence compartments</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPnEO</td>
<td>s/w</td>
<td>PCE</td>
<td>a</td>
<td>Atrazine</td>
<td>s/w</td>
</tr>
<tr>
<td>NP2EC</td>
<td>s/w</td>
<td>TCE</td>
<td>a</td>
<td>DEA</td>
<td>s/w</td>
</tr>
<tr>
<td>NP1EC</td>
<td>s/w</td>
<td>DCE</td>
<td>a</td>
<td>DIA</td>
<td>s/w</td>
</tr>
<tr>
<td>NP2EO</td>
<td>s/w</td>
<td>VC</td>
<td>a</td>
<td>HA</td>
<td>s/w</td>
</tr>
<tr>
<td>NP1EO</td>
<td>s/w</td>
<td>COCl₂</td>
<td>a</td>
<td>DIHA</td>
<td>s/w</td>
</tr>
<tr>
<td>NP</td>
<td>s/w/a</td>
<td>TCAC</td>
<td>w/a</td>
<td>DEHA</td>
<td>s/w</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TCA</td>
<td>s/w</td>
<td>DAA</td>
<td>s/w</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DCA</td>
<td>w</td>
<td>DAHA</td>
<td>s/w</td>
</tr>
<tr>
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<td></td>
<td>MCA</td>
<td>w</td>
<td>atra9</td>
<td>s/w</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>atra10</td>
<td>s/w</td>
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<td></td>
<td></td>
<td></td>
<td>atra11</td>
<td>s/w</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CYA</td>
<td>s/w</td>
</tr>
</tbody>
</table>

(TCE, DCE, VC), the results from modelling are in agreement with the distribution behavior predicted from the partition coefficients (see Table 5.8). The reason for this is that, according to our assumptions regarding reductive dechlorination (reactions 7–9 in the PCE case study), the lesser chlorinated ethylenes are only formed in the anaerobic part of the water compartment, and have to volatilize back into air. This is equivalent to assuming that their input is into the water compartment, which seems to change their distribution behavior as compared to that predicted from their partition coefficients.

The partitioning behavior of atrazine and its transformation products as predicted from their partition coefficients alone is similar to that of NPnEO and its transformation products in that the compounds of both substance families are predicted to partition between soil and water. However, while the model results for the atrazine substance family actually show partitioning between soil and water with varying relative shares, the results for the NPnEO substance family indicate that all compounds are mainly found in water. This different behavior as compared to the atrazine substance family, notwithstanding their similar partition coefficients, must be due to the fact that NPnEO is emitted to water and all transformation products...
are subsequently formed in water, while atrazine is emitted to soil and the transformation products of the first and second generation are mainly formed in soil. For higher generations of atrazine the tendency is towards partitioning into water, which agrees with the observations for the NPnEO case study that compounds with this sort of partitioning characteristics stay in water once they are emitted to or formed in water.

All in all, the mass distributions reflect the distribution behavior of parent compounds and transformation products that is to be expected from their partition coefficients and their particular emission and formation scenarios.

5.4.2 Primary, Secondary and Joint Persistence values

The same PP and JP values are obtained either from solving the level III or level IV system, as explained in Chapter 3.2. The values for the SP, however, can only be calculated from the time-dependent solutions of the level IV system. The resulting secondary concentration functions are converted to overall mass profiles for the individual compounds by multiplication with the compartments' volumes and summation over all compartments. The resulting mass profiles are given in Figure 5.7 for all three case studies. The persistence values deduced from these mass profiles according to Equations 4.5–4.7 in Chapter 4.2.2 are listed in Table 5.9. For the sake of simplicity and because each transformation product can be unambiguously attributed to one of the parent compounds NPnEO, PCE or atrazine, the index y/x for the Secondary Persistence will be shortened to y in the following case studies.

A comparison of the primary mass profiles (PMP) with the joint mass profiles (JMP) once more shows that the transformation products make up large parts of the JMP in the case of NPnEO, while, in the case of atrazine, the JMP is still dominated by the PMP of atrazine itself. With regard to the persistence values themselves, this translates into a quotient of 10.2 between JP and PP for NPnEO, of 2.72 for PCE and a quotient of only 1.31 for atrazine. These quotients reflect the importance of the transformation products in extending the persistence of the parent compound, i.e. they are representative of the extra amount of time the environment is exposed to chemicals due to the formation of transformation products.

The contribution of the individual transformation products to the JP ($R^y_{JP}$) is defined by the expression given in Equations 5.1. Consequently, $R^y_{JP}$ is exactly equivalent to the contributions to the total steady-state mass in the system depicted in Figure 5.6 (left graphs). The mass distribution graphs can therefore also be read as an...
illustration of the contribution of the single transformation products to the JP.

$$R_{JP}^{y} = \frac{\sum_{i} e_{i}^{y} \cdot v_{i}}{\sum_{i} e_{i}^{A} \cdot v_{i} + \sum_{y} \sum_{i} e_{i}^{y} \cdot v_{i}} = \frac{\sum_{i} c_{i}^{\text{stat},y} \cdot v_{i}}{\sum_{i} c_{i}^{\text{stat},A} \cdot v_{i} + \sum_{y} \sum_{i} c_{i}^{\text{stat},y} \cdot v_{i}} \quad (5.1)$$

Another interesting finding with regard to PP and JP values is that, according to the PP, NPnEO is the least persistent compound, PCE the second persistent compound and atrazine the most persistent compound, i.e. $\text{PP}(\text{NPnEO})<\text{PP}(\text{PCE})<\text{PP}(\text{atrazine})$. When the JP values are considered, however, atrazine and its transformation products form the least persistent substance family, the substance family of NPnEO the second persistent and that of PCE the most persistence substance family, i.e. $\text{JP}(\text{atrazine})<\text{JP}(\text{NPnEO})<\text{JP}(\text{PCE})$. If the chemicals were rank-ordered according to their persistence values, different rank orders would be derived, depending on whether the ranking is based on PP or JP values. In the case studies presented here, two of three rankings would be changed, i.e. $\text{PP}(\text{NPnEO})<\text{PP}(\text{atrazine})$ to $\text{JP}(\text{NPnEO})>\text{JP}(\text{atrazine})$ and $\text{PP}(\text{PCE})<\text{PP}(\text{atrazine})$ to $\text{JP}(\text{PCE})>\text{JP}(\text{atrazine})$, while $\text{PP}(\text{NPnEO})<\text{PP}(\text{PCE})$ stays.

The above discussion of the JP points out that the contribution of some of the transformation products, especially those of later generations, to the JP is marginal because they are formed in small amounts only. Still, this conclusion should not hide the fact that all of these transformation products are present in the environment and that they might display considerable persistence, albeit at low concentrations. In order to grasp that particular behavior, the SP was introduced as a second measure, which is calculated by normalizing the exposure by the actual maximal concentration in the environment. The SP is therefore able to reflect the temporal behavior of individual transformation products.

From the case study results in Table 5.9 it can be seen that the SP of the individual transformation products often surpasses the JP. This is, for example, the case for the SP of NP1EC and NP in the NPnEO case study, for the chloroacetic acids in the PCE case study and for all compounds in the atrazine case study. Especially in the case of DCA and MCA and in the case of most of the transformation products of atrazine, these are compounds which are only present in small amounts. The fact that their SP surpasses the JP, however, might be interpreted as a trigger to look beyond their importance for the JP and to examine those transformation products individually and in more detail. This examination might involve toxicity tests with particular attention to low-dose effects, and an examination of the substances' leaching potential. For NP, for example, with a contribution of only 10% to the JP,
Figure 5.7: Time-dependent mass profiles for the three case studies, obtained by solving the level IV system (PMP: Primary Mass Profile of the parent compound; JMP: Joint Mass Profile of all compounds; TP's: Transformation products).
Table 5.9: Point estimates for the Primary, Secondary and Joint persistence values for all three case studies.

<table>
<thead>
<tr>
<th></th>
<th>PP (d)</th>
<th>SP (d)</th>
<th>JP (d)</th>
<th>JP/PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPnEO</td>
<td>9.98</td>
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</tr>
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<th>SP (d)</th>
<th>JP (d)</th>
<th>JP/PP</th>
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<tr>
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<td>TCE</td>
<td>88.1</td>
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<td>DCE</td>
<td>95.8</td>
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<td>VC</td>
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<td>TCAC</td>
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</tr>
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</tr>
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<td>MCA</td>
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<td></td>
</tr>
<tr>
<td>All</td>
<td>122</td>
<td>2.72</td>
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<table>
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<tr>
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<th>PP (d)</th>
<th>SP (d)</th>
<th>JP (d)</th>
<th>JP/PP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
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<td></td>
</tr>
<tr>
<td>DEA</td>
<td>116</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>DIA</td>
<td>116</td>
<td></td>
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</tr>
<tr>
<td>HA</td>
<td>222</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DIHA</td>
<td>176</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DEHA</td>
<td>170</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>DAA</td>
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</tr>
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<tr>
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<tr>
<td>atra10</td>
<td>173</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>atra11</td>
<td>145</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CYA</td>
<td>126</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>All</td>
<td>78.6</td>
<td>1.31</td>
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</tr>
</tbody>
</table>
but a SP of 135 d, this examination would lead to the realization that NP has a potential for endocrine disrupting activity and that the low concentrations might still be problematic. Similarly, the chloroacetic acids TCA, DCA and MCA have a considerable phytotoxic potential and, due to their long SP, might therefore also prove to be harmful to ecosystems. Further, the chloro-triazines display quite a high mobility in soil, which, given their considerable SP, might lead to leaching and explain their presence in many aquifers.

These examples underpin the importance of the SP as an additional measure, besides the JP, that describes the characteristic temporal behavior of the transformation products. Especially in the case of low-dose effects as described in Chapter 1.2, the knowledge of the SP as an indicator of the potential for chronic, low-dose exposure might be of importance.

5.4.3 Sensitivity analysis

Many of the substance and landscape parameters that go into the model are highly uncertain and their best possible determination requires a lot of time and effort from both the scientists who experimentally determine the input parameters and the modelers who compile the experimentally measured data in order to use them as model inputs. Thus, in order to focus these data collection efforts, it is helpful to know which input parameters impact the model results most. Some first information on this question can be obtained from a sensitivity analysis. In the sensitivity analysis, each input parameter is modified individually while all others are held constant, and the change in the output parameters, here in the persistence values, is monitored. The sensitivity is then calculated as the dimensionless elasticity $U_E$ according to Morgan and Henrion (1990) (with $x$ as input parameter and $y$ as output parameter):

$$U_E(x, y) = \left[ \frac{\Delta y}{\Delta x} \right]_0 \times \frac{x_0}{y_0}$$

(5.2)

An elasticity of 0.1 thus indicates that a 1% change in one of the input parameters leads to a 0.1% change in one of the output parameters. Disadvantages of the elasticity are that it cannot account for the influence of simultaneous changes in several input parameters nor does it include any information on the extent of uncertainty in different input parameters.

In this work, the sensitivity analysis is focused on the JP only because it is regarded as the central criterion for the evaluation of the persistence of substance families.
as compared to the PP of the parent compound. In Figure 5.8, the results of the sensitivity analysis for the three case studies are summarized as sensitivity plots, which rank the different substance-specific input parameters for each case study according to their influence on the JP. For the sake of clarity, only sensitivities exceeding $U_E = 0.01$ are shown.

The sensitivities to landscape parameters are not shown in Figure 5.8 since they are generally much lower than the sensitivities to half-lives and fractions of formation. For PCE, all landscape parameters have sensitivities $< 0.01$ and for NPnEO only the depth of the water compartment ($U_E = 0.05$), the temperature ($U_E = 0.04$), the transfer velocity in air above water ($U_E = -0.04$), and the transfer velocity in water ($U_E = -0.01$) show sensitivities $> 0.01$. Similarly, in the case of atrazine only three landscape parameters have a sensitivity $> 0.01$, i.e. the depth of the soil compartment ($U_E = 0.06$), the fraction of organic carbon in soil ($U_E = 0.06$), and the velocity of water leaching from soil ($U_E = -0.06$). In this case, however, they are more important because there are only four more substance-specific input parameters with sensitivities $> 0.06$. Still, landscape parameters are excluded in the further assessment and discussion of sensitivities since their overall impact on the model results seems minor, albeit with a certain dependence on the compounds' distribution behavior, and since the predominant aim of this analysis is to differentiate between the impacts of the parent compound and the different transformation products on the model results.

The sensitivity analyses have been conducted for different ratios of $\Delta x/x_0$, and the results, especially the ranking of the input parameters according to their sensitivities, did not change considerably. This finding suggests that the system behaves fairly linearly for each single input parameter.

As was to be expected, the sensitivity of the JP to different input parameters seems to largely depend on whether a compound is present in notable amounts ($> 1\%$), i.e. the relative contribution of each compound to the total mass in the system, and its distribution between different compartments. Therefore only few parameters show a sensitivity exceeding 0.01 in the case of PCE where only four compounds out of nine are found in amounts greater than 1%, while in the case of atrazine eight out of twelve compounds contribute at least 1% to the JP, which is reflected in the higher amount of parameters with a sensitivity greater than 0.01. Because in the case of NPnEO all transformation products contribute significantly to the JP, all degradation rates and all fractions of formation in water show some influence on the JP. The ranking of the sensitivities of the degradation rates reflects nearly
Figure 5.8: Sensitivity plot of the Joint Persistence towards degradation rates ($k_i$ in graph), partition coefficients ($K_{H-x}$, $K_{ow-x}$ and $K_{oc-x}$ in graph), and fractions of formation ($theta_i$ in graph) for all three case studies. Only sensitivities exceeding 0.01 are shown.
completely the contribution of the individual compounds to the total mass in the system. Also, the most influential fractions of formation are those between the most prevalent transformation products. Generally, the sensitivity to the fractions of formation and to the degradation rates is stronger than the sensitivity to partition coefficients. The only partition coefficient with an influence exceeding 0.01 in the case of NPnEO, for example, is the Henry's law constant of NP. Obviously in the case of NP, $K_H$ is large enough to be decisive for the distribution of the compound between air and water and therefore also for its contribution to the JP since the degradation rate in air is much higher than that in water.

For the NPnEO and the PCE case study, the sensitivities to the fractions of formation and to the degradation rates are similarly large. This is not the case for the atrazine substance family, where the persistence of the parent compound atrazine dominates the JP and therefore makes the half-lives of atrazine in soil and water clearly the most influential input parameters, while the amounts of transformation products formed are of lesser importance.

In summary, the sensitivities of the JP to the properties of a single compound depend heavily on the amount of compound present and on its distribution between compartments. Generally, among the most important input parameters are the degradation rates in the favorite residence compartments of those compounds that have the biggest mass shares in the system. Similarly, the fractions of formation in the favorite residence compartments and between the most prevalent compounds are the most important fractions of formation. Regarding the chemical properties, the sensitivity of the JP to degradation rates is generally stronger than to partition coefficients.

5.5 Conclusions

The results from the three case studies have shown that, in some cases, the JP can be considerably larger than the PP. In these case studies the quotient between JP and PP was maximally around 10, but theoretically there is no upper limit to it. The value of the quotient depends on the number of generations of transformation products, on the persistence of each transformation product and on the magnitude of the fractions of formation, i.e. the transformation scheme. Further it is influenced by the emission scenario of the parent compound.
According to the case studies it could be shown that the JP allows one to obtain a more comprehensive depiction of the exposure situation in that it does not pretend that exposure to a chemical ceases after its primary degradation, but integrates the exposure to all selected compounds until the onset of ultimate biodegradation, which leads to complete mineralization. Therefore it is suggested that the JP should be used as the central criterion for the description of the persistence of substance families.

The SP is seen as a second criterion, which allows one to learn more about the temporal course of exposure to individual transformation products in the environment. As mentioned earlier, it might be instrumental in identifying specific effects such as chronic toxicity, low-dose effects or leaching, but it might also be useful in the prioritization of the transformation products of a specific parent compound for further examination. The prioritization of transformation products according to their SP could be used in addition to or instead of the purely mass-based criterion employed for the identification of potentially relevant transformation products of agrochemicals (see Chapter 2.3.1). If all known transformation products were first ranked according to their SP, this would allow for a more precautionary selection procedure in that those transformation products with a high SP but a low share of the total mass could also be singled out to undergo further assessment, i.e. be considered potentially relevant.

One point frequently discussed in the context of persistence as a hazard-based indicator for chemical assessment is whether persistence can be regarded as an inherent property of a specific compound. For the PP, the general agreement is to consider it as such although the actual persistence values depend on the emission scenario and model properties. For the case of SP and JP, the question is more complicated because both measures clearly depend on the transformation scheme.

The transformation scheme, in turn, depends on the conditions in the environment in which the transformation products are formed. Nevertheless, it is argued here that the transformation scheme should be regarded as substance-inherent property as well, because, depending on the molecular structure of the parent compound, the reactions with environmental agents lead to substance-specific transformation products and pathways. This assumption is not much different from characterizing reaction rates, which also depend heavily on environmental conditions, as substance-inherent properties. It is therefore argued that the JP at least should be regarded as substance-inherent property of the parent compound on the same grounds that the PP is considered as such.
In the case of the SP, the situation is even more complicated in that the SP of the same transformation product, e.g. DIA as transformation product of both atrazine and cyanazine, can assume different values. This leads to the special situation in which the SP is not an inherent property of the chemical compound, i.e. the transformation product, itself, but of a chemical compound as transformation product of a specific parent compound. This is another reason why the SP should not be used for the general assessment or ranking of a chemical, but only for the characterization of a transformation product in comparison to its parent compound or other transformation products of the same parent compound.

The results of the sensitivity analysis showed that, for these three case studies, the research focus should be on characterizing the degradation rates and fractions of formation as well as possible. The actual variance in the calculated persistence values, however, will not only depend on the sensitivities to the single parameters but also on the inherent uncertainty of those parameters. As the fractions of formation can only vary between 0 and 1, it is expected that the uncertainties in the degradation rates are larger than in the fractions of formation and that, therefore, research should primarily focus on the determination of degradation rates to make the model results as meaningful as possible. To further investigate the influence of uncertainty on model results and conclusions therefrom, such as, e.g., the prioritization of chemicals, a more comprehensive uncertainty analysis is conducted in the next chapter.

The actual calculation time for the determination of JP and SP is quite reasonable, i.e. approximately 5 minutes for the atrazine case study (Programming language: Mathematica 4.0.2.0 (Wolfram, 1999); Operating System: Windows 2000; Hardware: PentiumII, 350 MHz). However, due to the fact that the matrix S is inherently stiff, i.e. the entries for interphase transport and degradation sometimes differ by several orders of magnitude, severe numerical problems were encountered while solving the level IV system in Mathematica. However, the time effort for the actual calculation is still small compared to the time invested for the collection of the input data, which was on the order of several weeks for each case study. Therefore, another question to be discussed in Chapters 6 and 8 is whether the transformation scheme could be simplified at an early stage by roughly identifying those transformation products which will make large contributions to the JP and by excluding all others.
Chapter 6

Uncertainty Analysis of Primary and Joint Persistence

Every multimedia model is subject to large uncertainties which stem partly from uncertainties about the ability of the model itself to properly represent the environment and the processes therein, and partly from uncertainty or variability in the model input data. Typical uncertainties regarding multimedia models concern the appropriate selection and number of compartments to be modelled, the appropriate model geometry and the fact that average values are used to represent large and varied regions. In the context of this work, a number of additional questions arises concerning the selection of transformation products to be included, their substance-specific input data and their pattern of formation. All these uncertainties lead to an inevitable uncertainty adherent to the persistence values calculated as model outputs.

In the context of persistence, particularly the persistence of transformation products, two problems arise. First, it is of interest to learn how large the actual uncertainties in the persistence results are and to discuss what consequences this has for the applicability of persistence as hazard-based substance indicator, e.g. in the prioritization of chemicals. In other words, it is important to know how far apart two persistence values must lie in order for them to remain clearly distinguishable given all their inherent uncertainty. Only when two values are clearly distinguishable, do priority setting strategies like the ranking of substances make sense. As an example, it is of interest to note that the persistence values of the 12 POPs after release to soil calculated according to Scheringer (1996b) only differ by a factor of 1.1–1.8 between rank neighbors. The difference between the highest and the lowest persistence value
of the 12 POPs, however, amounts to a factor of 36. One of the aims of this chapter is to see whether any of these factors is high enough to claim that the substances display a clearly different persistence behavior.

The second reason for conducting an uncertainty analysis in this work has already been mentioned in the context of the sensitivity analysis in Chapter 5.4.3, i.e. to identify those input parameters that "drive" the model results in order to learn how to focus and possibly reduce data collection and data handling efforts. The results of the sensitivity analysis showed how the JP reacts to changes in single model input parameters. Additional questions to be answered in this context with the help of probabilistic uncertainty analysis are (i) how the output persistence values are correlated to changes in one input parameter when all other input parameters are simultaneously and collectively variable and uncertain, (ii) which input parameters contribute most to the overall uncertainty and should be researched more carefully in order to reduce uncertainty and obtain as reliable results as possible and (iii) which input parameters have so little influence that they can be given practically any value without changing the results. From these investigations, indications are obtained about how the number of transformation products could possibly be reduced without changing the value of the JP, and insight is gained into how JP could be roughly estimated from the raw substance data. The final aim of this step is to reduce the model complexity and to bring up ideas for the estimation of JP values.

After a general introduction to uncertainty analysis and its application in the context of transformation products, the chapter is split into two separate evaluations of the influence of parameter uncertainty and variability (Chapter 6.2) and of model uncertainty (Chapter 6.3). By doing so, it will be possible to discuss the comparative importance of these two types of uncertainty, which should also help to focus further research on transformation products and multimedia models (Chapter 6.4).

6.1 Framework for uncertainty analysis

According to Finkel’s framework for confronting uncertainty in risk management (Finkel, 1990), there are four types of uncertainty. These are as follows: decision rule uncertainty, model uncertainty, parameter uncertainty and parameter variability. Here, an attempt is made to attribute these four types of uncertainty to the specific problems related to the integration of transformation products into the evaluation of a substance’s persistence.
Decision rule uncertainty, also called scenario uncertainty, is related to possible judgment errors in decisions to be made, the omission of relevant facts thereby and possible errors in the methodologies chosen to determine the quantity on which decisions are based. A typical example for decision rule uncertainty is having to choose between different possible measures of persistence such as equivalence width, mean value and lifetime. The distinction between these measures and their advantages or disadvantages in characterizing the temporal exposure of the environment to a substance is discussed in Chapter 3.3 and in Chapter B.2 for the additional inclusion of transformation products. Another often discussed example of decision rule uncertainty is the question of how cut-off values for the purpose of priority setting should be determined.

Model uncertainty stems from a limited scientific understanding of the parameters governing environmental fate and transport. It is often neglected in sensitivity and uncertainty analysis because it is difficult to evaluate objectively. One sort of model uncertainty associated with transformation products is the uncertainty about the transformation scheme, i.e. about which transformation products are formed in each compartment and about which of the known transformation products need to be included at all. This question is dealt with in Chapter 6.3.2 concerning the different generations of transformation products. Another type of model uncertainty, not specifically linked to transformation products, is the number and relative size of the compartments considered. This uncertainty is investigated in Chapter 6.3.1 by comparing the PP and JP of the two case studies NPnEO and PCE in the usual 3-box model to their persistence in a, what is for these two substance families supposedly more suitable, 4-box model that includes a sediment compartment.

The main focus of the uncertainty analysis in this work though is on parameter uncertainty and variability. True parameter uncertainty is due to imprecisions in measurements or estimates of the model input parameters even though a single true value exists, whereas parameter variability stems from a stochastic variation in the data which is due to the fact that some input variables take on different values in time and space. As mentioned by Hertwich et al. (1999), these two types of uncertainty are often indistinguishable for chemical properties such as half-lives and partition coefficients. The same applies to the fractions of formation in the transformation scheme. It is difficult, even under laboratory conditions, to measure the exact relative share of each transformation product of the total load of transformation products, which results in parameter uncertainty, and at the same time the share of each transformation product depends on the environmental conditions and
is therefore variable. Further, the notion that true uncertainty is always reducible by means of more research, although correct on theoretic grounds, can often not be confirmed in practice. An overview of three decades of research on the $K_{ow}$ for DDT and DDE, for example, showed a shifting of the mean value but no reduction in the uncertainty range (Pontolillo and Eganhouse, unpublished results). In this work, true parameter uncertainty and parameter variability will therefore be treated together as overall uncertainty.

### 6.2 Parameter uncertainty and variability

To quantify the influence of parameter uncertainty and variability on the model output, a probabilistic uncertainty analysis is conducted. This is done by propagating the uncertainty in the input parameters through the model equations and thus mapping it onto the output parameters. In other words, the model can be thought of as a function $f$ of several input parameters $X_i$ producing an output $Y$, such as PP or JP, i.e. $Y = f(X_1, ..., X_n)$. Now, for the purpose of probabilistic uncertainty analysis, each uncertain and/or variable input parameter is described by means of a probabilistic distribution, indicating a range of possible values and their respective probability, instead of single point estimates.

In the uncertainty analysis in this work, only the substance-specific input parameters were attributed probabilistic distributions, while point estimates were used for the landscape parameters. The reason for this is two-fold. First, the focus of this analysis is on understanding the extent to which the parent compound and the different transformation products contribute to the uncertainty in the final JP value. Questions to be answered are whether it is true that the more substances are taken into account, the more uncertain the result becomes, and whether all substances are equally important in determining the range of the output values. Second, it has been shown by Hertwich et al. (1999) that for potential dose calculations in closed systems, most of the variance in the output is attributable to chemical-specific input parameters, especially half-lives, and that landscape parameters always contribute less than 10% and are therefore of minor importance. Because persistence calculations, as with the calculation of potential dose, are based on the exposure distribution of chemicals in the environment represented by a closed-system multimedia model, these findings are expected to apply to persistence calculations as well. Further, the results of the sensitivity analysis for the JP conducted in Chapter 5.4.3
also indicate that the landscape parameters generally have a low impact on the JP value and can therefore be left point estimates.

The methodology of probabilistic uncertainty analysis is explained in more detail in Appendix D. It is shown how the input distributions were constructed, how the uncertainty propagation was done and how the resulting output distributions were analyzed in order to answer the questions raised at the beginning of this chapter. Here, the results of the uncertainty analysis, i.e. the output distributions resulting from Monte Carlo analysis, are presented and discussed. As far as the input data entering the calculations are concerned, the values of the parameters of the distribution and the underlying data points are presented in the Appendices C.2.1-C.2.3 for the substance-specific input parameters of the three case studies and in Appendix D in Tables D.4-D.6 for the fractions of formation.

**Number of shots**

As explained in Appendix D, the optimal number of shots was determined empirically as a trade-off between calculation time needed and accuracy. For that purpose, Monte Carlo analyses with the number of shots, \( m \), varying between 100 and 10'000 were run and the two summary statistics of interest, i.e. the \( GM \) and \( GSD \), were determined for all three outputs PP, JP and Q. Three simulations were run for each case study and for each number of shots, \( m \), and the mean of the three simulations was plotted as a function of \( m \). The courses of the \( GM \) and the \( GSD \) obtained are illustrated in Figure 6.1 for three specific combinations of the NPnEO, PCE and atrazine case studies and the three outputs PP, JP and Q. Although the other cases were calculated too, they are not all depicted here because the patterns show the same tendency. While the \( GM \) and the \( GSD \) are still growing strongly when going from 100 to 1'000 shots, they clearly stabilize for \( m > 1'000 \). Assuming that the results for \( m=10'000 \) are closest to the correct result, a margin of ± 1% was drawn around that value. In all cases, the results for \( m=2'500 \) lie well within that margin. Since the calculation time grows slightly more than linear with \( m \), the value \( m=2'500 \) was chosen for all simulations. For the atrazine case study, this results in a calculation time of approximately 25 minutes as compared to 2 hours for \( m=10'000 \).

**Cumulative distribution functions**

The CDFs resulting from the Monte Carlo analyses for the PP, JP and Q are depicted in Figure 6.2 for all three case studies. The corresponding summary statistics are listed in Table 6.1 for the NPnEO, in Table 6.2 for the PCE and in Table 6.3 for the atrazine case study. For the CDFs and the calculation of their summary statistics
Figure 6.1: $GM$ and $GSD$ for PP, JP and Q, resulting from running different numbers of shots, $m$, for their determination. The grey area indicates ranges of ± 1% around the value for $m=10'000$, which is assumed to be the value that is closest to the correct value. From these graphs, $m=2'500$ was selected as a reasonable number of shots with respect to accuracy and calculation time.
and other measures like rank correlation coefficients, the arithmetic mean of the results of nine separate simulations was used in each case.

Table 6.1: Summary statistics for results of uncertainty analysis: PP, JP and Quotient Q for NPnEO case study.

<table>
<thead>
<tr>
<th></th>
<th>PP (d)</th>
<th>JP (d)</th>
<th>Q (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM</td>
<td>10.3</td>
<td>97.6</td>
<td>9.45</td>
</tr>
<tr>
<td>GSD</td>
<td>4.4</td>
<td>2.4</td>
<td>4.1</td>
</tr>
<tr>
<td>5th percentile</td>
<td>0.934</td>
<td>25.2</td>
<td>1.38</td>
</tr>
<tr>
<td>95th percentile</td>
<td>113</td>
<td>403</td>
<td>125</td>
</tr>
<tr>
<td>95th/5th percentile</td>
<td>121</td>
<td>16.1</td>
<td>90.4</td>
</tr>
</tbody>
</table>

Table 6.2: Summary statistics for results of uncertainty analysis: PP, JP and Quotient Q for perchloroethylene case study.

<table>
<thead>
<tr>
<th></th>
<th>PP (d)</th>
<th>JP (d)</th>
<th>Q (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM</td>
<td>62.7</td>
<td>155</td>
<td>2.47</td>
</tr>
<tr>
<td>GSD</td>
<td>2.0</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>5th percentile</td>
<td>20.7</td>
<td>54.0</td>
<td>1.13</td>
</tr>
<tr>
<td>95th percentile</td>
<td>187</td>
<td>674</td>
<td>11.9</td>
</tr>
<tr>
<td>95th/5th percentile</td>
<td>9.01</td>
<td>12.5</td>
<td>10.5</td>
</tr>
</tbody>
</table>

The first point to notice is the fact that all output distributions show large uncertainties with the GSD varying between 1.8 and 4.4. The corresponding 90% confidence interval factors range from 7 to 130. Thus, calculated persistence values can be uncertain by up to two orders of magnitude. Compared to the entire range of persistence values of 1–10'000 d spanned by a selection of environmentally relevant chemicals in Scheringer et al. (1999), the calculation of persistence values still seems to offer an information gain in that their uncertainty is narrow enough to specify a subrange that is two orders of magnitude smaller than the entire range of persistence values. If the calculated confidence intervals, however, are compared to the quotients between persistence values of, for example, individual POPs, it becomes obvious that the persistence of one POP might fall well within the confidence interval of a neighboring POP. Rather than assessing single compounds on
Figure 6.2: Cumulative distribution functions for PP and JP (left-hand graphs) and the quotient Q between JP and PP (right-hand graphs). Corresponding summary statistics are listed in Tables 6.1–6.3. The CDF of Q is truncated below 1 because the quotient JP/PP can never lie below 1 for a pair of JP and PP values from the same shot (see section on "Correlations between parameters" in Appendix D)
grounds of their persistence and other substance indicators, it might therefore be more appropriate to assign them to groups of chemicals which are defined by ranges of substance properties and to develop risk management strategies for the groups as a whole as it is done for POPs or PBTs. Along the same line of thought, ranking systems which attribute scores to ranges of persistence seem to be sufficiently adequate, given the large variance in the calculation of persistence values (O'Bryan and Ross, 1988; Ranke and Jastorff, 2000; Snyder et al., 2000).

The comparison of the GMs with the point values calculated in Chapter 5 (see Table 5.9) shows that the GMs lie between a factor slightly below 1 (0.91) up to nearly a factor of 2 lower and higher than the point estimates. The deviation of the GM from the point estimate has two reasons. First, the GM becomes larger than the point estimate if the uncertainty in the output value is dominated by highly skewed input distributions. The highly skewed input distributions lead to highly skewed output distributions in turn as can be seen, e.g., for the CDFs of the JP and PP of atrazine in Figure 6.2. Second, in the uncertainty analysis, all fractions of formation are described as triangular distributions varying between 0 and 1 and with the point estimates as most likely values. For fractions of formation with low point estimates, this might lead to average fractions of formation entering the uncertainty analysis that lie considerably higher than the point estimates, thus leading to higher JP values (see atrazine case study). Also, the contrary can be observed for fractions of formation with high point estimates, i.e. that their average from the distribution, entering the uncertainty analysis, lies lower than the point estimate. This must be the case for NPnEO, where the GM of the JP lies lower than the point estimate (GM(JP)=97.6 d vs. JP=102 d).

As a consequence of this, the ranking of the substance families with regard to their

<table>
<thead>
<tr>
<th></th>
<th>PP (d)</th>
<th>JP (d)</th>
<th>Q (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM</td>
<td>79.7</td>
<td>150</td>
<td>1.88</td>
</tr>
<tr>
<td>GSD</td>
<td>3.7</td>
<td>2.5</td>
<td>1.8</td>
</tr>
<tr>
<td>5th percentile</td>
<td>11.1</td>
<td>46.9</td>
<td>1.04</td>
</tr>
<tr>
<td>95th percentile</td>
<td>798</td>
<td>855</td>
<td>6.51</td>
</tr>
<tr>
<td>95th/5th percentile</td>
<td>71.9</td>
<td>18.2</td>
<td>6.26</td>
</tr>
</tbody>
</table>
PP and their JP is changed as compared to the point estimates, mainly because the GM of the JP of atrazine lies considerably higher than its point estimate. Now the rankings according to the GMs are PP(NPnEO)<PP(PCE)<PP(atrazine) and JP(NPnEO)<JP(atrazine)< JP(PCE). Thus, the ranking remains the same when going from PP to JP for the pair NPnEO and PCE and for the pair NPnEO and atrazine, and only changes for the pair PCE and atrazine.

Another important finding results from the comparison of the GSD for the PP with that of the JP. It shows that, in two of three cases (NPnEO and atrazine), the GSD of the JP is smaller than that of the PP. This clearly contradicts the usual presumption that through the additional inclusion of transformation products the model complexity and therefore also the uncertainty in the model outputs is augmented. The explanation for the smaller GSD for the JP of NPnEO and atrazine as compared to that of the PP is that, in these two cases, the most influential input parameters for the JP show smaller uncertainties than the most influential input parameters for the PP. This phenomenon will be further discussed in the context of the rank correlation coefficients (see next section). In summary, depending on the importance and uncertainty of individual input parameters, the variance of the JP can be smaller than that of the PP.

Results for rank correlation coefficients
Rank Correlation coefficients (RC) were determined as described in the previous chapter. As only rank correlation coefficients with absolute values greater than 0.1 indicate a significant dependence (Cullen and Frey, 1999), only those were depicted by means of Tornado plots in Figure 6.3 for all three case studies. In addition, it turned out that the selected parameters with |RC| > 0.1 corresponded exactly to those with a contribution to variance (CTV) of more than 1%.

When compared to the sensitivity charts in Figure 5.8 of Chapter 5.4, the charts for the RCs show a clearly reduced number of influential parameters. They are confined to the degradation rates of those transformation products whose relative mass share exceeds 5%-10% in their favorite residence compartment. Also, the few partition coefficients still present in the sensitivity analysis have disappeared completely from the picture. Fractions of formation with |RC| > 0.1 are only found for the transformation of the parent compound into transformation products of the first generation. In summary, only degradation data and fractions of formation concerning the transformation products of the first generation and those transformation products formed in amounts exceeding 5-10% seem to be important. This finding
Figure 6.3: Tornado plots for those input parameters with absolute rank correlation coefficients greater than 0.1 for all three case studies. $k_i$-$x$ stands for the degradation rates, and $\theta_{i}$ for the fractions of formation.
will be crucial in deciding how the complexity of the transformation scheme could be reduced, a point further discussed in Chapters 6.3.2 and 8.2.

Another point that stands out when the RCs are compared to the results of the sensitivity analysis is that the sequence of importance of some of the input parameters is changed. This results from the fact that RCs include both, the sensitivity of the model and the uncertainty of the input parameters. Thus it can, for example, be explained why the degradation rate of NP2EO in water with a GSD of 5.68 suddenly becomes more important than that of NP1EC with a GSD of 2.57.

Coming back to the observed reduction in variance between PP and JP for NPnEO and atrazine, this can now be explained with the help of the RCs. In Tables 6.4–6.6 the input parameters with $|RC| > 0.1$ for the PP and JP and the GSDs of all these input parameters are compiled. For each PP and JP, the weighted mean of the GSDs of the input parameters is calculated, with RC being used as weight. From the weighted averages it can be seen that the JP values in the case of NPnEO and atrazine are dominated by input parameters with less variance, i.e. smaller GSD values, than the corresponding PP. This leads to the lower GSD values of the output distributions of the JP as compared to the GSDs of the output distributions of the PP.

Table 6.4: List of GSDs for the most influential input parameters in the NPnEO case study. The values are used to calculate a weight-averaged GSD of all influential input parameters to predict the extent of variance in the output.

| PP     | $|RC|$ | GSD |
|--------|-------|-----|
| NPnEO, $\kappa_w$ | 1.0   | 4.30 |
| Weighted mean |       | 4.30 |

| JP     | $|RC|$ | GSD |
|--------|-------|-----|
| NP2EC, $\kappa_w$ | 0.41  | 2.80 |
| NPnEO, $\kappa_w$ | 0.36  | 4.30 |
| NP2EO, $\kappa_w$ | 0.29  | 5.68 |
| $\theta_{4,w}$    | 0.28  | 2.19 |
| $\theta_{1,w}$    | 0.21  | 2.13 |
| NP1EO, $\kappa_w$ | 0.21  | 9.22 |
| NP1EC, $\kappa_w$ | 0.17  | 2.57 |
| Weighted mean     |       | 4.03 |
Table 6.5: List of GSDs for the most influential input parameters in the PCE case study. The values are used to calculate a weight-averaged GSD of all influential input parameters to predict the extent of variance in the output.

| PP          | |RC| | GSD |
|-------------|-----------------|-----------------|
| PCE, $\kappa_a$ | 1.0             | 1.95            |
| Weighted mean |                 | 1.95            |

| JP          | |RC| | GSD |
|-------------|-----------------|-----------------|
| PCE, $\kappa_a$ | 0.54            | 1.95            |
| TCA, $\kappa_w$ | 0.42            | 14.5            |
| COCl$_2$, $\kappa_a$ | 0.38            | 2.30            |
| $\theta_{1,a}$ | 0.18            | 2.11            |
| $\theta_{2,a}$ | 0.18            | 2.58            |
| Weighted mean |                 | 5.21            |

Table 6.6: List of GSDs for the most influential input parameters in the atrazine case study. The values are used to calculate a weight-averaged GSD of all influential input parameters to predict the extent of variance in the output.

| PP          | |RC| | GSD |
|-------------|-----------------|-----------------|
| Atrazine, $\kappa_s$ | 0.75            | 3.15            |
| Atrazine, $\kappa_w$ | 0.51            | 12.4            |
| Weighted mean |                 | 6.89            |

| JP          | |RC| | GSD |
|-------------|-----------------|-----------------|
| Atrazine, $\kappa_s$ | 0.63            | 3.15            |
| Atrazine, $\kappa_w$ | 0.49            | 12.4            |
| $\theta_{3,s}$ | 0.21            | 2.54            |
| HA, $\kappa_s$ | 0.19            | 2.02            |
| Weighted mean |                 | 5.91            |
Contribution to variance

From the RCs the contribution to variance (CTV) was calculated as shown in Equation D.10 for all input parameters. As already mentioned, CTV values were $\geq 1\%$ for all input parameters with $|RC| > 0.1$. If the CTVs of the the input parameters are grouped into three groups according to the type of input parameter, i.e. degradation rates, partition coefficients and fractions of formation, the picture shown in Figure 6.4 results. In that picture the percentage contribution of each group of input parameters to the total variance in the output for all three case studies is shown.

![Figure 6.4: Contribution to variance (CTV) of the three main groups of substance-specific input parameters, i.e. degradation rates, partition coefficients and fractions of formation.](image)

It is most interesting to note that the degradation rates always contribute over 70% to the overall variance while the contribution of the partition coefficients lies below 1% in all three case studies. The same behavior has been observed for hydrophilic substances by Schwartz (2000) in an analysis of the CTVs in the EUSES exposure model. As most substances in our case studies, apart from the short-chain ethoxylates and NP, are rather hydrophilic, the results of these two studies are therefore in good agreement. The finding is further confirmed by the results of Hertwich et al. (1999), who showed that most of the variance in the calculated exposure values is due to chemical-specific input parameters and in particular to half-lives.

The contribution to variance of the parameter group of the fractions of formation lies between 6–26% in the three case studies. A comparison with the results of the sensitivity analysis, where they were about equally influential as the degradation rates, indicates that these lower CTVs must partly be due to their lower uncertainty
as they are always bounded by 0 and 1, while the degradation data can vary over much larger ranges. In the context of this work, it is important to note that the fractions of formation, which are often badly known and therefore have often been put forward as impediment for the dynamic modelling of transformation products, do not contribute greatly to the variance in the JP. Therefore it seems that reasonably good JP values can be calculated by using relatively rough guesses for the fractions of formation.

The results of the CTV analysis thus clearly show that most of the variance in the JP values is due to variance in the degradation rates, and that, in order to reduce the large variance in persistence calculations, the focus would need to be on reducing the variance in the determination of degradation rates. At this point, it would be crucial to know whether the variance is mainly due to true uncertainty or mainly due to variability. If uncertainty is dominant, there is a theoretical chance that it could be reduced by means of more and better research on degradation rates. If, however, the variability dominates, the variance in the persistence values is more inherent and could probably only be reduced in regional models for which region-specific degradation rates have actually been measured. In all other cases, it might be questionable to refine models to include regional singularities as long as generic, average values for degradation rates are used.

To obtain an estimate of the extent to which the large variance in the degradation rates can be classified as uncertainty or variability, the data set comprising the half-lives of atrazine in soil was analyzed in more detail. To do so, it was decomposed into subgroups whose data points were obtained by similar experimental methodologies. Because the largest part of the data points was measured by researchers from Ciba-Geigy Ltd. (short: Ciba), i.e. the producer of atrazine, these data points were separated from the measurements of other, independent research groups. A second distinction has been made between field and laboratory measurements. For the field measurements, those made in Europe were separated from those made in the US to reveal possible differences between these two regions. An illustration of the resulting sets of data points together with their geometric mean and standard deviation is given in Figure 6.5.

From the analysis of the data points, several qualitative statements on the importance of uncertainty versus variability can be made. First, all subgroups show a similar variance expressed by a GSD of 1.7–2. For the field and laboratory data of Ciba, this variance covers mainly variability of different soil types and possibly some measurement uncertainty, which cannot be quantified from the available data. As-
Figure 6.5: Decomposition of the entire data set of atrazine half-lives in soil (n = 91) into subgroups which have been measured with similar experimental methodologies. Measurements conducted by Ciba and other, independent research groups are separated as well as field and laboratory measurements. For each subgroup the single data points, their geometric mean and the range spanned by factoring in one geometric standard deviation is illustrated.

Assuming this measurement uncertainty to be small within the methodology employed at Ciba, one can thus tentatively assume that the spread of the Ciba data sets, covering around a factor of 10–15 for the 90% confidence interval, is mainly due to natural variability. As the GSDs of the measurements in the laboratory are similar to the GSDs of those in the field, both for the Ciba and the other data sets, one could argue that the laboratory experiments succeed in representing the variability found in natural environments.

Second, the comparison of the mean values obtained within Ciba for field and laboratory measurements shows that half-lives measured in the laboratory lie always about a factor of 2 higher than those measured in the field. Experts at Ciba attribute this to the lower viability and therefore lower microbial activity of soils transferred to the laboratory (Ciba, 1995b). This statement agrees well with the findings of Vink et al. (1997), who conducted a multivariate analysis of environmental factors influencing pesticide biotransformation and found that differences in microbial activity...
account for 40% of the total variance of measured rates. Thus, the methodological uncertainty of laboratory versus field measurements adds an additional uncertainty of a factor of 2 to the natural variability that covers a factor of 10–15. Third, when comparing the laboratory measurements conducted within Ciba with those of other research groups, it seems that methodological differences between different research groups might account for another uncertainty factor of 2.

All in all, for the case of atrazine half-lives in soil, the spread in the degradation rates seems to be dominated by the variability of different soils, which results in degradation rates differing by a factor of 10–15, whereas measurement uncertainties seem to be smaller but still considerable, accounting for differences in degradation rates of approximately a factor of 4. It remains an important task for further research to see whether the results of this preliminary analysis can be generalized for other substances and compartments and to possibly quantify the relative contribution of uncertainty and variability to overall variance by means of multivariate analysis.

6.3 Model uncertainty

In this chapter, different types of model uncertainty are investigated. This is, on the one hand, the influence of appending an additional sediment compartment to the multimedia model and, on the other hand, the effect of removing generations of transformation products from the transformation scheme.

Another often discussed model uncertainty, i.e. whether open- or closed-system models should be used, is not discussed in great detail. In my opinion, it is obvious that persistence calculations should always be conducted in closed systems because the persistence measure is supposed to indicate the time during which a substance can be found anywhere in the environment. The advective transport of a substance out of an open system, however, just shifts the problem to another location. Therefore, closed systems should be used in persistence calculations in order to properly represent the time any environment is exposed to a given substance.

Still, it is of interest to note that the decision between open and closed systems is even more influential in the calculation of the JP than in the calculation of PP. For the case of NPnEO, e.g., the PP in an open system amounts to 7.79 d as compared to 9.98 d in the closed system, while the JP in the open system amounts to 30.6 d as compared to 108 d in the closed system.* The reason for the higher sensitivity

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*The JP in the closed system is slightly different from the usual value because the model volumes
of the JP to the open or closed state of the model system is that the further down the generation sequence a given transformation product lies, the more it matters if all of its precursors are advected out of the system. The effect of advective outflow therefore gets, so to say, multiplied through the transformation scheme.

6.3.1 Inclusion of sediment compartment

A sediment compartment is added to the 3-box multimedia model. It is in contact with the water compartment and has therefore the same area as the water compartment and a height, \( h_{\text{sed}} \), of 0.02 m. It only represents the uppermost part of the sediment from which chemicals can still diffuse or resuspend into the water column. The permanent sediment, in which chemicals become permanently buried, is not included in the new 4-box model.

The exchange processes between the surface water and the sediment compartment are modelled according to the surface mixed sediment layer (SMSL) model described by Schwarzenbach et al. (1993). According to this model, the relevant exchange processes are as follows: (i) diffusion between the dissolved phase in the water and the pore water of the sediment, (ii) settling of particulate matter in the water column and (iii) resuspension of sediment particles into the water column. The mathematical expressions for the phase transfer coefficients between water and sediment are given in Table A.3 in Appendix A.2 and the corresponding model input parameters are quantified in Table A.2 in the same appendix.

In order to model the fate of the chemicals of the NPnEO and PCE substance families in the sediment compartment, half-lives in the sediment need to be known. For that purpose, degradation data measured in aerobic and anaerobic sediments were compiled for all compounds and geometric means were calculated to obtain average half-lives (see Table 6.7 for the NPnEO substance family and Table 6.8 for the PCE substance family). The underlying data bases can be found in Appendices C.2.1 and C.2.2. For the NPnEO substance family, the comparison of the average half-lives in soil and water (Table 5.2) and in sediment (Table 6.7) indicate that degradation in rather anaerobic media such as the sediment is generally slower than in aerobic media such as soil and water. Similarly, a much higher half-life of NP in sediment than in other environmental media has been assumed in two recent risk assessments for the Switzerland-specific model introduced in Chapter 7 were chosen for this quick modelling exercise. The reason for this choice is that outflow values in water and air are known for the Swiss model only.
on NP (E.C., 2000; UK EA, 2000).

*Table 6.7:* Half-lives of NPnEO and its transformation products in sediment. They were calculated as geometric means when more than one data point was available. The underlying data collection can be found in Appendix C.2.1.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$t_{1/2,\text{sed}}$ (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPnEO</td>
<td>3200</td>
</tr>
<tr>
<td>NP2EC</td>
<td>3200</td>
</tr>
<tr>
<td>NP1EC</td>
<td>3200</td>
</tr>
<tr>
<td>NP2EO</td>
<td>286</td>
</tr>
<tr>
<td>NP1EO</td>
<td>347</td>
</tr>
<tr>
<td>NP</td>
<td>327</td>
</tr>
</tbody>
</table>

*Table 6.8:* Half-lives of PCE and its transformation products in sediment. They were calculated as geometric means when more than one data point was available. The underlying data collection can be found in Appendix C.2.2.

<table>
<thead>
<tr>
<th>Substance</th>
<th>$t_{1/2,\text{sed}}$ (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>79.8</td>
</tr>
<tr>
<td>TCE</td>
<td>336</td>
</tr>
<tr>
<td>DCE</td>
<td>13000</td>
</tr>
<tr>
<td>VC</td>
<td>161</td>
</tr>
<tr>
<td>COCl$_2$</td>
<td>$1.01 \times 10^{-6}$</td>
</tr>
<tr>
<td>TCAC</td>
<td>$1.37 \times 10^{-7}$</td>
</tr>
<tr>
<td>TCA</td>
<td>53.8</td>
</tr>
<tr>
<td>DCA</td>
<td>3.50</td>
</tr>
<tr>
<td>MCA</td>
<td>3.08</td>
</tr>
</tbody>
</table>

The second prerequisite to model the fate of the substance families in the sediment is that their fractions of formation in sediment are known. For the NPnEO substance family they are given in Table 6.9 along with the fractions of formation in soil, water and air. The water compartment is now a purely aerobic compartment in which NP is expected to be mineralized quickly. So the fractions of formation of NP in water, $\theta_{3,w}$ and $\theta_{8,w}$ are reset to 0 (note, however, that the mineralization of NP1EC and
NP1EO proceeds through NP). In the sediment, where there are anaerobic spots, NP formed out of NP1EC and NP1EO may be more persistent. Because the exact fraction of persistent NP being formed is not known, the formation of persistent NP from NP1EC and NP1EO and direct mineralization of NP1EC and NP1EO are assumed to be equally important (\(\theta_{3,\text{sed}}\) is set to 0.5 and \(\theta_{8,\text{sed}}\) to 0.25). Also, under rather anaerobic conditions, the formation of NP2EO from NPnEO becomes more important and therefore the fractions of formation \(\theta_{1,\text{sed}}\) and \(\theta_{4,\text{sed}}\) are both set to 0.5.

For the PCE family, the new fractions of formation are listed in Table 6.10. Here, the changes concern mainly the formation of the chlorinated ethylenes because the higher chlorinated ones are exclusively formed under anaerobic conditions. Therefore, the fractions of formation for the chlorinated ethylenes in sediment \((\theta_{7,\text{sed}}, \theta_{8,\text{sed}}, \theta_{9,\text{sed}})\) have been set to 1, while their fractions of formation in water have been reset to zero.

**Table 6.9:** Fractions of formation for transformation products of NPnEO in the media soil, water, air and sediment. The main difference compared to the fractions of formation in Table 5.1 is the fact that NP is only formed in the sediment compartment but with higher shares. Also, the share of ethoxylates formed from NPnEO as compared to the formation of acids is enhanced under anaerobic conditions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Fractions of formation in soil ((\theta_{r,s}))</th>
<th>Fractions of formation in water ((\theta_{r,w}))</th>
<th>Fractions of formation in air ((\theta_{r,a}))</th>
<th>Fractions of formation in sediment ((\theta_{r,\text{sed}}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NPnEO → NP2EC</td>
<td>0.7</td>
<td>0.7</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>NP2EC → NP1EC</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>NP1EC → NP</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>4</td>
<td>NPnEO → NP2EO</td>
<td>0.3</td>
<td>0.3</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>5</td>
<td>NP2EO → NP2EC</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>6</td>
<td>NP2EO → NP1EO</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>7</td>
<td>NP1EO → NP1EC</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>8</td>
<td>NP1EO → NP</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.25</td>
</tr>
</tbody>
</table>

In Figure 6.6 the mass distributions in the 4-box model that includes a sediment boundary layer are depicted for the two case studies PCE and NPnEO. The corre-
Table 6.10: Fractions of formation for transformation products of PCE in the media soil, water, air and sediment. The main difference compared to Table 5.4 is the assumption of total reductive dechlorination of the chlorinated ethylenes in the sediment compartment.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Fractions of formation in soil ($\theta_{r,s}$)</th>
<th>Fractions of formation in water ($\theta_{r,w}$)</th>
<th>Fractions of formation in air ($\theta_{r,a}$)</th>
<th>Fractions of formation in sediment ($\theta_{r,sed}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PCE→COCl₂</td>
<td>0</td>
<td>0</td>
<td>0.9</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>PCE→TCAC</td>
<td>0</td>
<td>0</td>
<td>0.1</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>TCAC→COCl₂</td>
<td>0</td>
<td>0</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>TCE→COCl₂</td>
<td>0</td>
<td>0</td>
<td>0.28</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>TCE→DCA</td>
<td>0.04</td>
<td>0.04</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>TCAC→TCA</td>
<td>1.0</td>
<td>1.0</td>
<td>0.8</td>
<td>1.0</td>
</tr>
<tr>
<td>7</td>
<td>PCE→TCE</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>8</td>
<td>TCE→DCE</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>9</td>
<td>DCE→VC</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>10</td>
<td>PCE→TCA</td>
<td>0.15</td>
<td>0.15</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>TCA→DCA</td>
<td>0.3</td>
<td>0.3</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>12</td>
<td>DCA→MCA</td>
<td>0.3</td>
<td>0.3</td>
<td>0</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Corresponding newly calculated PP and JP values are given in Table 6.11.

Table 6.11: Primary and Joint persistence values for NPnEO and PCE case study, with and without inclusion of sediment compartment.

<table>
<thead>
<tr>
<th></th>
<th>With sediment</th>
<th>Without sediment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PP (d)</td>
<td>JP (d)</td>
</tr>
<tr>
<td>NPnEO</td>
<td>10.2</td>
<td>98.3</td>
</tr>
<tr>
<td>PCE</td>
<td>44.9</td>
<td>122</td>
</tr>
</tbody>
</table>

The mass distribution graphs clearly show that in both case studies some substances, i.e. NP, NP2EO and NP1EO in the NPnEO case study, and TCE, DCE and VC in the PCE case study, partition considerably into the sediment where all of them except TCE have longer half-lives than in the other compartments. Nevertheless,
Figure 6.6: Mass distributions for the case studies NPnEO and PCE in steady state in 4-box model including a sediment boundary layer. Left graphs show the contributions of parent compound and transformation products to the total mass in the system and right graphs show the mass distributions of all compounds between the compartments soil, water, air and sediment.
the PP and JP values are hardly changed compared to the 3-box model. In the case of PCE, the persistence values do not change at all. This is due to the fact that the amounts of chlorinated ethylenes formed are still so low that their contribution to the JP is simply negligible. The reason for their low formation rate is the volatility of their precursor PCE, which only partitions to water in very low amounts and from there in even lower amounts into the sediment, which is the only compartment where the lesser chlorinated ethylenes are formed. Thus, although these compounds have been measured in sediment and have been shown to contaminate aquifers, the amounts formed according to this model are not large enough to contribute to the JP.

For the NPnEO case study, it is a priori less clear why, albeit the considerable amounts of NP2EO and NP1EO found in sediment, the JP is even slightly lower than in the 3-box model. The low effect of the presence of NP2EO and NP1EO in sediment must have to do with the fact that the exchange processes between water and sediment in the SMSL model are nearly two orders of magnitude faster than the degradation in sediment. Therefore, only about 1% of all compounds are actually degraded in the sediment, the rest is resuspended into the water column and degraded there. Under these circumstances, the reason for the observed actual reduction in the JP value must be due to the fact that NP, which, in water, is the most persistent of all transformation products, is hardly formed anymore. This, by the way, is due to the fact that NP is now only formed from NP1EO and NP1EC in sediment, of which hardly any is actually present in there.

This finding leads to the question whether a surface mixed sediment layer is a proper representation of a sediment compartment for the purpose of persistence calculations. Rather, for persistence calculations, the permanent sediment should be included. This can be tentatively simulated by reducing the resuspension rate by a factor of 5. Doing this results in a rise of the JP to 116 d and an increase in the amount of NP2EO and NP1EO in sediment to 60% of their total mass present. Reducing the resuspension rate by a factor of 5 is only an approximation to demonstrate how large the effects of a permanent sediment compartment could be. The inclusion or omission of a permanent sediment layer therefore is clearly an important model uncertainty in calculating persistence values, which is, however, not further researched in this work.
6.3.2 Generations of transformation products

In order to organize data collection and calculation efforts most efficiently, it is of crucial importance to identify those transformation products which contribute so little to the JP that they can actually be neglected. The rank correlation coefficients for the degradation rates of the single transformation products, indicating the most influential substance input parameters, already give an idea of the importance of single transformation products (see Figure 6.3 in Chapter 6.2). Another way of finding out is to successively remove generations of transformation products, beginning with the last generation, and to calculate the JP of the remaining generations. The resulting effect on the JP is a measure of the importance of the removed generation and an indication of how large the model uncertainty with respect to that generation is.

Generations have been defined by the number of transformation steps, starting from the parent compound, that are minimally needed to reach the respective transformation products. The limits of each generation are indicated as dashed lines in the transformation schemes in Figures 5.2-5.5 in Chapters 5.1-5.3. The JP values resulting from the successive removal of generations of transformation products are calculated probabilistically by Monte Carlo analysis as already done in Chapter 6.2, and are presented as CDFs and geometric means therefrom. Also, the geometric mean of the quotient between the PP and JP of the remaining generations is calculated. Lastly, in order to quantify the overall horizontal distance between the original JP including all transformation products and the JP that only includes the remaining generations, S-Scores are calculated using the original JP as baseline (for explanation of the S-Score see Appendix D). The CDFs for the different cases are illustrated in Figure 6.7 for the three case studies, while the statistics and the S-Score are listed in Tables 6.12-6.14.

In the graphs in Figure 6.7, the curves lying on the outer right-hand side are the CDFs of the original JP, while the curves lying on the outer left-hand side are the CDFs of the PP. Thus, the CDFs in between those two, going from right to left, represent the JP values that result if each generation of transformation products is successively removed. Simply from comparing the three graphs, it becomes obvious that, in these three case studies, the first generation has by far the largest influence on the JP. This can be seen from the fact that a large shift of the CDF takes place when the first generation of transformation products is added to the parent compound, whereas the addition of further generations results in much smaller,
Figure 6.7: Cumulative distribution functions for all three case studies, illustrating the effect of the stepwise removal of generations of transformation products. The curves on the outer right-hand side represent the results of the probabilistic calculation of the JP, while the curves on the outer left-hand side are the results of the PP. In between lie the CDFs that are obtained when the remaining JP is calculated for reduced transformation schemes, from which generations have been removed successively.
Table 6.12: Statistics and S-Score for NPnEO case study, illustrating the effect of the stepwise removal of generations of transformation products.

<table>
<thead>
<tr>
<th></th>
<th>PC+1st + 2nd + 3rd generation (JP)</th>
<th>PC+1st + 2nd generation (d)</th>
<th>PC+1st generation (d)</th>
<th>PC (PP) (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gmJP</td>
<td>97.0</td>
<td>91.8</td>
<td>61.6</td>
<td>10.3</td>
</tr>
<tr>
<td>gmQ</td>
<td>9.39</td>
<td>8.89</td>
<td>5.97</td>
<td>(1.0)</td>
</tr>
<tr>
<td>s'-score</td>
<td></td>
<td>0.272</td>
<td>2.05</td>
<td>10.0</td>
</tr>
<tr>
<td>s_stop</td>
<td>0.090</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.13: Statistics and S-Score for PCE case study, illustrating the effect of the stepwise removal of generations of transformation products.

<table>
<thead>
<tr>
<th></th>
<th>PC+1st + 2nd + 3rd generation (JP)</th>
<th>PC+1st + 2nd generation (d)</th>
<th>PC+1st generation (d)</th>
<th>PC (PP) (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gmJP</td>
<td>157</td>
<td>157</td>
<td>156</td>
<td>62.7</td>
</tr>
<tr>
<td>gmQ</td>
<td>2.50</td>
<td>2.50</td>
<td>2.49</td>
<td>(1.0)</td>
</tr>
<tr>
<td>s'-score</td>
<td></td>
<td>0.004</td>
<td>0.017</td>
<td>3.85</td>
</tr>
<tr>
<td>s_stop</td>
<td>0.083</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.14: Statistics and S-Score for atrazine case study, illustrating the effect of the stepwise removal of generations of transformation products.

<table>
<thead>
<tr>
<th></th>
<th>PC+1st + 2nd + 3rd + 4th + 5th generation (JP)</th>
<th>PC+1st + 2nd + 3rd generation (d)</th>
<th>PC+1st + 2nd + 3rd generation (d)</th>
<th>PC+1st + 2nd + 3rd generation (d)</th>
<th>PC+1st + 2nd + 3rd generation (d)</th>
<th>PC (PP) (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gmJP</td>
<td>151</td>
<td>150</td>
<td>147</td>
<td>143</td>
<td>135</td>
<td>79.8</td>
</tr>
<tr>
<td>gmQ</td>
<td>1.90</td>
<td>1.88</td>
<td>1.84</td>
<td>1.79</td>
<td>1.69</td>
<td>(1.0)</td>
</tr>
<tr>
<td>s'-score</td>
<td>0.057</td>
<td>0.136</td>
<td>0.262</td>
<td>0.550</td>
<td>3.19</td>
<td></td>
</tr>
<tr>
<td>s_stop</td>
<td>0.082</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
sometimes even indistinguishable shifts to the right.
This change in the JP is captured quantitatively in the $GM$ of the JP, the $GM$ of the quotient and the $S$-Score. They all confirm the same tendency, i.e. that the biggest difference lies between whether the persistence is calculated for the parent compound alone or whether the first generation of transformation products is included. If the percent changes in the $GM$ of the JP and the quotient $Q$ for the removal of generations are studied in Tables 6.12–6.14, it can even be shown that the importance of the different generations increases steadily towards the parent compound. The last generation is thus always the least and the first generation the most important.

On a more restrictive basis, the $S$-Score allows a statement about whether or not a given CDF is at all distinguishable from the noise of the baseline CDF, which is only the case if the $S$-Score of the CDF compared to the CDF of the baseline JP distribution lies above $S_{\text{stop}}$. This algorithm can be used to identify those CDFs that are not distinguishable from the baseline CDF of the original JP on a statistically significant level although generations have been removed. The generations thus identified clearly do not contribute to the JP and can therefore be excluded from the transformation scheme. On these grounds, the second and third generation of PCE can be disregarded in the evaluation of the JP of that substance family. Also, the fifth generation of the atrazine substance family can be excluded. In the case of atrazine, all the other generations contribute to small extents but distinguishably to the JP, even if, when looking at the CDFs, all except the first seem negligible. For NPnEO, the removal of the last (3rd) generation already leads to distinguishable differences in the CDF as compared to the JP. Thus, one could conclude that in the case of NPnEO all generations contribute significantly to the JP and should be included in the calculation of the JP. However, as mentioned already, this is a very restrictive viewpoint and it has been shown before that, qualitatively, the contribution of the first generation is clearly dominant and might be sufficient for a first, efficient calculation of the JP.

It is interesting to discuss the results regarding the importance of different generations of transformation products in light of the factors influencing the JP, which are, on the one hand, the persistence of the respective transformation products and, on the other hand, the share with which they are formed relative to the parent compound. This relationship has been deduced analytically for the case of a one-dimensional system (see Equations B.17 and B.22 in Appendix B.2 for the case of strictly consecutive and for the case of parallel reactions, respectively). In the case of a multimedia model as it is used here, the situation is complicated by the fact that
degradation rates and fractions of formation differ between environmental compartments and that the persistence and fractions formed of a transformation product therefore depend on the partitioning behavior of its precursors. Still, an expression for the upper and lower limit of the JP that depends on half-lives and fractions of formation of the single compounds was found (see Equation 4.11 in Chapter 4.2.2). The relationships expressed in Equations B.17, B.22 and 4.11 might be helpful in explaining the decreasing importance of successive generations of transformation products.

In a first analysis of all three case studies, the largest fractions of formation of each triple of media-specific fractions of formation for each transformation step were selected and multiplied through the transformation scheme in order to obtain the share maximally formed of each transformation product. The shares of transformation products formed of the same generations were then added up to give the overall share of formation for each generation. In two of the three case studies (NPnEO and PCE), these shares diminish from generation to generation. This is due the fact that the model provides for situations in which only parts of the precursor are actually transformed into one of the transformation products in the transformation scheme while other parts are lost from the system either by mineralization, by formation of transformation products that are not considered relevant or by the formation of bound residues. For atrazine, the same pattern of diminishing shares as for PCE and NPnEO can be observed if the fractions of formation in soil and water are multiplied through the transformation scheme, which is a realistic assumption for atrazine and its transformation products because they are only found in those two compartments. Thus, one reason for the diminishing importance of later generations of transformation products certainly is the fact that they are formed in increasingly lower amounts due to the loss of chemical mass from generation to generation through other pathways.

In a second analysis, the half-lives for different generations of transformation products were compared. In the case of PCE, the half-lives of the 2nd and 3rd generation in soil and water, i.e. the relevant compartments for these compounds, are smaller than the half-lives of their precursors (TCE, TCA) in those same compartment, and also smaller than the half-life of the dominant, first generation transformation product COCl₂ in air. In this case, the smaller persistence of the later transformation products contributes, in addition to their lower shares of formation, to their diminishing importance for the JP. For atrazine and NPnEO, the picture is less clear cut. For atrazine, the half-lives of the 2nd to 5th generation in water are rather higher.
than those of the 1st generation, while they are definitely lower in soil. Also, the shares formed of each generation are the same from the 2nd to the 5th generation. Those generations are thus similar in their importance but still clearly less important than the 1st generation.\footnote{This similarity of the last four generations might also be an artefact because very little information on their half-lives and fractions of formation is available. Their fractions of formation have therefore been estimated as generic fractions of formation and their half-lives by means of QSPRs, which resulted in the same half-lives for nearly all transformation products.} For NPnEO, the 3rd generation transformation product, NP, is the most persistent compound of that substance family in water, while the parent compound is the least persistent. Regarding the 1st and 2nd generation, the 1st is more persistent for the acids and the 2nd more persistent for the ethoxylates. Thus, although persistence rather increases towards higher generations in this case study, the later generations still show a decreasing importance.

In summary, two reasons were discovered for the diminishing importance of successive generations of transformation products in the three case studies in this work. First, the shares of transformation products contributing to the JP decrease from generation to generation due to a certain amount of chemical mass that is lost in each transformation step through mineralization or through transformation into transformation products that are not considered relevant. This seems to be a fact that can be generalized for most substance families and will always lead to a decrease of the importance of later generations. Second, in some cases, the half-lives of 2nd and later generation transformation products are lower than the half-lives of their precursors. However, the NPnEO case study shows that this is not necessarily a general trend, but depends on the chemical structure of the parent compound and on the degradation pathways that are most likely for that structure.

\subsection*{6.4 Conclusions}

The probabilistic uncertainty analysis has shown that parameter uncertainties in persistence calculations amount to up to two orders of magnitude, i.e. factors of up to 130 for the 90\% confidence interval. This is considered a rather large uncertainty for use in a decision making context. It is mainly due to variance in the degradation rates. A reduction of uncertainty in persistence values would thus best be achieved by reducing variance in degradation rates. However, this variance in degradation rates stems only partly from reducible uncertainty, while another part stems from variability in the properties of the natural environment, such as pH.
and T, on which the degradation behavior of a substance strongly depends. The quantitative distinction of these two types of parameter uncertainty by means of two-dimensional probabilistic uncertainty analysis (Cullen and Frey, 2000) would have gone beyond the scope of this work. However, in Chapter 6.2, a preliminary analysis of the data set comprising the half-lives of atrazine in soil revealed that the overall uncertainty is dominated by the variability of the natural environments and that methodological uncertainties of different experimental setups are less influential but still considerable.

For the use of persistence as a hazard-based substance indicator upon which risk management decisions are based, the considerable uncertainty in the persistence values speaks rather for the classification of chemicals with similar properties into groups which are assessed collectively than for the assessment of single chemicals based on their individual properties. For the same reason, distributional information rather than single values should be used for the ranking of chemicals or the comparison of their persistence with cut-off values (Webster et al., 1998).

Regarding the difference in uncertainty of PP and JP, it was shown that JP values do not a priori have to be more uncertain than PP values, though they include more uncertain information on transformation schemes and substance properties. Rather, their uncertainty depends on how well their most influential input parameters are known. For PCE and NPnEO, the less common situation in which data on transformation products are known more exactly than the data on the parent compound seems to be the case.

The uncertainty in the exact value of the fractions of formation has much less influence on the JP than the degradation rates (CTV for fractions of formation between 6 to 26%). This is largely due to their natural restriction between 0 and 1, while degradation rates can vary between orders of magnitude. On the other hand, it was shown in the chapter on uncertainty in the transformations schemes (Chapter 6.3.2) that the decision concerning which generations of transformation products and which single transformation products to include has the largest influence of all uncertainties on the JP. This decision is the most important for transformation products of the first generation, while the importance of the decision whether or not to include them decreases towards later generations. This was explained by two trends: lower shares of formation for transformation products of later generations and, in some cases, their smaller persistence.

The question of whether or not to include a specific transformation product thus seems to be crucial for the calculation of JP and for the evaluation of persistence in
Uncertainty Analysis of Primary and Joint Persistence

This uncertainty in the transformation scheme leads to a far more general question of decision rule uncertainty. This is the basic question of whether it is justifiable to base decisions on PP alone, even if it can be shown that the inclusion of transformation products can change the persistence value in a much more profound way than the mere consideration of parameter uncertainty. In this work, a strong point is made that the important transformation products should always be included in persistence calculations.

Empirically, from the three case studies, the important transformation products were always found to be either transformation products of the first generation or transformation products that were formed in amounts exceeding 5–10% of the total mass in the system. This limit corresponds quite well to the 10% criteria which was selected in the guideline on transformation products of agrochemicals developed by the College voor de toelating van bestrijdingsmiddelen (CTB) (see Chapter 2.3.1). Suggestions for a more systematic, generalizable approach to identify influential transformation products with as little data as possible are discussed in Chapter 8.2.

Summarily, the analyses in this chapter show that there are three main factors influencing the JP. In order of decreasing importance, they are (i) the (number of) generations of transformation products considered, (ii) the persistence of the individual transformation products and (iii) the fractions of formation with which they are formed.

Regarding the relative importance of model versus parameter uncertainty, no generally valid statement can be made on grounds of the results of this chapter. If the choice of which transformation products to include into the persistence calculations is considered a model uncertainty as suggested in Chapter 6.1, it is relatively more important than parameter uncertainty. On the other hand, it was also shown that another model uncertainty, i.e. how many and which compartments to include in the model, was insignificant compared to parameter uncertainty. Overall, it should be noted that the evaluation of model uncertainty in this chapter remains very fragmentary and is focused on those model uncertainties that are considered most relevant in the context of this work.
Chapter 7

Including transformation products into chemical risk assessment

Although this work is focused on persistence as exposure-based hazard indicator, this chapter ventures into the quantification of risk for parent compound and transformation products, i.e. it applies the traditional approach of calculating the ratio between predicted environmental concentration (PEC) and predicted no-effect concentration (PNEC) as a measure of risk (see Figure 2.1 and description in Chapter 2.1) \(\text{(Fenner et al., 2002)}\). Since the PEC is equivalent to the steady-state concentrations in a level III model, it can be calculated using the same basic mathematical model structure as for the persistence calculations. This only leaves the quantification of the toxicity of the mixture of parent compound and transformation products (PNEC calculations) to be resolved.

This chapter further serves the following purposes. First, the framework for calculation of the combined risk of parent compound and transformation products, as proposed in this chapter, is considered as a useful suggestion how to meet the need stated in the TGD \(\text{(1996)}\) to include transformation products into risk assessment for chemicals. The modelling framework can be used to assess the regional risk of mixtures of agrochemicals as well as of other new and existing industrial chemicals and their respective transformation products. One of the prerequisites for applying the suggested framework is that the most likely transformation products are known, at least with respect to their molecular structure. Second, regarding the importance of different generations of transformation products, it is of interest to see, at least

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for one example, how the consideration of toxicity influences the picture. The NPnEO case study was chosen as a model example for risk calculation because its transformation products show both a high persistence and a high toxicity. Further, high concentrations of NPE have been measured in Swiss waters and questions regarding endocrine disrupting agents have a high actuality, especially in the context of a project called "Fischnetz", recently launched to clarify reasons for the continuous reduction of fish catchment yields in Swiss waters (Burkhardt-Holm and Studer, 2000). Therefore, in this chapter, the PEC to PNEC ratios for the aquatic environment and the sediment are calculated for the individual components of the dynamically formed mixture and the mixture itself. For this purpose, average release rates of NPnEO and its transformation products from Swiss sewage treatment plants were used. A combination of sensitivity and scenario analyses is employed to identify upper and lower bounds of the results. Although, to my knowledge, there are two more studies dealing with the risk of transformation products that include transformation kinetics in multimedia models (Yaffe et al., 2001; Yeh and Kastenberg, 1991), none of them tries to quantify the overall risk stemming from the complex mixture of parent compound and transformation products. Here, the toxicity of the emerging mixture of NPnEO and its transformation products is assessed under the assumption of similar mode of action of the single compounds and, therefore, concentration addition (Altenburger et al., 2000; Backhaus et al., 2000). This combination of fate modelling and toxicity assessment leads to a risk quotient for the entire group of chemicals. PECs were calculated for two sorts of regional models, i.e. one multimedia model representing the whole region of Switzerland and one model representing a river system only, such as, e.g., the river Rhein flowing through Switzerland and Germany.

7.1 Methodology

7.1.1 Regional-scale models

Multimedia model for Switzerland

In order to calculate predicted environmental concentrations (PECs) of NPnEO and its transformation products in Switzerland, the multimedia model for transformation products introduced in Chapter 4 has to be adapted to the specific region of Switzerland (see Figure 7.1). The PECs can then be obtained by solving the regional
model for Switzerland in steady state, i.e. as level III model.

Figure 7.1: Open four-compartment model for Switzerland. In each compartment (soil (s), water (w), air (a) and sediment (sed)) all chemicals x undergo first-order degradation ($\kappa_d^x$) and transformation ($\kappa_T^x = \varphi_T^x \cdot \kappa_d^x$), advective and diffusive phase transfer processes between the compartments ($u_{st}^x$) and advective transport out of the system ($\kappa_{out}^x$). Substances are emitted into the model system as secondary effluents into water ($I_w^x$) and, adsorbed to sewage sludge, into soil ($I_s^x$).

For that purpose, all media dimensions and some environmental properties have been modified to be specific to Switzerland. Additionally, a sediment compartment has been introduced because Swiss waters are often shallow enough for the substances to come into contact with the sediment layers, and because the $K_{ow}$ values of some of the transformation products of NPnEO are high enough for them to partition considerably into the sediment. The exchange processes between the surface water and the sediment compartment are modelled according to the surface mixed sediment layer (SMSL) model described in Appendix A.2. A list of the media dimensions and all parameters deviating from the globally averaged properties according
to Scheringer (1996a) and Mackay and Paterson (1991), as used in the persistence calculations, is given in Tables 7.1A and 7.1B.

**Table 7.1: Model dimensions and transport parameters for Switzerland (CH).**

<table>
<thead>
<tr>
<th>A. Compartment dimensions</th>
<th>Value (m)</th>
<th>Value (m³)</th>
<th>Value (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase depth</td>
<td>Value</td>
<td>CH Compartment volume</td>
<td>CH Interfacial Area</td>
</tr>
<tr>
<td>Soil (hₔ)</td>
<td>0.1</td>
<td>Soil (vₔ)</td>
<td>3.96·10⁹</td>
</tr>
<tr>
<td>Water (hₔ)</td>
<td>3</td>
<td>Water (vₜ)</td>
<td>5.20·10⁹</td>
</tr>
<tr>
<td>Air (hₕ)</td>
<td>1000</td>
<td>Air (vₚ)</td>
<td>4.13·10¹³</td>
</tr>
<tr>
<td>Sediment (hₛed)</td>
<td>0.02</td>
<td>Sediment (vₛed)</td>
<td>3.47·10⁷</td>
</tr>
</tbody>
</table>

**B. Environmental properties different from values in Scheringer (1996a)**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rain rate CH</td>
<td>uₜrain</td>
<td>4·10⁻³ m/d</td>
</tr>
<tr>
<td>Wind velocity</td>
<td>uₜwind</td>
<td>8.64·10⁴ m/d</td>
</tr>
<tr>
<td>Water outflow CH</td>
<td>Uₜwater</td>
<td>1.46·10⁸ m³/d</td>
</tr>
<tr>
<td>Deposition flow</td>
<td>Uₜdep</td>
<td>5.1·10⁻³ kg/m²d</td>
</tr>
<tr>
<td>Sediment density</td>
<td>ρₜsed</td>
<td>2500 kg/m³</td>
</tr>
</tbody>
</table>

It is assumed that the chemicals can be transferred out of the model system through advective transport in the air and the water body. Also, loss of the chemicals through transfer to the permanent sediment is included. The calculation of these loss processes, including the deposition of chemicals into the permanent sediment, is described in Table 7.2.

**Table 7.2: Mathematical expressions for advective loss processes out of the system in water, air and sediment.** The parameters used in the expressions in this table are defined and quantified in Tables 7.1 and A.2.

<table>
<thead>
<tr>
<th>Process description (Kooijman, 2001)</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adveective outflow in air</td>
<td>( K_{out,a} = \frac{\sqrt{\text{area} \cdot hₔ \cdot uₜwind}}{vₔ} )</td>
</tr>
<tr>
<td>Adveective outflow in water</td>
<td>( K_{out,w} = \frac{Uₜwater}{vₚ} )</td>
</tr>
<tr>
<td>Burial to permanent sediment</td>
<td>( K_{out,sed} = \frac{Uₜdep}{(1 - \text{por}) \cdot \rhoₜsed \cdot hₜsed} )</td>
</tr>
</tbody>
</table>

With the additional sediment compartment, taking all transfer, formation, degrada-
Including transformation products into chemical risk assessment

Including transformation products into account leads to a system of $4m$ linear differential equations ($m$: number of chemical species in the system, i.e. parent compound and transformation products). According to Equation 3.4 in Chapter 3.2.2, the change of the concentrations as a function of time $\dot{c}(t)$ can be written as:

$$\dot{c}(t) = -Sc(t) + q$$  \hspace{1cm} (7.1)

The corresponding concentration vector $c(t)$ (in mol/m$^3$) in Equation 7.1 now also contains the concentrations in the sediment compartment, i.e. $c(t) = [c^A_a(t), c^B_a(t), ..., c^m_a(t), c^m_w(t), c^m_{sed}(t)]$. $q$ is the corresponding source term vector containing the continuous release fluxes of the parent compound and the transformation products out of the sewage treatment plant into receiving waters and for NP also into the soil compartment (in mol/m$^3$s), and $S$ is the $4m \times 4m$ square matrix containing all parameters $u_{ik}, \kappa^x_i, \kappa^{xy}_i = \theta^{xy}_i \cdot \kappa^x_i$ and $\kappa_{out,i}$. The steady-state solution ($\dot{c}(t) = 0$) can then be calculated as

$$c^{\text{stat}} = S^{-1}q.$$  \hspace{1cm} (7.2)

In Equation 7.2 the vector $c^{\text{stat}}$ contains all the steady-state concentrations for each chemical $x$ in each compartment $i$ that are used as predicted environmental concentrations (PECs) to calculate the risk quotients.

**River model**

Since the formation of transformation products is a dynamic process, the risk quotient is expected to vary in time and space. This phenomenon cannot be investigated in the regional model for Switzerland, which produces a spatially and temporally averaged risk quotient for Swiss waters. Therefore some additional calculations were conducted with a spatially resolved river model as it was set up by Scheringer et al. (2000).

In that model, a river of the length $L=700$ km is divided into $n$ boxes of equal length $l = L/n$ and increasing volume $v_i$ (see Figure 7.2). The volume of the river is assumed to increase by a factor of 4 between its beginning and its end due to the inflow of tributaries, which, in the model, are assumed to be equally distributed. Each box along the river is subdivided into three compartments, i.e. a compartment of moving water (w1), one of stagnant water (w2) and a sediment layer (sed) (see Figure 7.3). Only the stagnant water is in direct contact with the sediment. The exchange processes between the stagnant water layer and the sediment are modelled using the SMSL model (Pfister, 2000; Schwarzenbach et al., 1993) and therefore
the processes and the input parameters for the sediment-water exchange processes are the same as described in Tables A.2 and A.3 in Appendix A.2 for the regional model. Between the moving and the stagnant water compartment, water is exchanged at a constant rate ($k_{\text{exch}12}$). The water flow is modelled as exchange of water between adjacent boxes into the flow direction of the river. This exchange is given by the flow velocity of the water ($u = 1 \text{ m/s}$). Since all NPEs are nonvolatile and/or water-soluble compounds which do not significantly partition into the atmosphere, the fraction in air is disregarded. The dimensions of the compartments and the additional modelling parameters are summarized in Table 7.3.

Figure 7.2: Longitudinal section of the river model according to Scheringer et al. (2000).

Figure 7.3: Cross section of the first river box ($j = 1$) with moving water $w_1$, stagnant water $w_2$, and sediment $\text{sed}$. The three subcompartments of $w_2$ and $\text{sed}$ are not treated separately in the model (Scheringer et al., 2000).
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Table 7.3: Dimensions of river model and additional modelling parameters. The volume of the stagnant water is 12.2% of the moving water. $A_j$ is the cross section of the moving water. $d$ is calculated from the flow velocity $u$ and the cross section of the moving water. $k_{\text{exch12}}$ and $k_{\text{exch21}}$ describe inflow and outflow rates of water parcels of the same volume.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>River length</td>
<td>$L$</td>
<td>700 km</td>
</tr>
<tr>
<td>Number of boxes</td>
<td>$n$</td>
<td>70</td>
</tr>
<tr>
<td>Box length</td>
<td>$l$</td>
<td>10 km</td>
</tr>
<tr>
<td>Water flow velocity</td>
<td>$u$</td>
<td>1 m/s</td>
</tr>
<tr>
<td>Depth of moving water</td>
<td>$h_{w1}$</td>
<td>4.9 m</td>
</tr>
<tr>
<td>Depth of stagnant water</td>
<td>$h_{w2}$</td>
<td>0.4 m</td>
</tr>
<tr>
<td>Depth of sediment</td>
<td>$h_{\text{sed}}$</td>
<td>0.05 m</td>
</tr>
<tr>
<td>Cross section at beginning of box $j=1$</td>
<td>$A_1$</td>
<td>392 m$^2$</td>
</tr>
<tr>
<td>Cross section at beginning of box $j=1$</td>
<td>–</td>
<td>48 m$^2$</td>
</tr>
<tr>
<td>Cross section at end of box $j=n$</td>
<td>$A_{n+1}$</td>
<td>4 · $A_1$</td>
</tr>
<tr>
<td>Transport coefficient</td>
<td>$d$</td>
<td>$u \cdot A_{j+1}/V_j$</td>
</tr>
<tr>
<td>Exchange coefficient</td>
<td>$k_{\text{exch12}}$</td>
<td>$1 \cdot 10^{-5}$ s$^{-1}$</td>
</tr>
<tr>
<td>Exchange coefficient</td>
<td>$k_{\text{exch21}}$</td>
<td>$k_{\text{exch12}} \cdot V_{w1}/V_{w2}$</td>
</tr>
</tbody>
</table>

Just as for the regional model, the basic mathematical structure of the river model in Scheringer et al. (2000), describing the transport and fate of one substance, was extended to account for the dynamic formation and fate of transformation products as described in Chapter 4.2.

Regarding the input scenario, it is assumed that the emissions from sewage treatment plants of one or several substances are into the moving water compartment, $w_1$, of the first box. The quantification of the substance emissions was only done very roughly by assuming that only one of the approximately 1000 sewage treatment plants in Switzerland emits into the river. This might not be a very realistic scenario for such a large river. However, it is not within the scope of this study to model spatially resolved emissions along the river. Therefore, the focus in the river model calculations is not on the correct quantification of the magnitude of risk, but on the investigation of the spatial risk profiles. For that purpose, only the relative amounts of the different substances emitted matter.

The individual emissions are summarized in the emission vector $q$ (in mol/s) and, by solving Equation 7.2, steady-state concentrations for $3n$ compartments and $m$ compounds are calculated.
7.1.2 Risk quotient for a complex mixture of parent compound and transformation products

For a single compound $x$, the risk to the organisms living in a given environmental compartment is commonly expressed as risk quotient ($RQ^x$), which compares the concentration $c^x$ of the compound $x$ in that compartment to some measure of its toxicity, e.g. $EC_l^x$ ($EC$=effect concentration, $l$=effect level in percent of affected organisms).

To describe the environmental risk posed by that mixture of a chemical and its emerging transformation products, ways of predicting the risk of the mixture from the toxicity of the individual components are needed. To this end, the concept of mixture toxicity, up to now mainly used for the assessment of mixtures that were initially released as such, is applied. The components of a chemical mixture can act either interactively (synergistically or antagonistically) or without interaction (through similar or dissimilar modes of action) on a given target organism. Because information about the interaction between components is often lacking and difficult to deduce from the chemical structures, no interaction is assumed in most cases as a first estimate (Vouk et al., 1987) (pp. 107-111). Two basic concepts can be distinguished in this case. The first is independent action (IA; also: response addition), assuming that the mixture components act independently on different receptor systems. The second is concentration addition (CA), which means that the mixture components have the same mode of action and the same slope of their dose-effect curves so that - at each concentration level - one component can be substituted by an equi-effective amount of another component.

For our calculations of the risk of the mixture of parent compound and transformation products, we assume CA (although short-chain and long-chain NPEs have not strictly the same mode of action (E.C., 2000)). CA has been shown experimentally (Backhaus et al., 2000) and numerically (Faust et al., 2001) to be a conservative but not over-conservative assumption. It has been found that, with CA, the mixture toxicity of independently acting chemicals is overestimated by maximally a factor of 10 (Backhaus et al., 2000). With the precautionary principle justifying such an overestimation, CA might therefore be considered an appropriate approach for a routine effect assessment of chemical mixtures (Backhaus et al., 2000).

Given CA, the concentrations of all components of a mixture can be transformed into an equivalent concentration $c^ref_{EQ}$ of a reference compound by summing up the concentration of each component multiplied by its relative potency $RP^x$. The relative
potency $RP^x$ is defined as the ratio of the toxic potency of the reference compound ($EC^\text{ref}_t$) divided by that of the compound $x$ ($EC^x_t$). The total risk of the mixture can then be assessed by comparing the equivalent concentration $c^\text{ref}_\text{EQ}$ with a given toxicity threshold of the reference compound (see Equation 7.3).

$$RQ'_{\text{mix}} = \frac{c^\text{ref}_\text{EQ}}{EC^\text{ref}_t} = \frac{\sum_x c^x \cdot RP^x}{EC^\text{ref}_t} = \frac{\sum_x c^x \cdot EC^\text{ref}_t}{EC^\text{ref}_t} = \sum_x \frac{c^x}{EC^x_t} = \sum_x RQ^x$$  \hspace{1cm} (7.3)

Equation 7.3 shows the usual expression for the mixture risk quotient (E.C., 2000; TGD, 1996; Vouk et al., 1987) indicating that, under the assumption of concentration addition, the risk for exposure to a mixture can be expressed as the sum of the single risk quotients $RQ^x$ of all toxicants of concern. Equation 7.3 thus implies that several subthreshold, i.e. ineffective exposures could have a cumulative adverse effect.

In the methodology suggested here, the concentration of the single substances is not measured but predicted with the help of the multimedia model described above. Therefore predicted environmental concentrations $PEC^x$ are used instead of measured concentrations $c^x$ to determine the risk quotients. Also, not the measured toxic effect concentrations $EC^x_t$ are used as toxicity thresholds, but predicted no-effect concentrations $PNEC^x$, which are extrapolated from the $EC^x_t$ values by applying extrapolation factors $EF^x$ that account for inter- and intraspecies variability, acute to chronic extrapolation, and extrapolation from low observed effects to predicted no-effect levels, thus $PNEC^x = EC^x_t/EF^x$. Accordingly, the definition for the mixture risk quotient $RQ_{\text{mix}}$ as used here is given in Equation 7.4.

$$RQ_{\text{mix}} = \sum_x \frac{PEC^x}{PNEC^x} = \sum_x RQ^x$$  \hspace{1cm} (7.4)

According to the EU TGD (1996), an EF of 1000 is applied if only acute toxicity data (L(E)C$_{50}$) for a given substance are available. This EF can be lowered (100, 50 or 10) if long-term studies have been conducted. The value of the EF then depends on the number of trophic levels for which long-term endpoints were measured and on whether the species with the lowest NOEC (no-observed effect concentration) value also shows the lowest acute toxicity (TGD, 1996).
7.1.3 Model input data including emission rates and toxicities

Usage of nonylphenol ethoxylates in Switzerland

As mentioned in Chapter 5.1 already, NPEs were banned from use in domestic cleaning agents in Switzerland in 1987. However, industrial NPE usage in other products still exceeds 400 tons per year in Switzerland (Rimml et al., 2000). Nearly 60% of that amount are discharged into the waste water, which goes into sewage treatment plants. During waste water treatment, NPEs are degraded according to the same transformation scheme as in the environment, i.e. they are partially degraded by microorganisms to compounds with shorter ethoxy chains (NP1/2EO) and partly carboxylated ethoxy chains (NP1/2EC) and under anaerobic conditions further to nonylphenol (NP) (see Figure 5.2 in Chapter 5.1). The degradation of long-chain NPE (NPnEO) during wastewater treatment is quite efficient under aerobic conditions. The compounds with less ethoxy units, on the other hand, are more persistent.

Of the total NPE amount treated in sewage treatment plants in Switzerland (240 t/y) approximately 45% (i.e. 108 t/y) are still found in the secondary effluents and digested sewage (Ahel et al., 1994b). Of this amount, 60% (66.7 t/y) are released to the surface water with the secondary effluents, being present as a mixture of long-chain NPnEO, short-chain NP1/2EO, carboxylic acids NP1/2EC, and NP. The 40% (41.3 t/y) associated with the sewage sludge are mainly NP; 45% (18.7 t/y) of this amount are applied to the soil with the sewage sludge. The other part of the sewage sludge and the associated NP is burnt or stored (Fent, 1998; Gujer, 1999).

Ahel et al. (1994b) examined 11 sewage treatment plants in Switzerland for the composition of the secondary effluent and calculated fractions of 28% for NPnEO, 22% for the sum of NP1EO and NP2EO, 46% for the sum of NP1EC and NP2EC, and 4% for NP (weight average based values). To determine the chemical input into the water compartment of the model, we apply these percentages to the above 66.7 t/y released with the secondary effluent.

Concerning the relative amounts of NP1EC and NP2EC, Potter et al. (1999) found in brackish water samples five times more NP2EC than NP1EC (measured on a molar basis). This means that, on a weight basis, mass fractions of approximately 39% NP2EC (26.2 t/y) and 7% NP1EC (4.5 t/y) are released. Bennett and Metcalfe (2000) and Ejlertsson et al. (1999) investigated NP1EO and NP2EO in the sediment. The ratio of NP2EO to NP1EO was between 0.33 and
Table 7.4: Yearly releases of NPnEO and its transformation products in secondary effluents of Swiss sewage treatment plants (Aher et al., 1994b).

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>NPnEO</th>
<th>NP2EC</th>
<th>NP1EC</th>
<th>NP2EO</th>
<th>NP1EO</th>
<th>NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission into soil</td>
<td>tons/year</td>
<td>no input</td>
<td>no input</td>
<td>no input</td>
<td>no input</td>
<td>18.7</td>
</tr>
<tr>
<td></td>
<td>mol/d</td>
<td>233</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emission into water</td>
<td>tons/year</td>
<td>18.7</td>
<td>26.2</td>
<td>4.52</td>
<td>4.00</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>mol/d</td>
<td>77.7</td>
<td>223</td>
<td>44.6</td>
<td>35.4</td>
<td>111</td>
</tr>
</tbody>
</table>

0.4 (mass basis). We used the average of 0.37 and calculated mass fractions of 16% (10.7 t/y) for NP1EO and 6% (4.0 t/y) for NP2EO.

The yearly releases of the different NPE components in secondary effluents of Swiss sewage treatment plants are summarized in Table 7.4.

Environmental behavior of NPnEO and its transformation products

The Henry's law constant, $K_H$, octanol-water partition coefficient, $K_{ow}$, and degradation rate constants, $\kappa_i$, of the six chemical species investigated are the same as presented in Table 5.2 and in Table 6.7. The fractions of formation are the same as established in Chapter 6.3.1 in Table 6.9 for the presence of a sediment compartment.

Toxicity of NPnEO and its transformation products

To derive a "Predicted No-Effect Concentration" (PNEC) for every single substance, a broad set of toxicity data was evaluated, containing data from databases in E.C. (2000), UK EA (2000), Servos (1999), and Staples et al. (1998). The EU study (UK EA, 2000), Servos (1999) and Staples et al. (1998) distinguish between data points that are considered valid and well documented and those that should be used with care. Here, only "valid" data were included.

It is known that, besides general acute and chronic toxicity, NPE also cause estrogenic responses in aquatic organisms that occur at concentrations similar to those at which chronic effects occur (E.C., 2000). However, the relative intensity of this effect for the different compounds is still an unresolved issue, see Metcalfe et al. (2001) vs. Jobling et al. (1996). The risk through estrogenic behavior is therefore not assessed in this study.
For all substances, PNEC values were deduced only from acute toxicity data by applying an EF of 1000. This choice is based on the following consideration: Long-term NOECs that are eligible for lower EFs of 50 according to the recommendations of the EU TGD (1996) are available only for NP and NPnEO. Using EF = 50 for NP and NPnEO and EF = 1000 for the other compounds, however, distorts the relative toxicity of the chemicals because it makes NP and NPnEO relatively less toxic (the long-term NOECs of NP and NPnEO are lower than the LC50s by only a factor of 5, compared to a factor of 20 between the two generic EFs of 1000 and 50). In setting up a set of standard values as a basis for further discussions, we decided to conserve the relative toxicity reflected in the LC50 values and used constant EFs of 1000 for all six compounds. Derived that way, the PNEC values in water reflect the tendency of increasing toxicity with decreasing chain length reported by Servos (1999) with NP being the most toxic compound. The PNECs in water are given in Table 7.5 along with the underlying LC50 values. PNEC values for the sediment were derived from the PNECs in water by using the equilibrium partitioning approach (Di Toro et al., 1991). The resulting values in μg/kg sediment are also listed in Table 7.5.

Table 7.5: Toxicity values of NPnEO and its transformation products. Lowest acute lethal concentrations (LC50) were selected from a database that was compiled from refs (UK EA, 2000; E.C., 2000; Servos, 1999; Staples et al., 1998).

<table>
<thead>
<tr>
<th>Endpoint</th>
<th>NPnEO</th>
<th>NP2EC</th>
<th>NP1EC</th>
<th>NP2EO</th>
<th>NP1EO</th>
<th>NP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
<td>LC50</td>
<td>LC50</td>
<td>LC50</td>
<td>LC50</td>
<td>LC50</td>
<td>LC50</td>
</tr>
<tr>
<td></td>
<td>Mysisidopsis bahia magna promelas bahia bahia azteca</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test duration</td>
<td>h</td>
<td>96</td>
<td>48</td>
<td>96</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>Concentration</td>
<td>μg/l</td>
<td>900</td>
<td>900</td>
<td>2000</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>Extrapolation factor (EF)</td>
<td></td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>PNEC in water</td>
<td>μg/l</td>
<td>0.90</td>
<td>0.99</td>
<td>2.00</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>PNEC in sediment</td>
<td>μg/kg</td>
<td>83.3</td>
<td>3.43</td>
<td>6.93</td>
<td>86.0</td>
<td>79.8</td>
</tr>
</tbody>
</table>

For comparison with this standard set of PNECs, the PNECs derived for NP and NPnEO from long-term NOECs were included as scenario B1 in the scenario analysis, see below, Chapter 7.2.2 on sensitivity and scenario analysis and Table 7.7. The lowest NOEC values, the appropriate EFs used and resulting PNECs are 3.9 μg/l (endpoint: length, Mysisidopsis bahia, 28 d), EF = 50, and PNEC = 0.078 μg/l for NP.

A third approach for deducing PNECs is to analyze distributions of species sensitivities and to define the acceptable environmental concentration as the concentration at which 5% of the species are exposed above their toxicity threshold (*Smith and Cairns, 1993*). In *E.C.* (2000), a hazardous concentration for 5% of the species (HC₅) is determined for NP from the log-probit transformed distribution of acute toxicity data (40 µg/l). Extrapolation factors of 4 and 10 are applied that account for the acute to chronic ratio and for sublethal effects and species differences, resulting in a PNECₙₕₑₜ of 1 µg/l. The PNECs of the other substances are deduced by using factors between 2 and 200, expressing the relative toxicities of the chemicals. (This approach assumes the same slope of the distributional curve as for NP for all chemicals.) These PNECs lie by a factor of 20–200 higher than those listed in Table 7.5 as standard values. This third set of PNEC values is discussed in the scenario analysis as scenario B2.

### 7.2 Average risk in Swiss water systems

#### 7.2.1 Results

*Predicted concentrations*

Figure 7.4 shows the mole fractions of NPnEO and its transformation products in the compartments soil, water and sediment in steady state. In air, no relevant amounts of any of the compounds were found. All compounds except NP partition mainly between water and sediment with the acids NP₂EC and NP₁EC found predominantly in water due to their higher water solubility. NP, being the only compound emitted to soil (adsorbed to sewage sludge), is mainly found in the soil compartment.

Water concentrations range from 0.012 µg/l for NP to 0.36 µg/l for NP₂EC (see Table 7.6 for the concentrations of all compounds), while concentrations in sediment range from 0.13 µg/kg for NP₁EC to 8.6 µg/kg for NP₁EO.

To evaluate these results, the water concentrations obtained from the model are compared in Table 7.6 with measured concentrations for five locations in Swiss rivers (*Ahel et al.,* 2000). Only for the river Glatt measurements are presented that include NP, the short-chain ethoxylates as well as the acids. Our calculated concentrations for these five compounds deviate from the measured concentrations in
Figure 7.4: Mass fractions of NPE in the compartments soil, water and sediment (on a molar basis). Fractions in air are below 0.1% for each compound (not shown).

the Glatt by a factor of 1.7 to 5. Further, the calculated concentrations for NP2EO and NP1EO lie within the range of the measurements in all five locations, while the concentration calculated for NP lies below the detection limit of the measurements. The tendency towards underprediction in the model results might be due to the fact that the calculations represent averages of all Swiss waters, while the measurements were conducted in rivers with characteristically high anthropogenic loads. Sediment concentrations have not been extensively measured yet, so that a comparison with the predicted concentrations is not possible here.

Risk assessment
Risk quotients were calculated for water and sediment. The risk quotients of the individual compounds, RQ, and the mixture risk quotient, RQmix, in water are listed in Table 7.7 (scenario "standard"). The most relevant result here is that none of the single compounds' concentrations reaches the corresponding effect level (all RQ are below 1), but the mixture exhibits a risk quotient of 2.5 and must therefore be considered potentially harmful. It should be noted though that NP1EO itself comes very close to its effect level. The biggest contributors to the overall risk are at the same time the most toxic compounds, namely NP and the short-chain ethoxylates NP2EO and NP1EO. This is still the case although all their concentrations are lower than the concentrations of the other compounds (NPnEO and short-chain acids),
Including transformation products into chemical risk assessment

Table 7.6: Comparison of the steady-state concentrations $c^*$, and measured concentrations of NPE in the river Glatt (Switzerland) and different other Swiss rivers by Ahel et al. (2000).

<table>
<thead>
<tr>
<th></th>
<th>$c^{NPE\text{EO}}$</th>
<th>$c^{NP2\text{EC}}$</th>
<th>$c^{NP1\text{EC}}$</th>
<th>$c^{NP2\text{EO}}$</th>
<th>$c^{NP1\text{EO}}$</th>
<th>$c^\text{NP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated concentrations (µg/l)</td>
<td>0.077</td>
<td>0.36</td>
<td>0.17</td>
<td>0.042</td>
<td>0.11</td>
<td>0.012</td>
</tr>
<tr>
<td>Measured concentrations in the river Glatt (Switzerland) (µg/l)</td>
<td>–</td>
<td>0.60</td>
<td>0.70</td>
<td>0.095</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Measured concentrations at five locations in Swiss rivers over the period 1997–1998 (µg/l)*</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>nd–0.31</td>
<td>nd–0.35</td>
<td>nd–0.48</td>
</tr>
</tbody>
</table>

which are less toxic than NP by a factor of about 50–100. Risk quotients in sediment are generally lower. They vary between 0.011 for NPnEO and 0.108 for NP1EO. The sequence of compounds in order of decreasing risk in sediment is NP1EO, NP2EC, NP, NP2EO, NP1EC, NPnEO. The mixture risk quotient lies below 1 at a value of 0.327.

*nd: below detection limit of 0.03 µg/l
†Exceedingly high value, measured in small river with high loads
Table 7.7: Calculated $RQ^x$ values in water for single components $x$ and $RQ_{mix}$ for the mixture. Uncertain parameters such as degradation rates and fractions of formation as well as PNEC extrapolation models are varied in the different scenarios. The standard scenario relates to the input parameters as given in Tables 6.9, 7.1, 7.4, and 7.5.

<table>
<thead>
<tr>
<th>Uncertain parameter</th>
<th>Scenario description</th>
<th>$RQ_{NP_{nEO}}$</th>
<th>$RQ_{NP_{2EC}}$</th>
<th>$RQ_{NP_{1EC}}$</th>
<th>$RQ_{NP_{2EO}}$</th>
<th>$RQ_{NP_{1EO}}$</th>
<th>$RQ_{NP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Standard</td>
<td>0.085</td>
<td>0.364</td>
<td>0.084</td>
<td>0.383</td>
<td>0.985</td>
<td>0.565</td>
</tr>
<tr>
<td>Degradation rates</td>
<td>(A1) Upper limit degradation rates</td>
<td>0.014</td>
<td>0.274</td>
<td>0.125</td>
<td>0.083</td>
<td>0.168</td>
<td>0.395</td>
</tr>
<tr>
<td></td>
<td>(A2) Lower limit degradation rates</td>
<td>0.298</td>
<td>0.437</td>
<td>0.040</td>
<td>0.580</td>
<td>1.650</td>
<td>0.631</td>
</tr>
<tr>
<td>PNEC extrapolation models</td>
<td>(B1) PNEC$^x$ calculated strictly according to TGD</td>
<td>0.004</td>
<td>0.364</td>
<td>0.084</td>
<td>0.383</td>
<td>0.985</td>
<td>0.150</td>
</tr>
<tr>
<td></td>
<td>(B2) RQ calculated with PNEC$^*$ from the distributional assessment in E.C. (2000)</td>
<td>3.84*10$^{-4}$</td>
<td>0.002</td>
<td>8.43*10$^{-4}$</td>
<td>0.021</td>
<td>0.054</td>
<td>0.012</td>
</tr>
<tr>
<td>Fractions of formation</td>
<td>(C1) Equal shares for parallel reactions (reactions: $1=0.5$; $2=1$; $3=0.5$; $4=0.5$; $5=0.5$; $6=0.5$; $7=0.33$; $8=0.33$ for all compartments)</td>
<td>0.085</td>
<td>0.353</td>
<td>0.078</td>
<td>0.470</td>
<td>1.013</td>
<td>1.677</td>
</tr>
<tr>
<td></td>
<td>(C2) No reaction of NP1/2EO to NP1/2EC (without reactions 5,7)</td>
<td>0.085</td>
<td>0.343</td>
<td>0.068</td>
<td>0.363</td>
<td>1.111</td>
<td>0.591</td>
</tr>
<tr>
<td></td>
<td>(C3) No NP formation in the sediment (without reactions 3,8 in the sediment)</td>
<td>0.085</td>
<td>0.364</td>
<td>0.084</td>
<td>0.383</td>
<td>0.985</td>
<td>0.544</td>
</tr>
</tbody>
</table>


In the calculated mixture risk quotients, the contribution of directly emitted transformation products cannot be distinguished from the contribution of those that are formed after release from the sewage treatment plant. In order to analyze how much of the risk of the mixture is due to the direct emission of transformation products and how much is due to the formation of transformation products from their precursors, the mixture risk quotient was calculated once more under exclusion of the transformation reactions. Doing this resulted in a \( R_{\text{mix}} \) of 2.05. Thus, for the emission scenario in Switzerland, the contribution to \( R_{\text{mix}} \) through the actual formation of transformation products is small (only around 0.4). However, in order to point out the general importance of the formation of transformation products for other emission situations and possibly other substance families too, a second calculation was performed in which it was assumed that all NPE was emitted in the form of NPnEO. This resulted in a \( R_{\text{NPnEO}} \) for the parent compound itself of 0.58 and an \( R_{\text{mix}} \) of the resulting mixture of 2.23, which lies higher than the risk of the parent compound itself by a factor of 3.9. This hypothetical emission scenario clearly shows that simply through the formation of transformation products a mixture might result whose mixture risk quotient exceeds the critical limit of 1, while the parent compound itself exhibits no risk.

### 7.2.2 Sensitivity and scenario analysis

Here, investigations about uncertainty are conducted in water only, since the mixture risk quotient in water lies above the critical limit. The values of the risk quotients in water as given in Table 7.7 (scenario "standard") depend strongly on the assumptions and input parameters that enter the calculation of the PEC and PNEC values. The uncertainty in the PEC values is discussed extensively in Chapter 6. The uncertainty in the PNEC values stems from uncertainty about the completeness of the collected toxicity data and from the model chosen to extrapolate from effect concentrations to no-effect concentrations. In the following, we discuss the influence of the most important uncertainties on the risk quotients \( R^* \) and \( R_{\text{mix}} \).

First, the sensitivity of \( R_{\text{mix}} \) to 68 model input parameters related to the chemical compounds was investigated (i.e. emission rates, degradation rates, partition coefficients, fractions of formation, PNEC values). For that purpose the dimensionless elasticity \( U_E \), i.e. the normalized sensitivity of \( R_{\text{mix}} \) to a one percent change in each input parameter, was evaluated as described in Chapter 5.4.3 already. All sensitivities exceeding 0.01 are represented in the sensitivity plot in Figure 7.5.
As expected, the RQ_{mix} is very sensitive to the PNEC values and emission rates of the three most toxic compounds NP2EO, NP1EO and NP, because it is directly proportional to these two types of parameters. The only relevant sensitivity other than to the PNEC values and emission rates is to the degradation rates and fractions of formation in water. As the degradation rates and fractions of formation contribute only indirectly to the PEC and RQ values, they are less influential though. One surprising result is the quite high influence of the Henry's law constant of NP. A possible reason for this is that its absolute value of 11.0 Pa·m^3/mol is high enough that a slight change considerably influences the distribution of NP between water and air. This assumption is supported by the fact that NP has been measured in air occasionally (Dachs et al., 1999).

To relate the sensitivities given in Figure 7.5 to the actual uncertainties in the input parameters, we defined a number of different, yet still realistic scenarios for each type of input parameter that the mixture risk quotient was found to be sensitive to.
Including transformation products into chemical risk assessment

(degradation rates, PNEC extrapolation model, fractions of formation), and calculated the corresponding \( RQ^* \) and \( RQ_{\text{mix}} \) values (see Table 7.7, scenarios A1 to C3). For the emission rates no alternative scenarios were defined because it is believed that the current numbers best represent the momentary use and emission situation of NPnEO and NP in Switzerland.

Using only the fastest degradation rates from the data collection (scenario A1) reduced \( RQ_{\text{mix}} \) by about 57% to a value still above the critical limit of \( RQ_{\text{mix}}=1 \). Using the slowest degradation rates (scenario A2) increased the \( RQ_{\text{mix}} \) by 47%. The biggest contribution to these changes stem from changes in \( RQ^{\text{NP1EO}} \) and \( RQ^{\text{NP2EO}} \). This is due to their high toxicity, on the one hand, but also to a large spread in the degradation rate data especially for NP1EO, on the other hand. The temperatures at which the degradation rates reported in the literature were measured vary between 284 and 310 K. Since average temperatures in Switzerland are around 283 K, degradation rates in the standard scenario might be too high and the actual situation might be closer to scenario A2 (low degradation rates).

One alternative PNEC extrapolation model is to derive each PNEC* strictly according to data availability and TGD recommendations for extrapolation factors (scenario B1, as mentioned above in the toxicity section of Chapter 7.1.3). This led to higher PNEC values for NP and NPnEO and to a change in \( RQ_{\text{mix}} \) of about -20%.

A rather different picture is obtained (scenario B2) if the PNEC values are used that were obtained from the distributional assessment of toxicity values (scenario B2) as it was conducted by Environment Canada (E.C., 2000). This is the only scenario where \( RQ_{\text{mix}} \) drops well below 1 to a value of 0.09 due to the fact that the PNEC values in scenario B2 lie by a factor of 20 to 200 higher than those of the standard scenario (see Chapter 7.4 for discussion).

Scenario C1 for the case of different transformation schemes assumes a worst-case information situation where nothing is known about the importance of the different pathways. Therefore equal fractions of formation were attributed to all parallel reactions, i.e. 100% transformation in the case of single pathways, 50% transformation in the case of two parallel pathways and 33.3% transformation in the case of three parallel pathways. This assumption was made for the soil, water and sediment compartments equally. This scenario leads to a considerably higher \( RQ_{\text{mix}} \) of 3.68, which is mainly due to the scenario’s assumption that NP is formed in all compartments. Two other more realistic formation scenarios, C2 and C3, address the two main uncertainties about the transformation scheme as identified in the literature and during discussions with experts. Scenario C2 concerns the question
whether the acids are formed through the oxidation of short-chain ethoxylates (reac-
tions 5, 7 in Figure 5.2) or whether they are only formed directly from longer-chain
ethoxylates. Scenario C3 represents a situation in which the sediment environment
is not sufficiently anaerobic for NP to be formed, so that NP1EO and NP1EC are
directly mineralized (reactions 3a, 8a in Figure 5.2). Interestingly, both scenarios
show only small deviations from the standard scenario. Consequently, the impor-
tance of knowing the exact transformation scheme seems to be low compared to
other uncertainties.
Assuming that the different scenarios in Table 7.7 cover the most important uncer-
tainties, we conclude that, given a particular PNEC extrapolation model, the other
uncertainties change $RQ_{\text{mix}}$ and most $RQ^*$ values by maximally a factor of about 2.

7.2.3 Discussion

We first discuss our results in the light of two other recent risk assessments for the
same substance family. The first one is the EU risk assessment for nonylphenol (UK
EA, 2000) and the second one is a risk assessment for nonylphenol and its ethoxy-
lates, conducted by Environment Canada and Health Canada (E.C., 2000). A more
general discussion can be found in the conclusions (see Chapter 7.4).

In the EU risk assessment for nonylphenol, ethoxylates were only considered under
the aspect that their biotransformation contributes to the biggest part of NP re-
leased into the environment, but were not assessed themselves. The EU assessment
investigates a variety of possible release scenarios of NPE from households and indus-
try into water. Local and regional PECs for NP were calculated under standard
worst-case assumptions, as described in the TGD (1996) (part IV), thus reflecting
hot spot situations and overestimating average concentrations in most European
rivers and lakes. On the toxicity side, a moderately conservative PNEC of 0.33 \(\mu\text{g/l}\)
was used. Given these assumptions, the EU risk assessment identifies risks to the
environment for nearly all applications of NPEOs as well as for the production of
NP and NP derivatives (RQ values for NP range from <0.6 up to approx. 1400).

Accordingly, a ban of NPE usage in all water-relevant use categories is suggested (i.e.
washing detergents, cosmetics, industrial surfactants, textile and leather industry,
paper production, metal production and veterinary medicine).

In our regional model for Switzerland, the risk quotient of nonylphenol alone (which
also mainly stems from NPE biodegradation) is around 0.6. Obviously, if only
NP was considered, no high risk would be deduced from our generic, regional risk
assessment. However, in our analysis we find that NP only accounts for 2.2% of the total mass in the water compartment and for only 23% of the total risk stemming from NPnEO and all of its transformation products. Since all these compounds exist together as mixture in the environment and since assuming a similar mode of action for them seems reasonable (E.C., 2000), our results indicate that assessing the risk of the overall mixture (RQ_{mix}) is required. By doing so, we also identify a risk quotient from NPE usage exceeding 1 in the regional model and come to the same conclusion regarding the need of release reductions for NPEs as the EU risk assessment. This, in turn, means that the EU risk assessment would identify an even higher risk if all NPEOs and NPECs, present at the same time as NP, were included into the assessment.

In the Canadian study (E.C., 2000), concentrations in receiving waters for all compounds considered in our analysis were measured. These measured concentrations were used to calculate the risk from each single compound as well as the overall risk of the entire group of compounds.

Regarding the risk quotients of the single compounds, the relative magnitude of our RQ^x values corresponds to the relative frequency with which the single compounds exceed a risk quotient of 1 in the Canadian study. Both studies agree that NP1EO poses the highest single risk, followed by the other two more toxic compounds NP2EO and NP, and in that the acids NP2EC and NP1EC exhibit lower single risks. The only difference regarding the relative importance of the individual components is that in our study NPnEO is less important than NP2EC whereas in the Canadian study it exceeds a risk quotient of 1 more frequently than both acids. This difference might be due to a slightly differing composition of sewage treatment plant effluents in Canada and Switzerland. All in all, however, our model appears to be able to reflect the observed relative contributions of the single compounds to the overall risk.

7.3 Risk profiles in the river model

7.3.1 Results

Two different emission scenarios were investigated in the river model. In the first scenario (A), the same relative emission pattern of NPnEO and its transformation products from Swiss sewage treatment plants was used as for the regional-scale model. However, only 0.1% of the total amount of each compound was assumed
to enter that particular river since there are approximately 1000 sewage treatment plants in Switzerland. As mentioned in the methodology section, this is certainly too small an amount for the river Rhine. Therefore, this investigation will not focus on the absolute risk but on the shape of the risk profiles. The second emission scenario (B) assumes that the whole chemical mass is emitted as untransformed NPnEO. This scenario is less realistic, but it is of theoretical interest because it shows how the risk profiles change along the river through the successive formation of transformation products, isolated from the effects of dilution and degradation of initially released amounts of transformation products.

Generally, the shapes of the resulting spatial concentration profiles along the river look quite similar in all three compartments. Concentrations in the two water compartments, w1 and w2, are nearly identical, while those in sediment lie one to two orders of magnitude higher (in μg/l). The corresponding risk quotients are, on average, by about a factor of 150 smaller than those identified in the regional model, because the release is only 0.1% of the release into the regional model, but the volume of the river is at the same time about 7 times smaller than the total volume of Swiss waters. In the following, only the results for the risk in the flowing water compartment, w1, will be discussed in detail. In Figures 7.6 and 7.7 the risk profiles for each transformation product are depicted for emission scenarios A and B, respectively. The layout of the profiles in accordance with the transformation scheme clearly shows how the shape of the risk profiles changes from generation to generation. In Figures 7.8 and 7.9 the profile of RQmix as it changes along the river is given, again for both emission scenarios A and B, respectively.

7.3.2 Discussion

The spatial risk profile of the parent compound NPnEO is constantly falling in downstream direction in both scenarios A and B. It shows the shape of an exponential decay, due to degradation, transfer into other compartments and dilution in the increasing river volume.

The risk profiles of the individual transformation products in scenario A (see Figure 7.6) show the same spatial trend as the parent compound in that they are constantly falling. However, the short-chain acids and ethoxylates in particular show a pronouncedly less steep decline than the parent compound. This must be due to the fact that they are being formed at the same time as they are being diluted and degraded. Consequently, also the risk profile of RQmix of the entire mixture for
Including transformation products into chemical risk assessment

Figure 7.6: Longitudinal sections of the risk profiles of NPnEO and its transformation products along the river (moving water segment, w1) for the emission scenario A, i.e. 0.01% of the emissions listed in Table 7.4 are assumed to enter the river.
Figure 7.7: Longitudinal sections of the risk profiles of NPnEO and its transformation products along the river (moving water segment, w1) for the emission scenario B, i.e. the whole chemical mass is emitted as untransformed NPnEO.
Figure 7.8: Longitudinal sections of the profile of the mixture risk quotient, $RQ_{\text{mix}}$ of the entire mixture of NPnEO and its transformation products, along the river (moving water segment, w1) for the emission scenario A.

Figure 7.9: Longitudinal sections of the profile of the mixture risk quotient, $RQ_{\text{mix}}$ of the entire mixture of NPnEO and its transformation products, along the river (moving water segment, w1) for the emission scenario B.
scenario A (see Figure 7.8) shows a less steep decline than the parent compound itself. It follows that, due to the formation of toxic and persistent transformation products while the chemical is transported down the river, the risk in the water might recede slower than expected from dilution and degradation effects.

In order to isolate and clarify this phenomenon, scenario B was constructed, which assumes that no transformation products are actually emitted from the sewage treatment plant, but that they are only formed along the river. Now, the risk profiles of the transformation products all reach their maximum only somewhere along the river. For the first generation, this maximum is around the middle of the river at box \( n = 36 \). For the second generation it is towards the end. For the third generation it is not even reached before the end of the 700 km river length. Here, the formation of the transformation products clearly outweighs the dilution effect. Obviously, formation and advective flow are on a similar time scale since the maximum of each generation is located further down the river.

In the case of NPnEO, in which the transformation products dominate the risk of the mixture due to their persistence and toxicity, this also has consequences for the risk profile of \( \text{RQ}_{\text{mix}} \) (see Figure 7.9). The maximum of the mixture risk quotient now lies at boxes \( n = 26, 27 \) instead of at the beginning of the river. Thus, the spatially resolved model shows that the risk due to the presence of NPnEO and its transformation products becomes maximal at some location further downstream of the outfall location. To my knowledge, this has not been clearly demonstrated before, although the possibility of this phenomenon has already been mentioned in the Canadian study (E.C., 2000). The only instance, however, in which such an augmented risk further downstream can be observed, is if the transformation products are more toxic than the parent compound itself.

### 7.4 Conclusions

The results for the risk of NPnEO and its transformation products in the regional model for Switzerland and in the river model show that the inclusion of transformation products into the risk assessment of the parent compound can considerably increase the overall risk. For the special case of NPnEO, whose transformation products are more toxic and persistent than the parent compound itself, the transformation products even account for 97% of the overall risk. For other compounds, the effect might be less pronounced but still relevant.
If the contribution of the transformation products to the overall risk is compared to their contribution to the JP, they are more important in the first case for two reasons. First, in the regional model for Switzerland and in the scenario A of the river model, the transformation products themselves are emitted from the sewage treatment plant, along with the parent compound. Second, some of the transformation products of NPnEO are more toxic than NPnEO itself, which gives their exposure an additional weight as compared to the parent compound. It has also been shown that for the emission scenario specific to Swiss sewage treatment plants, the actual formation of transformation products in the environment only accounts for 0.4 of the total risk quotient of 2.47. For a more general emission scenario however, assuming all NPE to be emitted in the form of the parent compound NPnEO, the risk of the mixture resulting from the formation of transformation products lies by a factor of 3.9 higher than the risk of the parent compound alone. Generally, the consideration of the formation of transformation products will always lead to the identification of a higher risk than from the parent compound alone. The extent of the effect though depends on the toxicity of the transformation products relative to the toxicity of the parent compound.

Regarding the uncertainty of the mixture risk quotient, the results from the scenario analysis suggest that the uncertainty of RQmix is smallest due to uncertainties in the fractions of formation (±4% in more realistic scenarios C2 and C3 in Table 7.7), usually within a factor of 2 for different degradation rates, but on the order of at least one order of magnitude for different PNEC extrapolation models. Thus, basically the same results regarding the contribution to variance of degradation rates and fractions of formation to the exposure calculations were obtained from the scenario analysis in this chapter as from the probabilistic uncertainty analysis in Chapter 6.2. However, regarding the judgement about the existence of risk, a much larger uncertainty stems from the PNEC extrapolation models chosen. In this respect, EU TGD guidelines are more conservative than North American ones, which often use the distributional approach. PNEC values deduced with the distributional approach are usually larger for two reasons. First, the distributional assessment relies on the idea that protection of 95% of all species is sufficient, while the TGD approach aims at protecting all species by basing the PNEC on the effect level of the most sensitive species (here: HC5 of 40 μg/l (distributional) vs. LC50 of 20.7 μg/l (TGD)). Second, the distributional assessment uses lower extrapolation factors than the generic ones suggested in the TGD to account for the remaining uncertainties regarding acute to chronic ratio, sublethal effects and species differences (here: 40 (distributional) vs.
The comparison of our study with the EU risk assessment as well as the with Canadian study and the results of the scenario analysis reveal a second factor that heavily influences the judgment about the risk of a specific chemical. The comparison shows that the judgment about risk depends heavily on whether transformation products are considered and, if so, on how many. The same question has been found to be the main model uncertainty in the persistence calculations (see Chapter 6.3).

A third factor influencing the judgment about risk is the assumption of concentration addition, which was not addressed specifically in the scenario analysis. In those cases where it is not applicable but is still used as an estimate of mixture toxicity, it will overestimate the toxicity by maximally a factor of 10.

All in all, the mixture risk quotient in this study is subject to two conservative assumptions regarding PNEC extrapolation and evaluation of mixture toxicity, and one non-conservative assumption in that possible estrogenic effects at low concentrations are excluded.

Regarding the further applicability of the method presented here, the following assumptions need to be considered: the use of averaged landscape parameters (no local conditions), the steady-state conditions, the selection of transformation products and fractions of formation on the PEC side; the assumption of concentration addition and the choice of extrapolation factors on the PNEC side.

The agreement between measured and modelled concentrations in the regional model (see Chapter 7.2) as well as the correspondence between the relative risk of the single compounds in the Canadian study (E.C., 2000) and the relative risk identified in our model calculations, make it plausible that the model is able to describe the complex exposure and effect patterns of a set of transformation products correctly. We therefore suggest that it could be of use – within the above limitations – to assess the risk of other compounds with environmentally relevant transformation products, e.g., odorants such as nitro musks (Gatermann et al., 1998), surfactants used in shower gels and shampoos (Brunner et al., 2000), fluorinated alkanes (Martin et al., 2000), PAHs (Yaffe et al., 2001), or azo-dyes (O’Neill et al., 2000).
Chapter 8

Relevance of transformation products in chemical risk management

8.1 How do transformation products affect risk management decisions?

Chemical ranking and scoring systems such as the frameworks for the identification of POPs or PBT substances presented in Chapter 3.1 use diverse sets of substance indicators to prioritize chemicals for risk assessment or other risk management considerations. Prioritization allows for, among other things, (i) the identification of chemicals that need additional, refined analysis or whose use and releases should be reported on a regular basis, (ii) the realization of efficient risk reduction opportunities such as ban, phase-out or use reductions, (iii) the application of pollution prevention through the comparison of alternative chemicals for industrial processes, and (iv) the selection of candidate substances for intensified research during the early stages of the development of new chemicals (Swanson and Socha, 1995).

This work is focused on two substance indicators frequently used in chemical ranking and scoring, i.e. persistence as exposure-based hazard indicator and the risk quotient as risk-based indicator. Specific attention was given to the investigation of how the consideration of transformation products can change the judgment about a given chemical, i.e. the parent compound.
8.1.1 Joint persistence in priority setting

Persistence is used in priority setting, among other substance indicators, in two ways. One possibility is to use persistence as cut-off criterion. If a given chemical exceeds the cut-off value, it is identified as belonging to a group of chemicals which should become subject to some sort of risk management strategy. The two typical strategies applied in the context of high persistence are the setting up of reporting requirements or a set of more restrictive actions such as ban, phase-out or use/release reductions. A typical example for the setting up of cut-off values that trigger reporting is the Emergency Planning and Community Right-to-Know Act (EPCRA) in the American legislation. In the EPCRA, criteria are set forth to identify PBT chemicals. The persistence cut-off values are those listed in Table 3.1, Chapter 3.1 as US/EPA-P and US/EPA-VP criteria. The purpose of EPCRA is to provide the public with information on the release of toxic chemicals that have the potential to cause adverse effects in their communities. The persistence cut-off values are therefore quite low (2 months in soil, water and sediment, and 2 days in air). A set of higher persistence criteria (US/EPA-VP) (6 months in soil, water and sediment) has also been established to identify chemicals for which a lower reporting threshold should be applied.

Programs whose aim it is to exclude highly persistent and highly bioaccumulative chemicals from use are mostly international agreements on POPs and chemicals with high long-range transport potential. They generally apply higher persistence criteria in order to identify a very small subset of chemicals to which direct action should be applied.

In order to illustrate how the evaluation of JP can change the judgment regarding a specific parent compound, the comparison of the PP and JP values of the three case studies to the cut-off values listed in Table 3.1 was attempted. This is complicated by the fact that PP and JP are overall persistence values while the cut-off values are given as half-lives for single compartments. This difficulty was overcome by comparing PP and JP with the half-life criteria in the main residence compartments of the parent compound and the transformation products. In the case of NPnEO and atrazine it was found that the parent compounds are not persistent under any of the frameworks discussed in Chapter 3.1, Table 3.1. However, the JP values of NPnEO and atrazine both exceed the US/EPA-P criteria for persistence in water, respectively in water and soil for atrazine. Further, in water they even exceed Can-US and POP/UNEP criteria for persistence. In the case of PCE, the parent
compound itself would already have to be classified as persistent in air, and the consideration of the large JP due to the formation of COCl₂ in air would only aggravate this finding. It needs to be mentioned though that, in the case of atrazine and PCE, the BCF values estimated from log $K_{ow}$ values* lie clearly below 1'000 for all compounds where $BCF = 1'000$ is the criterion chosen for bioaccumulation in the EPCRA framework. They would thus, notwithstanding their persistence, not be classified as PBTs. Some of the transformation products of NPnEO (NP1/2EO and NP), however, have BCF values just around 1'000, which would speak for an inclusion of the substance family of NPnEO into the list of PBT chemicals. These findings illustrate the fact that the choice of JP as persistence indicator can considerably change the judgment about the temporal extent of exposure to a chemical. In this work, it is argued that using JP instead of PP as persistence indicator results in a more realistic depiction of overall exposure. Paying regard to the statement in Annex D of the POP convention (UNEP, 2000) that a chemical can still be judged persistent if it does not meet any of the persistence criteria but if there is enough evidence that it is otherwise sufficiently persistent, it is argued that the contribution of transformation products to the persistence of their parent compound could be regarded as an additional reason for consideration and should therefore always be included in the evaluation of the persistence of a substance.

Another possibility to use persistence for priority setting is to use it as ranking criterion. In this function, it helps to set relative priorities for source or release reduction projects or, more generally, to learn about the relative concern of different chemicals in order to allocate resources most efficiently. One example of this type of application is the Informal Working Group on Priority Setting (IPS) of the EU. The IPS ranking system serves as a basis for choosing substances that will undergo extensive risk assessment (Swanson and Socha, 1995; van Leeuwen et al., 1996). Regarding the effect that the consideration of JP can have on the ranking of chemicals, it was shown in Chapter 5.3 for the three case studies that, if the JP is evaluated instead of the PP, the priority between substances can be changed. Thus, entire substance families can show a different rank order than the parent compounds alone. This accelerates the argument that transformation products that are persistent enough and formed in large enough amounts to possibly change the rank of the parent compound in persistence rankings should be included in persistence calculations.

*Estimation of BCF according to $\log BCF = 0.85 \cdot \log K_{ow} - 0.70$ (Schwarzenbach et al., 1993)
Whenever persistence is used as criterion for priority setting, the uncertainty inherent in the persistence values should be taken into account. One should be aware of the fact that the 90% confidence interval is often enclosed by factors as broad as up to 10 around the geometric mean of the distributions of PP or JP. For the use of persistence as ranking criterion this entails that two point values that only lie by a factor of 2–3 apart are not distinguishable with certainty. Rather, in agreement with Webster et al. (1998), it is preferable in these situations to either work with broad persistence classes to which chemicals are assigned on the basis of their persistence ranges, or to examine and compare distributions of persistence values rather than single point values. In this way, the environmental reality is better represented and, at the same time, a distinction between two chemicals is still possible on the basis of their persistence distributions.

Similar considerations apply to the use of persistence in combination with rigid cut-off criteria. Even if the average persistence value evaluated lies above a given cut-off criterion, there is a certain probability that it might lie below that same criterion under certain circumstances. The JP of NPnEO, for example, lies above the criterion for persistence according to US/EPA-P. If, however, the JP is divided by the $GSD$ with the resulting value representing the lower limit of the 67% confidence interval, it lies below that cut-off value. There are thus certain instances in which the substance family of NPnEO would not be judged persistent. Again, in these situations, it might be preferable to evaluate distributions of persistence values and to formulate the cut-off criteria as probabilistic criteria, i.e., as suggested by Webster et al. (1998), to give them the form of "the environmental persistence should be less than 100 d, with a frequency of at least 50%, and with a frequency of 90% less than 200 d".

### 8.1.2 Mixture risk quotient for parent compound and transformation products

Risk assessment according to the TGD (1996) can be regarded as a quantitative scoring system, which is clearly regulated in the risk assessment Directive 93/67/EEC (EEC, 1993) and in the supporting TGD. The risk quotient calculated is a cut-off criterion with a physically interpretable meaning as it indicates whether a concentration found in the environment exceeds a certain threshold concentration above which damage is assumed to be likely to occur. As illustrated in Figure 2.1 of Chapter 2.1.1, depending on the value of the risk quotient, a set of risk manage-
ment measures is triggered. It has to be noted in this context that the risk quotient is a rather hybrid construction in that it is a rigid cut-off criterion, on one hand, distinguishing between harm and no harm, whereas, on the other hand, it can also be used as gradual measure of risk that, depending on its value, entails actions of varying degrees of severity (see Figure 1, "Decision Scheme for Aquatic Risk Characterization", in Chapter 11, "Environmental Risk Assessment of New Substances", in TGD (1996)).

For the case of NPnEO it could be shown that the mixture of parent compound, transformation products emitted and transformation products formed in the environment results in a risk quotient greater than 1 ($RQ_{mix}=2.47$) in the regional scale model for Switzerland, while none of the single compounds exhibits a risk quotient above 1. According to the risk quotient for the entire substance family, there is thus a risk present that needs to be addressed and which would not have been indicated by the risk quotient of the parent compound alone. Of course, the decision regarding the management of NPnEO use and releases would not be based on a single value like the one calculated in Chapter 7. It should, however, trigger further investigations on the subject and the conduction of monitoring studies. If this complementary set of studies, taking all uncertainties into account, confirms that NPnEO and its transformation products present a risk for the region of Switzerland, this could lead to a ban of NPnEO in all water-relevant applications as it was decided in the EU risk assessment on nonylphenol (UK EA, 2000).

In conclusion, the inclusion of transformation products into risk assessment allows for a more realistic representation of the actual environmental conditions and therefore the calculation of the mixture risk quotient of parent compound and transformation products results in a more comprehensive risk assessment. This mixture risk quotient will always lie higher than the risk quotient of the parent compound alone and might thus trigger more stringent risk management decisions. It is therefore argued that decisions based on the mixture risk quotient of the whole substance family should always be given priority over decisions based on the risk quotient of single compounds such as the parent compound.

In the context of risk quotients, it should be noted again that large uncertainties exist regarding the PNEC extrapolation model. The mixture risk quotient can lie as low as 0.09 for the NPnEO case study if PNEC values are deduced by means of distributional assessment (E.C., 2000). Similarly as for the persistence criterion, it might therefore be more sensible to define the presence of risk as a probability that a risk quotient of 1 is exceeded in a probabilistic assessment rather than by means
of a rigid cut-off value of 1.

8.2 Procedure for identifying influential transformation products

Despite the obvious importance of evaluating the JP that was pointed out in the preceding chapters, it was also demonstrated that the calculations are very data and time intensive. At the same time, sensitivity and uncertainty analyses show that only a limited number of input parameters and compounds actually determine the final value of the JP. These findings suggest that JP should be evaluated besides the PP wherever possible, but that means should be found to reduce the amount of input data needed. To achieve this, a less data intensive procedure needs to be developed that allows for a preliminary identification of the most influential transformation products.

8.2.1 Development of the procedure

In Chapter 6 it was empirically shown in the three case studies that it is always the first generation of transformation products and the later generation transformation products that are formed in amounts exceeding 5–10% of the total mass in the system at steady state which make up the biggest part of the JP. The intention here is to investigate whether this finding can be used as a rule to identify the most influential transformation products. For that purpose, an easy-to-use method has first to be developed that allows one to identify those transformation products whose relative mass in steady state exceeds 10%.

As elaborated on in Chapter 6, the main factors influencing the JP, once all transformation products have been identified and the basic structure of the transformation scheme is known, are the persistence of the individual transformation products and their fractions of formation. Both factors depend heavily on the main residence compartments of the compound under question, which in turn are a function of the physico-chemical properties of the compound and its emission or formation compartments.

To identify the main residence compartments in a generic manner, it is suggested that the two-dimensional plot of log $K_H$ versus log $K_{ow}$ presented by Gouin et al. (2000) is employed. The main residence compartments for each compound in the
three case studies are listed in Table 5.8 of Chapter 5.4.1. To obtain an estimate of the persistence of a compound, given the information on its main residence compartments, approximate persistence values $P_x$ for each compound $x$ have been estimated as the geometric mean of the half-lives of that compound in all its relevant residence compartments. If the compound has only one main residence compartment, the half-life in that compartment can be used as such. Regarding the fractions of formation, two information situations are distinguished. In the first situation, individual fractions of formation have been determined for each transformation reaction and for each compartment. They are therefore termed known fractions of formation. In that case and for multicompartmental partitioning of the precursor, approximate fractions of formation ($\text{FF}_{xy}$) are estimated as arithmetic means of the fractions of formation in all relevant residence compartments of the precursor. The second situation is assumed to be a worst-case information situation in which nothing about the relative importance of the single reactions pathways is known. To represent that situation, generic, equal fractions of formation ($\text{GFF}_{xy}$) are attributed to all parallel reactions as described in scenario C1 in Chapter 7.2.2. They are further assumed to be the same in all compartments. The quantities that finally go into the estimation of the JP are not the fractions of formation themselves, but the shares formed ($\text{SF}_x$ for known fractions of formation, or $\text{GSF}_x$ for generic fractions of formation) of each transformation product. They are obtained by multiplication of the fractions of formation of a given transformation product with the shares formed of its precursor and, in the case of converging reaction pathways, subsequent addition of the shares of transformation product resulting from the different pathways. The whole procedure is illustrated in Figure 8.1 for the case of NPnEO. The JP is finally estimated by the approximations given in Equation 8.1 for known fractions of formation and in Equation 8.2 for generic fractions of formation.

$$\text{JP}_{\text{est}} = \text{PP} + \sum_x P_x \cdot \text{SF}_x \quad (8.1)$$

$$\text{JP}_{\text{est}} = \text{PP} + \sum_x P_x \cdot \text{GSF}_x \quad (8.2)$$

### 8.2.2 Results

The results of the estimation procedure for NPnEO are given in Table 8.1, together with the results from running the full model. In the last column, the JP of the full
Figure 8.1: Transformation scheme for NPnEO illustrating the procedure to estimate JP values. Different combinations of s/w/a indicate the main residence compartments for each compound. \( P \) stands for the approximate persistence of each compound given its main residence compartments. \( FF \) are the approximate known fractions of formation and GFF the generic fractions of formation, with which the transformation products are formed out of their precursors given the main residence compartments of the precursors. SF and GSF are the shares formed of each compound, obtained through multiplication of the fractions of formation (known or generic) of that compound with the shares formed of its precursor and, in the case of converging reactions, subsequent addition of the shares of transformation product formed.
model calculation ("true" JP) as well as the two estimated JP values are shown. In the preceding columns, the contribution of each transformation product to the JP is given in absolute and relative terms. Additionally, the rankings of all compounds (parent compound and transformation products) according to their contribution to the JP are given as ordinal numbers. In Tables 8.2 and 8.3 the same results are compiled for the other two case studies.

There are several points of interest worth noting which concern the predictive power of the estimation procedure proposed. First, the estimates for the absolute values of the JP are not quite satisfactory even if the known fractions of formation are used. Compared to the "true" JP, the JP estimated with known fractions of formation only accounts for 61.9%, 79.8% and 86.8% in the case of NPnEO, PCE and atrazine, respectively. The predictions with known fractions of formation, however, are good with regard to the relative importance of the transformation products. In all three case studies, the four most important compounds can be identified correctly and for PCE and atrazine even in the right order with respect to the full model calculations. If the model is run with just those four compounds identified, the "true" JP can be reconstructed to 83.3% for NPnEO, to 99.9% for PCE and to 93.6% for atrazine.

Still, the preceding procedure requires the identification of the fractions of formation, which in turn requires much investigation and literature research. Therefore, it is also of interest to examine the predictive capabilities of the generic fractions of formation. Doing so allows for, in the case of PCE, the identification of the three most important compounds, but not in the correct order. For atrazine and NPnEO, only the two most important contributors are identified correctly. If only the compounds whose rank order is correctly predicted by the generic fractions of formation are included to run the model, this results in 98.6% of the "true" JP for PCE and 89.0% for atrazine. Thus, although these values are lower than those obtained with the known fractions of formation, the generic fractions of formation still allow one to identify enough transformation products to account for nearly 90% of the "true" JP in these two cases. For NPnEO, the two most important contributors correctly identified by the generic fractions of formation only make up 54.2% of the "true" JP. However, the generic fractions of formation are able to predict the percent contribution of the single compounds in the NPnEO case study very well, which is more decisive with regard to the importance of the single transformation products than their rank order.

Given the predictive capability of the generic fractions of formation and knowing that the first generation transformation products and all others accounting for more than
5–10% of the total mass are most important for the JP, a model simulation was run which included only the first generation transformation products and those whose relative masses were found to exceed 10% under the assumption of generic fractions of formation. For the NPnEO case study, this led to the selection of all compounds except NP1EO, which in turn resulted in a calculated JP that accounted for 90.1% of the "true" JP. For PCE and atrazine, only the first generation transformation products were selected according to the above selection criteria, which resulted in JP values accounting for 99.9% and 93.4% of the "true" value, respectively.

It is concluded that the selection procedure proposed, using generic fractions of formation, performs well enough to identify those transformation products that should be included in the full model calculations. It is expected that, in most cases, this will lead to a JP that represents at least 90% of the "true" JP.
Table 8.1: "True" JP (bold) as well as two estimates of JP using known and generic fractions of formation for the NPnEO case study. Additionally, the absolute and relative contributions of each compound are given as well as rank orders indicating the relative importance of the individual compounds.

<table>
<thead>
<tr>
<th></th>
<th>NPnEO</th>
<th>NP2EC</th>
<th>NP1EC</th>
<th>NP2EO</th>
<th>NP1EO</th>
<th>NP</th>
<th>Total (JP)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model calculations</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contribution to JP (d)</td>
<td>9.98</td>
<td>42.0</td>
<td>28.2</td>
<td>7.09</td>
<td>5.57</td>
<td>8.68</td>
<td>102</td>
</tr>
<tr>
<td>% contribution</td>
<td>10%</td>
<td>41%</td>
<td>28%</td>
<td>7%</td>
<td>5%</td>
<td>9%</td>
<td>100%</td>
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<td>4</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>6</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td><strong>Estimation with known fractions of formation (FF)</strong></td>
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<td></td>
</tr>
<tr>
<td>( \bar{P}_x \cdot SF_x ) (d)</td>
<td>9.98</td>
<td>23.0</td>
<td>19.6</td>
<td>5.28</td>
<td>4.17</td>
<td>1.15</td>
<td>63.1</td>
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<tr>
<td>% contribution</td>
<td>16%</td>
<td>36%</td>
<td>31%</td>
<td>8%</td>
<td>7%</td>
<td>2%</td>
<td>100%</td>
</tr>
<tr>
<td>Rank</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td></td>
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<tr>
<td><strong>Estimation with generic fractions of formation (GFF)</strong></td>
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<td></td>
</tr>
<tr>
<td>( \bar{P}_x \cdot GSF_x ) (d)</td>
<td>9.98</td>
<td>20.3</td>
<td>18.6</td>
<td>8.80</td>
<td>6.95</td>
<td>7.17</td>
<td>71.7</td>
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<tr>
<td>% contribution</td>
<td>14%</td>
<td>28%</td>
<td>26%</td>
<td>12.5%</td>
<td>9.5%</td>
<td>10%</td>
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<td>4</td>
<td>6</td>
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Table 8.2: "True" JP (bold) as well as two estimates of JP using known and generic fractions of formation for the PCE case study. Additionally, the absolute and relative contributions of each compound are given as well as rank orders indicating the relative importance of the individual compounds.

<table>
<thead>
<tr>
<th></th>
<th>PCE</th>
<th>TCE</th>
<th>DCE</th>
<th>VC</th>
<th>COCl₂</th>
<th>TCAC</th>
<th>TCA</th>
<th>DCA</th>
<th>MCA</th>
<th>Total (JP)</th>
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</tr>
<tr>
<td>Contribution to JP</td>
<td>44.9</td>
<td>1.9·10⁻³</td>
<td>3.2·10⁻⁶</td>
<td>1.2·10⁻⁷</td>
<td>69.2</td>
<td>1.60</td>
<td>6.07</td>
<td>0.120</td>
<td>0.031</td>
<td><strong>122</strong></td>
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<td>% contribution</td>
<td>37%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>57%</td>
<td>1%</td>
<td>5%</td>
<td>0%</td>
<td>0%</td>
<td><strong>100%</strong></td>
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<td>Rank</td>
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<td>5</td>
<td>1</td>
<td>4</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td></td>
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<tr>
<td>Estimation with known fractions of formation (FF)</td>
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<td></td>
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</tr>
<tr>
<td>Pₓ · SFₓ (d)</td>
<td>44.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>48.3</td>
<td>1.2·10⁻⁴</td>
<td>3.97</td>
<td>0.095</td>
<td>0.025</td>
<td><strong>97.3</strong></td>
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<tr>
<td>% contribution</td>
<td>46%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>50%</td>
<td>0%</td>
<td>4%</td>
<td>0%</td>
<td>0%</td>
<td><strong>100%</strong></td>
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<tr>
<td>Rank</td>
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<td>4</td>
<td>4</td>
<td>1</td>
<td>4</td>
<td>3</td>
<td>4</td>
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<tr>
<td>Estimation with generic fractions of formation (GFF)</td>
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</tr>
<tr>
<td>Pₓ · GSFₓ (d)</td>
<td>44.9</td>
<td>0.428</td>
<td>0.178</td>
<td>0.096</td>
<td>24.4</td>
<td>3.1·10⁻⁴</td>
<td>16.8</td>
<td>1.61</td>
<td>1.42</td>
<td><strong>91.1</strong></td>
</tr>
<tr>
<td>% contribution</td>
<td>49%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>27%</td>
<td>0%</td>
<td>18%</td>
<td>2%</td>
<td>2%</td>
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</tr>
<tr>
<td>Rank</td>
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<td>5</td>
<td>5</td>
<td>5</td>
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<td>3</td>
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<td>4</td>
<td></td>
</tr>
</tbody>
</table>
Table 8.3: "True" JP (bold) as well as two estimates of JP using known and generic fractions of formation for the atrazine case study. Additionally, the absolute and relative contributions of each compound are given as well as rank orders indicating the relative importance of the individual compounds.

<table>
<thead>
<tr>
<th></th>
<th>Atrazine</th>
<th>DEA</th>
<th>DIA</th>
<th>HA</th>
<th>DIHA</th>
<th>DEHA</th>
<th>DAA</th>
<th>DAHA</th>
<th>atral9</th>
<th>atral0</th>
<th>atral11</th>
<th>CYA</th>
<th>Total (JP)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model calculations</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Contribution to JP (d)</td>
<td>60.1</td>
<td>2.48</td>
<td>0.919</td>
<td>9.82</td>
<td>0.179</td>
<td>0.534</td>
<td>1.01</td>
<td>0.935</td>
<td>0.223</td>
<td>1.05</td>
<td>0.112</td>
<td>1.16</td>
<td><strong>78.6</strong></td>
</tr>
<tr>
<td>% contribution</td>
<td>77%</td>
<td>3%</td>
<td>1%</td>
<td>13%</td>
<td>0%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>0%</td>
<td>1%</td>
<td>0%</td>
<td>1%</td>
<td>100%</td>
</tr>
<tr>
<td>Rank</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>2</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td>5</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Estimation with known fractions of formation (FF)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>( P_x \cdot SF_x ) (d)</td>
<td>60.1</td>
<td>1.10</td>
<td>0.436</td>
<td>2.37</td>
<td>0.162</td>
<td>0.428</td>
<td>0.815</td>
<td>0.766</td>
<td>0.175</td>
<td>0.853</td>
<td>0.088</td>
<td>0.927</td>
<td><strong>68.2</strong></td>
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<tr>
<td>% contribution</td>
<td>88%</td>
<td>2%</td>
<td>1%</td>
<td>3%</td>
<td>0%</td>
<td>1%</td>
<td>1%</td>
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<td>4</td>
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<td>5</td>
<td>4</td>
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<td></td>
</tr>
<tr>
<td><strong>Estimation with generic fractions of formation (GFF)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \tilde{P}_x \cdot GSF_x ) (d)</td>
<td>60.1</td>
<td>4.03</td>
<td>3.60</td>
<td>8.22</td>
<td>2.31</td>
<td>5.38</td>
<td>5.78</td>
<td>1.16</td>
<td>6.35</td>
<td>0.578</td>
<td>6.90</td>
<td><strong>106.7</strong></td>
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<tr>
<td>% contribution</td>
<td>56%</td>
<td>4%</td>
<td>3%</td>
<td>8%</td>
<td>2%</td>
<td>2%</td>
<td>5%</td>
<td>5%</td>
<td>1%</td>
<td>6%</td>
<td>1%</td>
<td>6%</td>
<td>100%</td>
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<tr>
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<td>7</td>
<td>4</td>
<td>8</td>
<td>3</td>
<td>8</td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
8.2.3 Calculation of Joint Persistence with reduced data set

From the above considerations, a procedure can be deduced to calculate the JP of a chemical substance family with reduced data effort, but which will still allow for the representation of at least 90% of the "true" JP that accounts for all known transformation products.

The prerequisite for this procedure is that all specific transformation products are known (for a definition of specific transformation products see Chapters 2.2 and 2.3.1), and that the transformation scheme is known to such an extent that the consecutive order of the transformation products is properly represented. Once this information has been gathered, the following 10-step procedure must be run through:

1. Measurement/Estimation of $K_H$ and $K_{ow}$ values for all compounds.

2. Identification of main residence compartments according to Gouin et al. (2000) for all compounds.

3. Measurement/Estimation of the half-lives in the relevant residence compartments for all compounds.

4. Calculation of approximate persistence ($P_x$) as geometric mean of the half-lives in all relevant residence compartments for all compounds.

5. Calculation of the shares formed using generic fractions of formation ($GSF_x$) for all compounds.

6. Calculation of the estimated JP as

   
   \[ JP_{est} = PP + \sum_{x} P_x \cdot GSF_x. \]

7. Calculation of the percent contribution of each transformation product to the $JP_{est}$ and subsequent selection of those transformation products with a contribution $>10\%$.

8. Measurement/Estimation of the remaining unknown half-lives in all compartments for the parent compound, the first generation transformation products and all compounds selected under 7.
9. Identification of fractions of formation in all compartments between the parent compound, the first generation transformation products and all compounds selected under 7.

10. Run of the full model to calculate the JP including the parent compound, the first generation transformation products and all compounds selected under 7.

8.3 Conclusions

In this chapter, it has been demonstrated how the consideration of the JP or RQ_{mix} of an entire substance family as compared to the PP or RQ_{x} of the parent compound alone can lead to differing judgments regarding the presence of hazard or risk for the environment. It is thus postulated that efforts should be made to find ways that are feasible with regard to data requirements to include transformation products in the hazard and risk assessment of chemicals. The JP is proposed as one important instrument in doing so.

However, the competent authorities or the risk assessors in chemical industry, who are responsible for the compilation of registration dossiers need to be supplied with a manageable and easy-to-use instrument to calculate the JP. For this reason, a simplified procedure based on a reduced data set for the identification of influential transformation products was developed in Chapter 8.2.

The suggested procedure assists in identifying those transformation products that are formed in amounts exceeding 10% of the total mass in the system, while using only two partition coefficients, K_{H} and K_{ow}, generic fractions of formation and half-lives in the main residence compartments as input data. Ultimately, the 10% limit for the distinction of influential transformation products corresponds exactly to the 10% limit for the distinction of major and minor metabolites in the draft document on the identification of relevant metabolites of pesticides proposed by CTB. The difference lies in the fact that, here, multimedia behavior is explicitly accounted for. Therefore, the question of whether or not a certain transformation product surpasses the 10% limit cannot be answered by single-media measurements or modelling, but needs to be predicted by means of a multimedia model. Thus, the sequence of decision steps in the procedure used for the identification of transformation products that are influential in the calculation of JP as suggested here (see Figure 8.2) is different from the sequence of decision steps used to identify relevant transformation products for risk assessment as suggested by CTB (see Figures 2.5 and 2.6).
Figure 8.2: Decision scheme leading from the identification of environmental transformation products of a given parent compound to the calculation of an estimate of the JP that covers all influential transformation products.
The procedure as suggested here is illustrated in Figure 8.2 and includes the following elements and decision steps. First, all possible transformation products in all environmental compartments need to be identified and their sequence in the transformation scheme needs to be established. This should be done with paying as much attention as possible to completing the mass balance (i.e. the whole mass emitted should possibly be accounted for by the transformation products found). In the following first decision step, specific transformation products (for definition see Chapters 2.2 and 2.3.1) are separated from unspecific transformation products. The specific transformation products then enter the 10-step procedure as suggested in Chapter 8.2.3 and steps 1–7 are run through. In a subsequent decision step, all transformation products that do not belong to the first generation nor exceed a contribution of 10% to the JP according to the suggested procedure, are classified as not influential and excluded from the transformation scheme. Finally, steps 8–10 are run through with the remaining influential transformation products and an estimate for the JP is calculated. This estimate should be able to cover at least an approximate 90% of the true value of the JP.
Chapter 9

Conclusions and Outlook

9.1 Conclusions

In Chapter 2.1 at the beginning of this work, persistence and hazard-based indicators in general were postulated as more suitable tools for the preliminary assessment of chemicals than effect-based measures such as the risk quotient. It was suggested that they could be used as screening tools in the prioritization of chemicals for a subsequent, detailed risk assessment (see also Figure 2.4). In order to learn more about their different features, the hazard-based Joint Persistence (JP) and the risk-based mixture risk quotient (RQ\textsubscript{mix}) as calculated for NPnEO are compared in Table 9.1.

The calculation of both indicators, JP and RQ\textsubscript{mix}, is based on exposure patterns. Their main difference lies in the fact that the risk quotient additionally includes effect data. For its calculation, an additional set of toxicity data and extrapolation models for predicting no-effect concentrations (PNECs) is thus needed. The other important difference between the two indicators is the fact that JP is an intensive property and, as such, is only dependent on the media-specific relative amounts released, while the risk quotient is an extensive property that is directly proportional to the absolute amounts released.

These differences manifest themselves in the results for the two indicators. Different rankings for the generations of transformation products and the individual transformation products are obtained with regard to the importance of their contribution to the JP and to the RQ\textsubscript{mix}, respectively. Thus, the 2\textsuperscript{nd} generation of transformation products of NPnEO is the most important contributor to RQ\textsubscript{mix}, while, for the JP, the 1\textsuperscript{st} generation has been identified as the most important contributor in
Table 9.1: Comparison of JP as exposure-based hazard indicator with RQ_{mix} as risk indicator for the case study of NPnEO.

<table>
<thead>
<tr>
<th></th>
<th>JP</th>
<th>RQ_{mix}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assessment level</td>
<td>Exposure-based; Hazard indicator</td>
<td>Effect-based; Risk indicator</td>
</tr>
<tr>
<td>Model system</td>
<td>Closed system; Generic, world-averaged landscape parameters</td>
<td>Open system; Regional-specific landscape parameters</td>
</tr>
<tr>
<td>Emission scenario</td>
<td>Parent compound emitted to water</td>
<td>Parent compound and transformation products emitted to water and NP to soil</td>
</tr>
<tr>
<td>Quotients</td>
<td>JP/PP=10.2</td>
<td>RQ_{mix}/RQ^{NPnEO}=29.1</td>
</tr>
<tr>
<td>Main sensitivities</td>
<td>Degradation rates and fractions of formation</td>
<td>PNECs and amounts emitted</td>
</tr>
<tr>
<td>Main uncertainties</td>
<td>Degradation rates</td>
<td>PNEC extrapolation model</td>
</tr>
<tr>
<td>Importance of genera-tions</td>
<td>1^{st} &gt; 2^{nd} &gt; 3^{rd}</td>
<td>2^{nd} &gt; 1^{st} &gt; 3^{rd}</td>
</tr>
<tr>
<td>Importance of single transformation products</td>
<td>NP2EC&gt;NP1EC&gt;NP2EO&gt;NP1EO&gt;NP</td>
<td>NP1EO&gt;NP&gt;NP2EO&gt;NP2EC&gt;NPnEO&gt;NP1EC</td>
</tr>
</tbody>
</table>
the three case studies hitherto considered. The effect is even more noticeable for the single transformation products. There, NP1EO and NP show the highest single risks, while they contribute the least to the JP. Apart from the different emission scenarios used for the calculation of the two indicators, this change of importance of NP1EO and NP is primarily due to their higher toxicity in comparison to the parent compound and to the other transformation products.

The example of NPnEO thus clearly shows that the inclusion of effect data into chemical assessment can lead to vastly different statements regarding the overall and relative importance of transformation products as compared to exposure-based assessment. Seen from this point of view, effect data, if available, provides important information to assess the actual level of risk, which is excluded from exposure-based hazard indicators.

At the same time, however, the scenario analysis in Chapter 7 showed that, although important, effect data is also highly uncertain and difficult to obtain. Its particular weakness lies in the necessity to use extrapolation factors in extrapolating from toxicity endpoints for single species to no-effect concentrations that protect all species in an ecosystem. Although rationales for these factors have been given, a closer look shows that they are not supported by any scientific reasoning concerning the underlying mechanisms of toxic action. As a consequence of this, different extrapolation models are used in different political contexts. They have been shown to produce PNEC values that differ by two to three orders of magnitude. In contrast, the total uncertainty for the JP values was shown to amount to only about two orders of magnitude for the 90% confidence interval. Furthermore, the calculation of risk by means of PNEC values is flawed by the fundamental problem of normative indeterminacy as discussed in Chapter 2.1.1.

The purpose of preliminary screening of chemicals is to use as little data as possible to obtain as much relevant information about the hazard of a chemical compound as possible. Thus, due to the fact that persistence calculations need less data, are easier to perform and include fewer uncertain parameters while still providing the exposure information that is common to both indicators, the JP is, in my opinion, a more suitable tool in the preliminarily screening of the environmental hazard potential of a parent compound and its transformation products than the mixture risk quotient.
9.2 Outlook

In this work, it has been illustrated that the consideration of transformation products in the evaluation of the indicators persistence and risk quotient can lead to remarkably different results than for the parent compound alone. These results generally indicate a higher risk and can entail more stringent risk management decisions. As a consequence of these findings, it is postulated that transformation products should, wherever possible, be included in the risk assessment of environmental pollutants. Moreover, their dynamic formation should be taken into account in order to correctly reflect the time during which the environment is exposed to chemicals that are formed out of the originally released compound. Only by doing so can a more comprehensive picture of the persistence or the risk of a chemical release be obtained. This postulate, however, will not be fulfilled unless chemical legislation explicitly asks for the identification of transformation products for all chemicals. In order for this to happen, the awareness of the importance of transformation products needs to be further stimulated. Additionally, easier and faster methods for the identification of transformation products need to be developed.

To learn more about the importance of transformation products, the methodology developed in this work for the calculation of SP, JP and mixture risk quotients should be applied to other chemical examples, preferably to newer substances as well. The conclusions drawn from the three case studies should be reexamined with particular regard to their generalization. This especially concerns the discovery that the first generation of transformation products contributes most to the JP, and the rules for the identification of the most influential transformation products introduced in Chapter 8.

Another interesting application of the JP would be to test the hypothesis that the development of new industrial chemicals and agrochemicals tends more and more towards substances with short temporal and spatial ranges. While this is actually the case for the parent compounds in some applications (see, e.g., the substitution of CFCs with HCFCs), it is not clear whether this still holds true if the whole substance family is regarded.

In order to make the tools developed in this work applicable, and thus to fulfill the postulate that transformation products should be increasingly considered in chemical assessment, metabolism and degradation research was identified as the second, important research need. Thereby, the two main focuses should be on establishing transformation schemes and on the characterization of representative half-lives for
all influential transformation products. Ways of establishing transformation schemes are (i) the conducting of experimental degradation studies in the laboratory or field, (ii) the theoretical prediction of transformation products by means of expert systems or structure-activity relationships, or (iii) a combination of the two approaches. If experimental studies are conducted, particular attention should be paid to best possibly closing the mass balances (i.e. to make sure that the complete mass of the parent compound released into the system is recovered in the form of mineralization or specific transformation products). To monitor the efficiency of recovery, the experiments are usually carried out with $^{14}$C-labelled compounds. The biggest difficulty in the experimental determination of transformation schemes stems from the fact that the scope of the generally applied analytical methods is often not broad enough to cover all transformation products. Thus, some transformation products will escape identification unless other methods are applied, which, in many cases, need first to be developed. This, however, presupposes that the experimenter knows what kind of compound he is looking for, which is often not the case. All in all, the experimental identification of transformation schemes is an expensive and time-consuming task and often not very successful in closing the mass balances. To improve the results, it is necessary to further develop the analytical methods, especially for very low concentrations, and to find ways of roughly predicting the structures of possible transformation products. Methods to theoretically predict transformation schemes have been suggested, e.g., by Störmann and Jastorff (1993) and Behrendt et al. (1999). Most of these methods comprise a set of reaction rules that specify the types of bonds that are likely to be broken given a specific environmental reactant or enzymatic system, and how the bonds are rearranged in the course of the reaction. So far, these methods have only been able to predict the transformation products of a limited number of well understood compounds such as, e.g., atrazine. Due to the enormous variety of chemical structures, it will not be an easy task to develop more generally applicable predictive tools. Potentially promising approaches are the use of multivariate analysis of known compounds and their reaction pathways and the deduction of structure-activity relationships therefrom. Also, with the speed of computers constantly growing, it might become feasible to conduct proper quantum-chemical calculations to predict reaction pathways and degradation rates on a broad basis. Uncertainties in calculated persistence values amounting to up to two orders of magnitude for the 90% confidence interval were identified in this work. In all three case
studies, at least 70% of the total variance in the JP values was due to variance in the degradation rates. Reasons for the sizeable variance in the degradation rates might be manifold. Possibilities are: a lack of agreed standards about how to conduct degradation studies in the laboratory and field, and about how to interpret the results; natural variability due to different environmental conditions; methodological problems specific to multimedia modelling, e.g., the question how degradation rates that have been measured in a specific environmental matrix, such as sediment, groundwater or soil, should be assigned to a certain compartment in the multimedia model to represent the degradation rates therein. Research efforts should be intensified to disentangle these different influences. As a first approach, two-dimensional uncertainty analysis might be instrumental in differentiating uncertainty and natural variability.

A reduction in the uncertainty of measured degradation rates is very difficult to achieve since widely differing opinions exist about how to properly conduct such experiments and the feasibility of extrapolation from laboratory studies to field conditions (Kishi et al., 1994; Washington and Cameron, 2001). Still, research endeavors should be directed towards understanding the underlying reasons for the differences in the results, such as adsorption phenomena or adaptation of microbial communities. Natural variability cannot be reduced, but attention can be paid in choosing only those measured values for modelling that are representative of the environmental conditions in the modelled system (temperature, pH, organic carbon content etc.). In that context, guidelines need to be developed in collaboration with the environmental chemists conducting the degradation studies that help in selecting those measured degradation rates that properly represent a given environmental compartment.

Other uncertainties in the calculated persistence values and the risk quotients are discussed and the corresponding research needs are identified in Chapters 7 and 8. They concern mainly model uncertainties such as the number and choice of compartments modelled, and uncertainty about differing methodologies to extrapolate predicted no-effect concentrations for the calculation of risk quotients.

Using basically the same mathematical structure for the dynamic formation of transformation products as suggested in this work, it is also possible to calculate spatially resolved exposure patterns of the transformation products. From these, spatial ranges of the single transformation products and of the whole substance family can be deduced. This has already been done by Quartier and Müller-Herold (2000) for only one transformation product and under the assumption of instantaneous equi-
Conclusions and Outlook

librium partitioning. It might be of interest to apply the mathematical framework developed here in order to obtain spatial patterns for more complex transformation schemes and for non-equilibrium partitioning. Especially where short-lived transformation products of long-lived parent compounds are concerned, considerably larger secondary spatial ranges of the single transformation products as compared to their characteristic spatial ranges are to be expected.
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Appendix A

Multimedia models

A.1 Fate models for PEC predictions

Predicted environmental concentrations (PECs) for use in chemical risk assessment should be calculated for a minimal set of compartments including soil, water and air. Preferably the compartments sediment and biota are also considered. For a first assessment only a few physico-chemical parameters (i.e. molecular weight ($MW$), solubility ($S$), melting and/or boiling point ($T_m$ or $T_b$)) are required substance-wise. Also, the mode of entry of the substance into the environment and the amount released need to be known. In the TGD (1996), instructions are given about how to predict concentrations for each compartment separately. Nevertheless, the manual conduction of a full exposure assessment for each single compartment can be a time-and resource-consuming exercise and still neglects the transport of the substance between the compartments.

Therefore, computerized models that allow a quick prediction of the fate of chemicals in a multimedia environment have been developed. For this kind of models, usually an extended set of substance properties, including their vapor pressure ($p_v$) or Henry’s law constant ($K_H$), the octanol-water partition coefficient ($K_{ow}$) and their degradation rates ($\kappa_i$) in each environmental compartment, is required.

The basic structure of most multimedia fate models is based on the multi-compartmental fugacity models first introduced by Mackay et al. (Mackay, 1979; Mackay and Paterson, 1981; Mackay and Paterson, 1982) (also termed unit world models). In this set of models, environmental media (also termed compartments) are represented as well-mixed boxes that are interconnected with each other. Chemicals are degraded in those boxes with their media-specific first order degradation rates and
are transported between them due to advection and diffusion. The chemicals are introduced into the model system through emission into any of the compartments and are lost either through degradation or advection out of the system. In Figure A.1 the basic structure of a multimedia model is illustrated. In Chapter 3.2, the assumptions behind the different levels of fugacity models (level I-IV) are discussed in more details.

Some of the publicly available modelling systems are briefly described in Table A.1. The main distinction is between regional scale models that allow a preliminary assessment of the chemicals’ fate and distribution in the environment (Mackay, EU-SES, CalTOX, ChemCAN), and refined models that represent the environment on a local scale (GREAT-ER, AQUASIM).
**Table A.1:** Short overview over selected computerized modelling systems for PEC calculations.

<table>
<thead>
<tr>
<th>Name</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mackay <em>(Mackay, 1991)</em></td>
<td>Set of fugacity models in a unit world concept. Depending on assumptions regarding equilibrium and steady-state conditions, different levels (I-IV) are distinguished. Calculation of $\text{PEC}_{\text{regional}}$.</td>
</tr>
<tr>
<td>EUSES <em>(EUSES, 1999)</em></td>
<td>Decision support system integrating models presented in the TGD <em>(1996)</em> into a Windows 95/NT-based software product. Calculation of $\text{PEC}_{\text{regional}}$ with SimpleBox (Mackay level III model with nested continental and regional scale).</td>
</tr>
<tr>
<td>CalTOX <em>(McKone, 1993)</em></td>
<td>Multimedia total exposure model for hazardous waste sites, including multimedia transport and transformation model, and exposure scenario model. Includes uncertainty analysis. Calculation of time-varying $\text{PEC}_{\text{regional}}$ for contaminants introduced initially to lower soil layers or/and released continuously to air, surface soil or water.</td>
</tr>
<tr>
<td>ChemCAN <em>(Mackay et al., 1996)</em></td>
<td>Model based on Mackay level III model for 24 regions of Canada (written in Visual Basic). Other regions can be defined by the user and added to the database. Calculation of $\text{PEC}_{\text{regional}}$.</td>
</tr>
<tr>
<td>AQUASIM <em>(Reichert, 1994)</em></td>
<td>Dynamic box model for simulation and data analysis of aquatic systems (lakes, rivers). Includes sensitivity analysis. Calculation of time-varying $\text{PEC}_{\text{local}}$ for different depths.</td>
</tr>
<tr>
<td>GREATER <em>(ECETOC, 1999a)</em></td>
<td>Geographically referenced regional exposure assessment tool for European rivers. Simulates fate and transport of detergent ingredients using GIS data for river systems and temporally and spatially resolved emission data. Calculation of time-varying $\text{PEC}_{\text{regional}}$ in river systems.</td>
</tr>
</tbody>
</table>
A.2 Surface mixed sediment layer (SMSL) model

The SMSL model is used here to describe the exchange processes between the surface water and the top layer of the sediment compartment. In the SMSL model, the top layer of the sediment is described as completely mixed box. It is defined by the mixing depth $h_{sed}$, within which the assumption of complete mixing holds. Below the mixing depth lies the permanent sediment from which no back transport into the water column is possible. Transport to the permanent sediment is therefore modelled as loss term (sediment burial). The exchange processes between the surface water and the SMSL compartment are described by Schwarzenbach et al. (1993). The relevant exchange processes are (i) diffusion between the dissolved phase in the water and the pore water of the sediment, (ii) settling of particulate matter in the water column and (iii) resuspension of sediment particles into the water column. The mathematical expressions for these phase transfer coefficients are given in Table A.3 and the corresponding model input parameters are quantified in Table A.2.

Table A.2: Input parameters for SMSL model, describing sediment-water exchange processes according to Schwarzenbach et al. (1993) (pp. 591–597) and Schnoor et al. (1992).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Mixing depth</td>
<td>$h_{sed}$</td>
<td>0.02 m</td>
</tr>
<tr>
<td>% organic carbon in sediment</td>
<td>$f_{sed}$</td>
<td>0.1</td>
</tr>
<tr>
<td>Porosity of sediment</td>
<td>$por$</td>
<td>0.9</td>
</tr>
<tr>
<td>Concentration of particulate organic matter in water</td>
<td>$POC$</td>
<td>0.002 kg/m$^3$</td>
</tr>
<tr>
<td>Sediment density</td>
<td>$\rho_{sed}$</td>
<td>2500 kg/m$^3$</td>
</tr>
<tr>
<td>Sedimentation velocity</td>
<td>$u_{sed}$</td>
<td>0.68 m/d</td>
</tr>
<tr>
<td>Resuspension flow</td>
<td>$U_{resusp}$</td>
<td>$1\times10^{-4}$ kg/m$^2$d</td>
</tr>
<tr>
<td>Diffusion velocity</td>
<td>$u_{diff}$</td>
<td>0.16 m/d</td>
</tr>
</tbody>
</table>
Table A.3: Mathematical expressions for phase transfer coefficients describing diffusive and advective phase transfer processes between the water and sediment compartment. The organic carbon-water partition coefficient $K_{oc}^x$ is deduced from the $K_{ow}^x$ with the linear correlation $\log K_{oc} = 0.82 \log K_{ow} + 0.14$ (Schwarzenbach et al., 1993) (p. 275). The other parameters used in the expressions in this table are defined and quantified in Table A.2.

<table>
<thead>
<tr>
<th>Process description</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction of substance adsorbing to particles in the water column</td>
<td>$frac_p^x = \frac{POC \cdot K_{oc}^x}{1 + POC \cdot K_{oc}^x}$</td>
</tr>
<tr>
<td>Fraction of substance adsorbing to particles in sediment</td>
<td>$frac_{sed}^x = \frac{(1 - \text{por}) \cdot \rho_{sed} \cdot f_{sed} \cdot K_{oc}^x}{\text{por} + (1 - \text{por}) \cdot \rho_{sed} \cdot f_{sed} \cdot K_{oc}^x}$</td>
</tr>
<tr>
<td>Total transport of substance from water into sediment</td>
<td>$u^{sed}<em>{w} = \frac{u^{sed}}{h</em>{w}} \cdot frac_p^x + \frac{u^{diff}}{h_{sed}} \cdot (1 - frac_{sed}^x)$</td>
</tr>
<tr>
<td>Total transport of substance from sediment into water</td>
<td>$u^{sedw}<em>{w} = \frac{U</em>{resusp}}{(1 - \text{por}) \cdot \rho_{sed} \cdot h_{sed}} \cdot frac_{sed}^x + \frac{u^{diff}}{h_{sed} \cdot (1 - frac_{sed}^x)}$</td>
</tr>
</tbody>
</table>
Appendix B

Persistence of transformation products in a single medium environment

All substances in the single medium environment are assumed to be degraded and formed by first order kinetics, which means that the rate of removal of the substance is proportional to its concentration. As a consequence of the removal of the parent compound A at a given rate $k^A$ a transformation product B is formed at a rate $k^{AB}$ that is proportional or equal to $k^A$, depending on the value of the proportionality factor $\theta^{AB}$, i.e. $k^{AB} = \theta^{AB} \cdot k^A$. Here, $\theta^{AB}$ is termed fraction of formation. This relationship can be represented symbolically by

Transformation Scheme 1: $c^A \xrightarrow{k^{AB}} c^B \xrightarrow{k^B}$

If this process is generalized for a sequence of $n$ first order sequential reaction it is written as

Transformation Scheme 2: $c^A \xrightarrow{k^{AB}} c^B \xrightarrow{k^{BC}} \ldots \xrightarrow{k^{n-1,n}} c^n \xrightarrow{k^n}$

This type of reactions is typical for decay series of radionuclides and has been discussed extensively in the respective technical literature (Lieser, 1997).

B.1 Analytical solutions

Given full conversion from A to B, i.e. $\theta^{AB} = 1$, the first order differential equations for A and B that correspond to Transformation Scheme 1 are

$$\frac{dc^A(t)}{dt} = -k^A c^A(t) \quad (B.1)$$
\[
\frac{dc^A_B(t)}{dt} = k^A c^A(t) - k^B c^B(t) \tag{B.2}
\]

The solution of Equation B.1 (i.e. the primary concentration function) is well known and is given in Equation B.3*. The solution for \( c^B(t) \) (i.e. the secondary concentration function for B formed out of A) with the initial condition \( c^B_0 = 0 \) (i.e. no transformation product present at time zero) is given in Equation B.4. For the case of just one transformation product B, the joint concentration function \( c^{AB}(t) \) is the sum of \( c^A(t) \) and \( c^B(t) \) as given in Equation B.5.

\[
c^A(t) = c^A_0 e^{-k^A t} \tag{B.3}
\]

\[
c^B(t) = c^A_0 \frac{k^A}{k_B - k^A} \left( e^{-k^A t} - e^{-k^B t} \right) \tag{B.4}
\]

\[
c^{AB}(t) = c^A(t) + c^B(t) = \frac{c^A_0}{k_B - k^A} (k^B e^{-k^A t} - k^A e^{-k^B t}) \tag{B.5}
\]

An illustration of the temporal course of the concentration functions \( c^A(t) \), \( c^B(t) \) and \( c^{AB}(t) \) is given in Figure B.1, where they are depicted for three different quotients of \( k^A/k^B(=\alpha) \).

For a longer sequence of \( n \) successive transformations as in Transformation Scheme 2, a general form of the concentration function \( c^n(t) \) can be found (see Equation B.6).

\[
c^n(t) = a^A e^{-k^A t} + a^B e^{-k^B t} + \ldots + a^n e^{-k^n t} \tag{B.6}
\]

The coefficients in this equation are

\[
a^A = \frac{k^A k^B \ldots k^{n-1}}{(k^B - k^A)(k^C - k^A) \ldots (k^n - k^A)} c^A_0
\]

\[
a^B = \frac{k^A k^B \ldots k^{n-1}}{(k^A - k^B)(k^C - k^B) \ldots (k^n - k^B)} c^A_0
\]

\[
\ldots
\]

\[
a^n = \frac{k^A k^B \ldots k^{n-1}}{(k^A - k^n)(k^B - k^n) \ldots (k^{n-1} - k^n)} c^A_0
\]

From these concentration functions, analytical solutions for the PP, SP and JP can be deduced. With the equivalence width as persistence measure, the PP and JP can be defined as follows:

\[
PP : \tau^A = \frac{1}{c^A_0} \int_0^\infty c^A(t) \ dt = \frac{1}{c^A_0} \int_0^\infty c^A_0 e^{-k^A t} dt = \frac{1}{k^A} \tag{B.7}
\]

*Mass profiles are obtained from concentration functions by multiplication of the concentrations with the respective compartments' volumes. Henceforth, the two modes of presentation will be used equivalently, depending on the context.
Figure B.1: Primary, secondary and joint concentration functions for A, B and AB for the cases $\alpha = 0.1, 2$ and 10 with $\alpha = \frac{k_A}{k_B}$.

As mentioned before, the SP of B cannot be defined in exact analogy to the equivalence width of A, because the starting concentration of B is zero. Instead, the concentration $c_B(t)$ builds up over time as long as formation exceeds decay and diminishes again when the opposite becomes the case. The maximum of $c_B(t)$ is defined by its time to maximum $t_{max}$ and its maximal concentration $c_{max}^B$ as given in Equations B.9 and B.10.

$$t_{max} = \frac{\ln k_A - \ln k_B}{k_A - k_B} \quad (B.9)$$

$$c_{max}^B = c_0^A \left( \frac{k_B}{k_A} \right)^{\frac{k_B}{k_A - k_B}} \quad (B.10)$$

In best possible analogy to the equivalence width, the SP is therefore defined as the
time integral of the concentration function $c^B(t)$ divided by the maximum concentration $c_{\text{max}}^B$ (see Equation B.11, where $\tau^{B/A}$ stands for the Secondary Persistence of B formed out of A). Like this, both measures, $\tau^A$ and $\tau^{B/A}$, are such that the area of the rectangle formed when they are multiplied with their maximum times ($c_{\text{max}}^A$, and $c_{\text{max}}^B$ respectively) equals the time integral of the concentration functions $c^A(t)$ and $c^B(t)$ respectively. This analogy is depicted in Figure B.2.

$$\text{SP : } \tau^{B/A} = \frac{1}{c_{\text{max}}^B} \int_0^\infty c^B(t) \, dt = \left(\frac{k_B}{k_A}\right) \frac{x^B}{x^A} \int_0^\infty \frac{k_A}{k_B - k_A} (e^{-k_A t} - e^{-k_B t}) \, dt \quad (B.11)$$

$$= \frac{1}{k_B} \left(\frac{k_B}{k_A}\right) \frac{x^B}{x^A}$$

Figure B.2: Illustration of the analogy in the definition of PP and SP based on the equivalence width measure.

With the mean time $\mu$ as persistence measure, all persistence definitions PP, SP and JP can be formulated equivalently and solved analytically (see Equations B.12-B.14).

$$\text{PP : } \mu^A = \frac{\int_0^\infty c^A(t) \cdot t \, dt}{\int_0^\infty c^A(t) \, dt} = \frac{\int_0^\infty e^{-k_A t} \cdot t \, dt}{\int_0^\infty e^{-k_A t} \, dt} = \frac{1}{k_A} \quad (B.12)$$

$$\text{JP : } \mu^{AB} = \frac{\int_0^\infty c^{AB}(t) \cdot t \, dt}{\int_0^\infty c^{AB}(t) \, dt} = \frac{\int_0^\infty (k_B e^{-k_A t} - k_A e^{-k_B t}) \cdot t \, dt}{\int_0^\infty (k_B e^{-k_A t} - k_A e^{-k_B t}) \, dt} = \frac{k_A^2 + k_A k_B + k_B^2}{k_A k_B (k_A + k_B)} \quad (B.13)$$

$$\text{SP : } \mu^{B/A} = \frac{\int_0^\infty c^B(t) \cdot t \, dt}{\int_0^\infty c^B(t) \, dt} = \frac{\int_0^\infty (e^{-k_A t} - e^{-k_B t}) \cdot t \, dt}{\int_0^\infty (e^{-k_A t} - e^{-k_B t}) \, dt} = \frac{k_A + k_B}{k_A k_B} \quad (B.14)$$

The analytical solutions for the PP, SP and JP using both equivalence width and mean time as persistence measures are compiled in Table B.1. It is interesting to note that, for the mean time, the SP is always larger than the JP, because the relationship $\mu^{AB} = \mu^{B/A} - \frac{1}{k_A + k_B}$ exists.
Table B.1: Analytical solutions for the persistence measures $\tau^{\text{equiv}}$ and $\mu$, expressing the PP based on $c^A(t)$, the SP based on $c^B(t)$ and the JP based on $c^{AB}(t)$.

<table>
<thead>
<tr>
<th>Persistence measure</th>
<th>PP</th>
<th>JP</th>
<th>SP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau^A = \frac{1}{k^A}$</td>
<td>$\tau^{AB} = \frac{k^A + k^B}{k^Ak^B}$</td>
<td>$\tau^{B/A} = \frac{1}{k^B} (\frac{k^B}{k^A})^\frac{k^B}{k^A}$</td>
</tr>
<tr>
<td>Mean Time</td>
<td>$\mu^A = \frac{1}{k^A}$</td>
<td>$\mu^{AB} = \frac{k^A^2 + k^Ak^B + k^B^2}{k^Ak^B(k^A + k^B)}$</td>
<td>$\mu^{B/A} = \frac{k^A + k^B}{k^Ak^B}$</td>
</tr>
</tbody>
</table>

B.2 Suitability of different persistence measures for transformation products

In order to better understand the suitability of $\tau^{\text{equiv}}$ and $\mu$ to express PP, SP and JP, different limiting cases are investigated in a next step. Based on the solutions in Table B.1, limes for the special cases of short-lived ($\alpha \ll 1$) and long-lived ($\alpha \gg 1$) transformation products $B$ can be deduced. These limes are given in Table B.2. As can be seen from Table B.2, the persistence measures $\tau^{\text{equiv}}$ and $\mu$ are not distinguishable for the cases of a relatively short-lived or relatively long-lived transformation product $B$.

Table B.2: Limes of the analytical solutions for the PP, SP and JP expressed by means of $\tau^{\text{equiv}}$ and $\mu$ for the limiting cases of $\alpha \ll 1$ and $\alpha \gg 1$ with $\alpha = \frac{k^A}{k^B}$.

<table>
<thead>
<tr>
<th>Persistence measure</th>
<th>$\alpha$</th>
<th>PP</th>
<th>JP</th>
<th>SP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalence Width</td>
<td>$\ll 1$</td>
<td>$\tau^A = \frac{1}{k^A}$</td>
<td>$\tau^{AB} = \frac{1}{k^A}$</td>
<td>$\tau^{B/A} = \frac{1}{k^A}$</td>
</tr>
<tr>
<td>Mean Time</td>
<td>$\ll 1$</td>
<td>$\mu^A = \frac{1}{k^A}$</td>
<td>$\mu^{AB} = \frac{1}{k^A}$</td>
<td>$\mu^{B/A} = \frac{1}{k^A}$</td>
</tr>
<tr>
<td>Equivalence Width</td>
<td>$\gg 1$</td>
<td>$\tau^A = \frac{1}{k^A}$</td>
<td>$\tau^{AB} = \frac{1}{k^B}$</td>
<td>$\tau^{B/A} = \frac{1}{k^B}$</td>
</tr>
<tr>
<td>Mean Time</td>
<td>$\gg 1$</td>
<td>$\mu^A = \frac{1}{k^A}$</td>
<td>$\mu^{AB} = \frac{1}{k^B}$</td>
<td>$\mu^{B/A} = \frac{1}{k^B}$</td>
</tr>
</tbody>
</table>

Different results are obtained for the case $k^A = k^B$ ($\alpha = 1$) however. The solutions for this case were obtained by solving the first-order differential equations, i.e. Equations B.1 and B.2, for $k^A = k^B$, resulting in different concentration functions.
$c^B(t)$ and $c^{AB}(t)$, which are given in Equations B.15-B.16.

\[ c^B(t) = c_0^A k^A t e^{-k^A t} \quad (B.15) \]
\[ c^{AB}(t) = c_0^A e^{-k^A t} (1 + k^A t) \quad (B.16) \]

The equivalence widths and mean times deduced for the case of equal degradation rates are compiled in Table B.3. Apart from $\tau^{B/A}$ these formulas are the same as they would have been obtained by equaling $k^A = k^B$ in Table B.1. Therefore, we assume that the formulas in Table B.1 are valid in most cases and that the requirement that there be no equal $k^x$ is of small practical importance since the formulas hold for nearly equal $k^x$ and in most cases there is no practical significance to a small change in one of the equal $k^x$ (Di Toro, 1972).

\[ \begin{array}{|c|c|c|c|}
\hline
\text{Persistence measure} & \alpha & \text{PP} & \text{JP} & \text{SP} \\
\hline
\text{Equivalence Width}  & 1 & \tau^{A} = \frac{1}{k^A} & \tau^{AB} = \frac{2}{k^A} & \tau^{B/A} = \frac{e}{k^A} \\
\text{Mean Time} & 1 & \mu^{A} = \frac{1}{k^B} & \mu^{AB} = \frac{3}{2k^B} & \mu^{B/A} = \frac{2}{k^A} \\
\hline
\end{array} \]

For nearly equal $k^A$ and $k^B$ obviously different results are obtained for the SP and JP depending on which persistence measure is chosen. Still, it is hard to say which measure is more suitable to describe the temporal course of the concentration functions. However, it seems reasonable that the JP for $k^A = k^B$ should be twice the PP, which is the case for $\tau^{\text{equiv}}$ but not for $\mu$.

For the JP expressed as equivalence width, this finding can be expanded to an interesting rule which extends to higher numbers of sequential reactions. It can be found that for any number of generations of transformation products the JP can be expressed as a multiple of the PP, $\tau^A$, where the factor is the sum of the quotients between $k^A$ and $k^i$ (see Equation B.17). This rule allows one to predict the JP for any number of sequential reactions as long as the quotients $k^A$ and $k^x$ are known. It also shows that there is a lower limit for the JP, which is $\tau^A$, but no upper limit, even for the case of just one transformation product $B^\dagger$.

\[ \tau^A = \frac{1}{k^A} \quad (B.17) \]

\dagger This is of course only true for the unrealistic case where $k^B$ tends towards 0.
Another opportunity to evaluate the difference between the persistence measures $\tau_{\text{equiv}}$ and $\mu$ is to compare them for the case of parallel reactions. In that case it is assumed that A decays not only to B, but also to another product P, which is assumed not to be part of the system under consideration ($\theta_{AB} + \theta_{AP} = 1$, $\theta_{AB} = k_{AB}/(k_{AB} + k_{AP}) = k_{AB}/k^A \leq 1$). The transformation scheme then looks as follows:

This leads to a different formulation of the equation for the formation of B (see Equation B.18) as well as of the concentration functions $c_{B*}$ and $c_{AB*}$ (see Equations B.19–B.20, where * marks the concentration functions and persistence values of B when other transformation products are formed out of A in parallel), which in turn leads to a different maximum concentration $c_{B*_{\text{max}}}$ for B (see Equation B.21). Accordingly, different results are obtained for the persistence values too. They are compiled in Table B.4 for the case of different $k^A$ and $k^B$.

\[
\frac{dc_{B*}}{dt} = \theta_{AB} k^A c_A^* - k^B c_{B*} \quad \text{(B.18)}
\]

\[
c_{B*}(t) = \frac{\theta_{AB} k^A c_0^*}{k^B - k^A} \left(e^{-k^A t} - e^{-k^B t}\right) = \theta_{AB} c_B(t) \quad \text{(B.19)}
\]

\[
c_{AB*}(t) = \frac{c_0^*}{k^B - k^A} \left((k^B - (1 - \theta_{AB})k^A)e^{-k^A t} - \theta_{AB} k^A e^{-k^B t}\right) \quad \text{(B.20)}
\]

\[
c_{B*_{\text{max}}} = \theta_{AB} c_0^* \left(\frac{k^B}{k^A}\right) k^B_{\text{max}} = \theta_{AB} c_{B*_{\text{max}}} \quad \text{(B.21)}
\]

Obviously, the persistence values for the PP and SP do not change when compared to the case of $\theta_{AB} = 1$. While this was to be expected for the PP, which is not influenced by the following formation of B, this is not self-evident for the SP. It
Table B.4: Analytical solutions for the PP, SP and JP expressed by means of $\tau^{\text{equiv}}$ and $\mu$ for the case of parallel reactions, i.e. $\theta^{AB} \leq 1$.

<table>
<thead>
<tr>
<th>Equivalence Width</th>
<th>PP</th>
<th>JP</th>
<th>SP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau^A = \frac{1}{k_A}$</td>
<td>$\tau^{AB*} = \frac{\theta^{AB}k_A + k_B}{k_Ak_B}$</td>
<td>$\tau^{B/A*} = \frac{k_B}{k_A}(k_B - k_A)$</td>
<td></td>
</tr>
<tr>
<td>Mean Time</td>
<td>$\mu^A = \frac{1}{k_A}$</td>
<td>$\mu^{AB*} = \frac{\theta^{AB}k_A^2 + \theta^{AB}k_Ak_B + k_B^2}{k_Ak_B(\theta^{AB}k_A + k_B)}$</td>
<td>$\mu^{B/A*} = \frac{k_A + k_B}{k_Ak_B}$</td>
</tr>
</tbody>
</table>

implies that the absolute amount of B becomes less with smaller $\theta^{AB}$, but that the course of the concentration function relative to the time axis remains the same. Hence, $\theta^{AB}$ only influences the JP. In order to better understand that influence, the limiting cases of $\alpha \gg 1$ and $\alpha \ll 1$ were investigated again for the JP and are compiled in Table B.5. Now, $\tau^{\text{equiv}}$ and $\mu$ show a distinctively different behavior for long-lived transformation products. This is further illustrated in Figure B.3, where five plots with the concentration functions $c^A(t)$, $c^{B*}(t)$ and $c^{AB*}(t)$ are depicted for the cases $\alpha = 10$ and $\theta^{AB} = 1, 0.8, 0.6, 0.4, \text{ and } 0.2$, and the corresponding JP values for $\tau^{AB*}$ and $\mu^{AB*}$ are plotted.

Table B.5: Limes of the analytical solutions for the JP, expressed by means of $\tau^{\text{equiv}}$ and $\mu$ for the limiting cases of $\alpha \ll 1$ and $\alpha \gg 1$ and for parallel reactions.

<table>
<thead>
<tr>
<th>Equivalence Width</th>
<th>$\alpha \ll 1$</th>
<th>$\alpha \gg 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau^{AB*} = \frac{1}{k_A}$</td>
<td>$\tau^{AB*} = \frac{\theta^{AB}}{k_B}$</td>
<td></td>
</tr>
<tr>
<td>Mean Time</td>
<td>$\mu^{AB*} = \frac{1}{k_A}$</td>
<td>$\mu^{AB*} = \frac{1}{k_B}$</td>
</tr>
</tbody>
</table>

From the investigation of the behavior of $\tau^{\text{equiv}}$ and $\mu$ it can be concluded that, for parallel reactions, the JP measure $\tau^{AB}$ behaves differently from $\mu^{AB}$, whose value does not change significantly with diminishing $\theta^{AB}$. While $\tau^{AB}$ reflects the fact that the overall concentration falls relatively fast to small concentrations for small values of $\theta^{AB}$, $\mu^{AB}$ does not react to that but rather represents the fact that the transformation product B is comparably persistent and therefore remains for a long time at low concentrations.
Regarding the general solution for the JP, expressed as equivalence width, of higher numbers of generations of transformation products as given in Equation B.17, those expressions can be generalized for the case of parallel reactions, i.e. if the precursor does not react entirely into the successor under consideration. The respective expressions are given in Equation B.22.

\[
\tau_{AB}^{*} = \tau^{A}(1 + \theta^{AB}\alpha) \quad \text{(B.22)}
\]

\[
\tau_{ABC}^{*} = \frac{1}{k^{A}} + \frac{\theta_{AB}^{B}}{k^{B}} + \frac{\theta_{AB}^{B} \theta_{BC}^{C}}{k^{C}} = \tau^{A}(1 + \theta^{AB}\alpha + \theta^{AB}\theta^{BC}\beta)
\]

\[
\tau_{A\ldots n}^{*} = \sum_{x=A}^{n} \frac{1}{k^{x}} = \sum_{x=A}^{n} \prod_{j=A}^{x-1} \theta^{j+1} = \tau^{A}(1 + \theta^{AB}\alpha + \theta^{AB}\theta^{BC}\beta + \ldots \prod_{x=A}^{n-1} \theta^{x+1}\nu)
\]

with \(\alpha = \frac{k^{A}}{k^{B}}, \beta = \frac{k^{A}}{k^{C}}, \ldots \nu = \frac{k^{A}}{k^{n}}\)
From the above elaborations on the suitability of the equivalence width and the mean time as persistence measures for the PP, SP and JP of a parent compound and its relevant transformation products, we conclude that the equivalence width is better suited for two reasons. First, according to the expressions in Equation B.17 it behaves as one would expect for several generations of transformation products, i.e. it doubles in case of an equipersistent transformation product (i.e. \( k^A = k^B \)), triples in the case of a transformation product that is twice as persistent, and also triples in the case of two consecutive generations of equipersistent transformation products. This is not the case for the mean time. Second, the equivalence width for the JP reacts to the fact that in parallel reactions lesser amount of the transformation product under consideration are formed, which is hardly reflected in the value of the mean time. Consequently, we have chosen the equivalence width as the measure that is better suited to express the JP. It will therefore also be used to calculate SP values, although, in the multimedia model, this means solving the level IV system in order to evaluate the maximal concentration of the concentration functions of the transformation products.
Appendix C

Substance-specific input data

C.1 Methods for substance data collection

The first step in identifying data needs is to gain an overview of the transformation pathways of the parent compound in each environmental compartment. This information is obtained mainly from literature and from discussions with scientists and experts from the industry. From this collection of possible transformation products, those that should be part of the transformation scheme for the model calculations need to be identified in a following step. This selection procedure is necessary in order to reduce data intensity and complexity and, at the same time, to achieve optimal transparency and comparability of different substance families. For that purpose, the following rules have been set up:

- Transformation products that were only measured rarely, under certain circumstances or are still disputed were not considered (e.g. dicarboxylated transformation products of nonylphenol ethoxylates, acetamide-alkylamino transformation products of atrazine).

- To decide how many generations of transformation products to consider and where to end the transformation scheme, the following cut-off criteria for specific transformation products were applied (for rationale see Chapters 2.2 and 2.3.1): A chemical is not further included if
  - it has a chain length of less than four carbon atoms, is not an epoxide or aldehyde, and contains no other elements than C, H, N or O, or
  - it is known to be degradable through an ubiquitous enzymatic pathway, or
— it is otherwise known to be efficiently mineralized by microorganisms.

Once the basic pathways and all specific transformation products in each environmental compartment have been identified, an extensive literature search has to be conducted to obtain the following model input parameters for the parent compound and each of its transformation products:

- Octanol-water partition coefficient, \( K_{ow} \), (or organic carbon-water partition coefficient, \( K_{oc} \)), and Henry’s law constant, \( K_H \).

- 3 (or 4) media-specific half-lives for soil, water, air and, depending on the choice of compartments modelled, sediment.

- Media-specific fractions of formation for all transformation reactions.

The aim of the data search is to gather the maximal available number of data points for each input parameter in order to get as complete a picture of the range of possible values for each parameter as possible. Sources of information for data gathering are:

- Literature databases (e.g., CAS, Web of Science, Current Contents)

- Handbooks (e.g., Illustrated Handbook of Physico-Chemical Properties and Environmental Fate for Organic Chemicals by Mackay et al. (1993), Handbook of Environmental Degradation Rates by Howard et al. (1991), Handbook of Environmental Fate and Exposure Data for Organic Chemicals by Howard (1991))

- Online substance databases (e.g., ECDIN*, ChemFinder†, Environmental Fate Data Base (EFDB)‡, and hyperlinks therein)

- Industry information (e.g., registration dossiers)

- BUA reports (BUA, 1989)

For the three case studies, the number of data points found for each input parameter varied between 0 (e.g. for half-lives in soil, water and air for all 3\(^{\text{rd}}\) and 4\(^{\text{th}}\) generation transformation products of atrazine) and 100 (e.g. for the half-life of atrazine in soil). Generally, the data availability was good for octanol-water partition coefficients and

*http://ecdin.etomep.net/
†http://chemfinder.cambridgesoft.com/
‡http://esc.syrres.com/efdb.htm
half-lives in those compartments where the compounds are found preferentially, as well as half-lives in air. For the Henry's law constant and for the half-lives in all other compartments, data availability was medium, while data on the fractions of formation is practically non-existent except for a few well known transformation steps. In addition, there was generally more data available for the early generation transformation products and those transformation products that have been found repeatedly in the environment, and less for later generations.

If no data point could be retrieved for a certain model input parameter, quantitative structure-property relationships (QSPR) were used to estimate that parameter. These are mathematical relationships, obtained from regression analysis of measured values of a certain physico-chemical property for a number of chemicals, called a training set, against a set of descriptors that are based on the molecular structure of a chemical. QSPR thus allow the extrapolation of different properties of chemical compounds solely from their molecular structure. Currently, the most comprehensive and reliable collection of such estimation methods is the commercially available estimation software package EPIWIN by Meylan and Howard (1999). It contains a set of 10 QSPR methods to estimate 7 physico-chemical parameters (BCF, $K_H$, log $K_{ow}$, $T_m$, $T_b$, $p_v$, $S$), 3 degradation rates (biodegradation, atmospheric oxidation and hydrolysis) and the toxicity to aquatic organisms (e.g. LC50 for fish, daphnia, and green algea). All parameter estimations are based on the SMILES notation (Simplified Molecular Identification and Line Entry System) of the chemical compounds. For our model, the physico-chemical parameters $K_{ow}$ and $K_H$, the degradation rates in air (rate for atmospheric oxidation) and biodegradability as a surrogate for degradation in soil and water were estimated, where necessary, with the help of EPIWIN. In Table C.2 an overview of the estimation methods used and their respective reliability is given. The semi-quantitative scale for biodegradation in BioWin (Boethling et al., 1994) was translated into half-lives according to the list given in Table C.1. In those cases where more than one data point is available for a certain model input parameter, the set of all collected points needs to be represented by means of a statistical summary measure. For this purpose, the geometric mean ($GM$) was used for all five types of substance input data as opposed to the often used arithmetic mean ($\mu$). In the case of $K_H$ and $K_{ow}$ the geometric mean was chosen for its ability to better represent the central tendency of a set of data that spreads over several orders of magnitude, which is often the case for partition coefficients. For the degradation rates or half-lives, the geometric mean was chosen as a summary measure because identical mean values for the degradation velocity were obtained for the geometric
mean only, independent of whether they were based on degradation rates or on their half-lives (see Equation 3.1 in Chapter 3.1). This is due to the fact that the $GM$ is based on multiplication as opposed to addition, which is the case for the arithmetic mean. For the arithmetic mean the inequality between $\mu(k)$ and $\mu^*(k)$, where $\mu^*(k)$ results from $\mu(t_{1/2})$ as $\mu^*(k)=\ln 2/\mu(t_{1/2})$, is shown in Equation C.1. In contrast, the equality of $GM(k)$ and $GM^*(k)$, where $GM^*(k)$ again results from $GM(t_{1/2})$ as $GM^*(k)=\ln 2/GM(t_{1/2})$, is shown in Equation C.2.

\[
\mu(k) = \frac{1}{n} \sum k_i \quad \text{and} \quad \mu(t_{1/2}) = \frac{1}{n} \sum t_{1/2,i} \quad \text{(C.1)}
\]

\[
\mu^*(k) = \frac{\ln 2}{\frac{1}{n} \sum t_{1/2,i}} = n \cdot \ln 2 \cdot \frac{1}{\sum \frac{\ln 2}{k_i}} = n \cdot \frac{1}{\sum \frac{1}{k_i}} \neq \mu(k)
\]

\[
GM(k) = \left( \prod k_i \right)^{1/n} \quad \text{and} \quad GM(t_{1/2}) = \left( \prod t_{1/2,i} \right)^{1/n} \quad \text{(C.2)}
\]

\[
GM^*(k) = \frac{\ln 2}{\left( \prod t_{1/2,i} \right)^{1/n}} = \ln 2 \cdot \frac{1}{\left( \prod \frac{\ln 2}{k_i} \right)^{1/n}} = \frac{1}{\left( \prod \frac{1}{k_i} \right)^{1/n}} = \left( \prod k_i \right)^{1/n} = GM(k)
\]

Table C.1: Translation of semi-quantitative scale used in BioWin (Boethling et al., 1994) into half-lives that can be used as model input parameters for biodegradation in soil and water.

<table>
<thead>
<tr>
<th>Semi-quantitative score</th>
<th>Time required for primary biodegradation according to BioWin</th>
<th>Half-live used as model input (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>Hours</td>
<td>0.5</td>
</tr>
<tr>
<td>4.5</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>4.0</td>
<td>Days</td>
<td>3.5</td>
</tr>
<tr>
<td>3.5</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>3.0</td>
<td>Weeks</td>
<td>14</td>
</tr>
<tr>
<td>2.5</td>
<td></td>
<td>28</td>
</tr>
<tr>
<td>2.0</td>
<td>Months</td>
<td>182.5</td>
</tr>
<tr>
<td>1.5</td>
<td></td>
<td>365</td>
</tr>
<tr>
<td>1.0</td>
<td>&gt;1 Year</td>
<td>1825</td>
</tr>
</tbody>
</table>
Table C.2: Short descriptions of parameter estimation methods from EPIWIN (Meylan and Howard, 1999) that were used where no measured values were available as substance input parameters ($r^2$: Correlation coefficient, SD: Standard deviation in log units).

<table>
<thead>
<tr>
<th>Estimated parameter</th>
<th>Method</th>
<th>Training set (number of compounds)</th>
<th>$r^2$</th>
<th>SD</th>
<th>Validation set (number of compounds)</th>
<th>$r^2$</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-water partition coefficient (Meylan and Howard, 1991)</td>
<td>$\log K_{H2O}$</td>
<td>Bond contribution</td>
<td>345</td>
<td>0.94/0.97$^\S$</td>
<td>0.45/0.34</td>
<td>74</td>
<td>0.96</td>
</tr>
<tr>
<td>Octanol-water partition coefficient (Meylan and Howard, 1995)</td>
<td>$\log K_{ow}$</td>
<td>Atom/fragment contribution</td>
<td>2351</td>
<td>0.98</td>
<td>0.22</td>
<td>6055</td>
<td>0.94</td>
</tr>
<tr>
<td>Organic carbon-water partition coefficient (Meylan et al., 1992)</td>
<td>$\log K_{oc}$</td>
<td>Molecular topology/fragment contribution</td>
<td>189</td>
<td>0.96</td>
<td>0.23</td>
<td>205</td>
<td>0.86</td>
</tr>
<tr>
<td>Atmospheric oxidation (Meylan and Howard, 1993)</td>
<td>$k_{OH}$, $k_{O3}$</td>
<td>Atkinson (1988)</td>
<td>For training set see Atkinson (1988)</td>
<td>77</td>
<td>0.89</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>Biodegradation (Boethling et al., 1994)</td>
<td>Time frame (1–5) for primary and ultimate biodegradation</td>
<td>Group contribution</td>
<td>Estimates for 200 chemicals from 17 experts</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

$^\S$For inclusion of correction factors.
C.2 Data collections

C.2.1 Data collection for NPnEO

In the NPnEO case study, substance-specific input data for NPnEO was deduced using data points for NPnEO with $n=9-15$. NP is represented by those compounds with branched nonyl chains (CAS Registry Number: 84852-15-3).

The input data for NPnEO and its transformation products can be downloaded as Excel sheet (NPnEO_data.xls) from http://ltcmail.ethz.ch/hungerb/publications/pu2001.html#dissertations. The references in the data sheet are listed in the bibliography in this work.

C.2.2 Data collection for perchloroethylene

The input data for perchloroethylene and its transformation products can be downloaded as Excel sheet (PCE.data.xls) from http://ltcmail.ethz.ch/hungerb/publications/pu2001.html#dissertations. The references in the data sheet are listed in the bibliography in this work.

C.2.3 Data collection for atrazine

The input data for atrazine and its transformation products can be downloaded as Excel sheet (atrazine_data.xls) from http://ltcmail.ethz.ch/hungerb/publications/pu2001.html#dissertations. The references in the data sheet are listed in the bibliography in this work.

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esc.syrres in PCE_data.xls stands for the following URL: http://esc.syrres.com/interkow/physdemo.htm
Appendix D

Methodology of probabilistic uncertainty analysis

Probability distributions for input parameters
The validity of any uncertainty analysis is contingent upon the validity of its inputs. Characterizing the type of input distributions is a major task in probabilistic uncertainty analysis because it will transmit the input information directly to the final results. Decisive for the choice of input distributions is their ability to properly represent a set of known values and their physical meaningfulness. Convenient tools for representing probability distributions are the probability density function (PDF) and the cumulative distribution function (CDF). The CDF is obtained by integrating the PDF over the random variable $X$.

In this analysis, lognormal distributions were chosen to represent the distributions of the degradation data as well as those of the partition coefficients. The lognormal distribution is said to be a good representation for physical quantities that are constrained to being non-negative, and to be appropriate for representing large uncertainties that are expressed on an order-of-magnitude basis (Morgan and Henrion, 1990). Both cases apply for partition coefficients and degradation data. The description of the logarithm of the random variable $X$ by means of a normal distribution results in a lognormal distribution for $X$. The lognormal distribution is thus based on logtransformed input data. This has the further advantage that it results in the same distribution for the degradation data, independently of whether it is based on logtransformed half-lives or degradation rates. Although the claim to obtain the same distribution of input values for degradation, independent of whether it is based on degradation rates or half-live, seems to be self-evident, this is not the case for
any distribution that is not based on logtransformed data.

The parameters of the lognormal distribution are equivalent to the mean and standard deviation of the logtransformed data, and are therefore called logarithmic mean, \( \mu_{\ln} \), and logarithmic standard deviation, \( \sigma_{\ln} \). They were estimated differently for the different model input parameters in each case study, depending on the number of data points, \( n \), available. Other measures that describe the same distribution are the geometric mean (\( GM \)) and geometric standard deviations (\( GSD \)), the arithmetic mean (\( \mu \)) and the arithmetic standard deviation (\( \sigma \)), and the coefficient of variation (\( CV \)) deduced therefrom. These alternative parameters are interrelated with the parameters of the lognormal distribution \( \mu_{\ln} \) and \( \sigma_{\ln} \) according to Equations D.1–D.6 (McKone, 1994).

\[
GM = \exp(\mu_{\ln}) \quad (D.1)
\]

\[
GSD = \exp(\sigma_{\ln}) \quad (D.2)
\]

\[
\mu = \exp(\mu_{\ln} + \frac{1}{2}\sigma_{\ln}^2) \quad (D.3)
\]

\[
\sigma = \sqrt{\exp(2\mu_{\ln} + \sigma_{\ln}^2)[\exp(\sigma_{\ln}^2) - 1]} \quad (D.4)
\]

\[
CV = \frac{\sigma}{\mu} \quad (D.5)
\]

\[
CV = \sqrt{\exp(\ln GSD^2 - 1)} \quad (D.6)
\]

If \( n \geq 3 \), the maximum likelihood procedure according to Morgan and Henrion (1990) for the estimation of the parameters of a lognormal distribution is applied. If \( x_i \) is one data point of the input parameter \( X \), the parameters of the input distribution are defined as follows:

\[
\mu_{\ln}(X) = \ln \bar{X} = \frac{1}{n} \sum_{i=1}^{n} \ln x_i \quad (D.7)
\]

\[
\sigma_{\ln}(X) = \left( \frac{1}{n} \sum_{i=1}^{n} (\ln x_i - \mu_{\ln}(X)) \right)^{1/2} \quad (D.8)
\]

If \( n = 2 \), the logarithmic mean, \( \mu_{\ln} \), is calculated as for \( n \geq 3 \) according to Equation D.7. The logarithmic standard deviation, \( \sigma_{\ln} \), is calculated by assuming that the two data points represent the 5\(^{th} \) and 95\(^{th} \) percentile of the lognormal distribution. If this assumption results in a smaller \( CV \) than the default \( CV \)s suggested in CalTOX (McKone, 1993), the default \( CV \) from CalTOX is used instead to determine \( \sigma_{\ln} \).
Table D.1: Default coefficients of variation (CVs) for degradation data and partition coefficients as used in CalTOX (McKone, 1993). They are evaluated as the arithmetic mean of the CVs of eight chemicals. The corresponding GSD and $\sigma_in$ values were calculated according to Equations D.6 and D.2.

<table>
<thead>
<tr>
<th>Input parameter</th>
<th>CV</th>
<th>GSD (calc.)</th>
<th>$\sigma_{in}$ (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa_s$</td>
<td>1.1</td>
<td>2.44</td>
<td>0.89</td>
</tr>
<tr>
<td>$\kappa_w$</td>
<td>1.2</td>
<td>2.57</td>
<td>0.94</td>
</tr>
<tr>
<td>$\kappa_a$</td>
<td>1.0</td>
<td>2.30</td>
<td>0.83</td>
</tr>
<tr>
<td>$K_H$</td>
<td>0.45</td>
<td>1.54</td>
<td>0.43</td>
</tr>
<tr>
<td>$K_{ow}$</td>
<td>0.37</td>
<td>1.43</td>
<td>0.36</td>
</tr>
</tbody>
</table>

If $n = 1$, the logtransformed data point is taken to be $\mu_{in}$ and the default CVs from CalTOX are used to determine $\sigma_{in}$ (McKone, 1993). The default CVs suggested in CalTOX are given in Table D.1.

The CVs in CalTOX were determined as arithmetic means of the CVs of eight substances for which thorough data collections had been constructed, i.e. 1,1-dichloroethylene, 1,2-dichloroethane, benzene, benzoapyrene, PCE, TCDD, TCE, and VC. In addition to the fact that these data collections are still not very extensive and comprehensive, the main problem with these CVs is that they were calculated as quotients of $\sigma$ and $\mu$ of the untransformed, i.e. not logtransformed, half-lives. Different CVs would thus be obtained if they were based on the degradation rates instead. In this form, they are therefore not appropriate to describe the spread of the distributions of the degradation data. Still, determining the spread of a lognormal distribution in cases where only one data point is available is a matter of expert judgment anyway. In this sense, the CVs in CalTOX quite probably represent reasonable estimates for the spread of degradation data. Other estimates for the same parameters have been proposed by Webster et al. (1998) in the form of 95% confidence interval factors for the distributions of degradation data. These intervals can be translated into GSDs by using the relationship that the 95% confidence interval corresponds to the GM divided/multiplied by $GSD^{1.96}$. The confidence interval factors suggested and the corresponding GSD and CV values are given in Table D.2.

The values for the CV calculated in Table D.2 show the same tendency as the CVs from CalTOX in that the degradation data in air is the least and that in water the
Table D.2: 95% confidence intervals for degradation rates in soil, water and air as suggested by Webster et al. (1998). The GSD was calculated using the relationship that the 95% confidence interval corresponds to the GM divided/multiplied by GSD\(^{1.96}\). The corresponding CV and \(\sigma_{in}\) values were calculated according to Equations D.6 and D.2.

<table>
<thead>
<tr>
<th>Input parameter</th>
<th>95% confidence interval factor</th>
<th>GSD (calc.)</th>
<th>CV (calc.)</th>
<th>(\sigma_{in}) (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\kappa_s)</td>
<td>3</td>
<td>1.75</td>
<td>0.59</td>
<td>0.56</td>
</tr>
<tr>
<td>(\kappa_w)</td>
<td>4</td>
<td>2.03</td>
<td>0.81</td>
<td>0.71</td>
</tr>
<tr>
<td>(\kappa_a)</td>
<td>2</td>
<td>1.42</td>
<td>0.36</td>
<td>0.35</td>
</tr>
</tbody>
</table>

most uncertain, but they are generally smaller. To be on the conservative side regarding the uncertainties, CalTOX values were therefore chosen for the probabilistic analyses in this work.

In those cases where no input data was available at all and the EPIWIN package (Meylan and Howard, 1999) was therefore used to estimate the input parameters, the measures of accuracy of the respective estimation method, given as standard deviation (SD) of the logtransformed estimated properties from the known properties of the compounds of the validation test set, were translated into GSDs. They are listed in Table D.3. For \(K_{oc}\) and \(k_{OH}\), the GSDs of the estimation methods lie in the same range as the GSDs describing the uncertainty of a set of measured values, i.e. GSD=2–3 for \(K_{oc}\) and GSD=1–2 for \(k_{OH}\). In contrast, the estimation method for \(K_H\) has an inaccuracy that is about one order of magnitude larger than the uncertainty of a set of measured values, e.g. GSD\((K_H) = 1 – 2\) for the chlorinated ethylenes in the PCE cases study.

The fractions of formation in the uncertainty analysis are all described by means of triangular distributions between 0 and 1. Triangular distributions are the distributions with maximum entropy if only the upper and lower bound and a most likely value of a parameter are known. This is exactly the case for the fractions of formation. The fractions of formation used as point estimates in Chapter 5 (see Table 5.1, Table 5.4 and Table 5.6) were used as the most likely values of the triangular distributions.

*For \(K_H > 10^{-8}\) atm m\(^3\)/mol

\(^{1}\)For \(K_H < 10^{-8}\) atm m\(^3\)/mol
Table D.3: Standard deviations, $SD$, for the estimation methods of the EPIWIN package (Meylan and Howard, 1999) used to deduce GSD values for the input distributions of estimated input parameters. $SD$ is the standard deviation of the logtransformed estimated properties from the known properties of the compounds of the validation test set.

<table>
<thead>
<tr>
<th>Input parameter</th>
<th>EPIWIN package</th>
<th>$SD$</th>
<th>GSD (calc.)</th>
<th>CV (calc.)</th>
<th>$\sigma_H$ (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{H^+}$</td>
<td>HenryWin</td>
<td>0.87</td>
<td>7.41</td>
<td>7.37</td>
<td>2.00</td>
</tr>
<tr>
<td>$K_{H^-}$</td>
<td>HenryWin</td>
<td>1.43</td>
<td>26.9</td>
<td>226</td>
<td>3.29</td>
</tr>
<tr>
<td>$K_{oc}$</td>
<td>PCKocWin</td>
<td>0.477</td>
<td>3.00</td>
<td>1.53</td>
<td>1.10</td>
</tr>
<tr>
<td>$k_{OH}$</td>
<td>AOP</td>
<td>0.218</td>
<td>1.65</td>
<td>0.54</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Monte Carlo analysis

Monte Carlo analysis is the method commonly used to propagate input distributions through a model. The idea behind it is to approximate the probability distribution for the model output by selecting a number of random samples of scenarios for evaluation. This is done by a simultaneous, repeated random sampling of all input distributions and storing of the corresponding output values. This procedure results in a distribution for each output value, which, for a large number of simulations, so-called shots, is likely to provide a good representation of the true output distribution. Outputs analyzed for the case studies in this work are the PP, the JP and the quotient Q between the two.

In Monte Carlo analysis one of two sampling schemes is generally employed: Simple random sampling or Latin hypercube sampling (Morgan and Henrion, 1990). Latin hypercube sampling may be viewed as a stratified sampling scheme designed to ensure that the upper and lower ends of the distributions used in the analysis are well represented. It is considered to be more efficient than simple random sampling, that is, it requires fewer simulations to produce the same level of precision. It was therefore selected as the method of choice for the analyses in this work.

Advantages of Monte Carlo analysis are that the model can be used in its original form, that summary statistics and confidence intervals for calculated outputs can be constructed easily and that several methods for ranking uncertainties in the inputs, such as correlation coefficients and rank correlations, can be applied directly to the results of the Monte Carlo analysis, i.e. a set of lists containing the sampled values from each input parameter distribution and lists of corresponding output values. The precision of the Monte Carlo analysis can easily be enhanced by raising the number
of shots. Morgan and Henrion (1990) discuss how the number of shots required for a certain precision in the output can be estimated. However, the number of shots and therefore the accuracy of the resulting distributions is limited by the practical disadvantage of Monte Carlo analysis, which is that it requires large amounts of time to carry out the calculations. Finding the ideal number of shots is therefore always a trade-off between accuracy and time needed for the calculations. For the analyses in this work, the optimal number of shots was not determined analytically but by running different numbers of simulations and determining the tendency of the corresponding summary statistics. As it is shown in Chapter 6.2, the optimal number of shots was determined to be 2500, which resulted in a calculation time of approximately 25 minutes for the atrazine case study.

Correlations between parameters
Correlations between input parameters (e.g. the interdependence of pH and the hydrolysis rate in water) or between output parameters have an impact on the results and must therefore be considered in uncertainty analysis. Two possibilities may be used to handle correlations between input parameters. The first is to integrate the correlations explicitly into the mathematical model and the second is to use correlation matrices which coordinate the random sampling between correlated variables according to the correlation coefficients in the matrix (Morgan and Henrion, 1990). In theory, correlations between physico-chemical parameters might exist, but they are generally so weak that they were not considered in this work. Since functional dependencies of degradation rates and partition coefficients on environmental parameters such as temperature and pH are not explicitly modelled in our system, these correlations do not need to be taken into account either. However, there is one special case of correlation for the parallel decay of atrazine to DEA and DIA. It is known that the fractions of formation for these two processes, i.e. $\theta_{1,s/w}$ and $\theta_{2,s/w}$, always show a ratio of approximately 2:1 in water and 3:1 in soil for deethylation versus deisopropylation. This correlation was allowed for by assuming total correlation and explicitly integrating it into the model. In the uncertainty analysis, the sum of the two fractions of formation in soil and water is thus treated as one single variable.

There also exists a correlation between parallel fractions of formation, which stems from the fact that the mass balance of each precursor in the transformation scheme has to be respected. Thus, even if the single fractions of formation are uncertain, their sum must never exceed 1 (unless the precursor decays into two parts which each
constitute individual transformation products). Hence, the values of the different fractions of formation for parallel reactions are not independent. Although this problem is easily solved for two fractions of formation which always add up to 1, the situation here is more complicated because it is assumed that they do not necessarily need to add up to 1. This is equivalent to saying that one or more unknown or irrelevant transformation products might be formed at the same time. This problem was solved as follows: First, all fractions of formation were attributed individual triangular input distributions as discussed above. Next, each precursor was given another triangular distribution representing the probability distribution of the overall decay, i.e. representing the share that goes into those transformation products that are actually part of the transformation scheme. This distribution is also assumed to vary between 0 and 1, and was given the sum of the fractions of formation of all parallel reactions as a most likely value or, in the case of atrazine and its transformation products, that fraction of the compound that is not immobilized in the form of bound residues. In the Monte Carlo analysis, the overall decay distribution was sampled first, the sampled value indicating how many relevant transformation products are formed at all in that specific scenario. Then, a random number generator was used to decide from which distribution of the individual transformation products the fraction of formation should be sampled first. This fraction of formation was then multiplied by the sampled overall decay, and the fraction of formation for the other transformation product was obtained by subtraction from the upper limit given by the sampled overall decay. This procedure is illustrated in Figure D.1 for the decay of atrazine in soil into DEA, DIA and HA. This illustration shows both the general handling of parallel reactions, such as the decay of atrazine into HA on one hand and DEA and DIA on the other hand, as well as how the special interdependence between the formation of DIA and DEA was handled. The parameters of the triangular distributions for all decay and formation processes are given in Tables D.4-D.6 for the three case studies. Since the model yields results for both the PP and the JP, possible correlations between output parameters also need to be investigated. If the two distributions obtained for the JP and the PP are simply compared with each other without paying attention to belonging pairs of PP and JP values, it is possible that the JP of one scenario might be smaller than the PP of another scenario. It was shown, however, that on theoretical grounds, the JP must always be equal or bigger than the PP. This correlation was taken into account by calculating the quotient of JP and PP for each scenario separately, which resulted in a third output distribution representing
Figure D.1: Illustration of how input distributions for fractions of formation of parallel reactions are generated for the case of atrazine transformation in soil. For the parallel reaction of DEA and DIA a fixed ratio of approximately 3:1 has been observed.

the quotient Q of JP and PP. Wherever the ratio between JP and PP needs to be investigated, the discussion should be based on the distribution of the quotient and not on the ratio of the summary statistics of the individual PP and JP distributions.

Analysis of results
The three output parameters of the uncertainty analysis, namely the PP, JP and quotient Q are analyzed in various ways in order to answer the questions raised at the beginning of this chapter.

In order to learn about the location and the width of the output distributions, the geometric mean, $GM$, was calculated as a measure of central tendency and the geometric standard deviation, $GSD$, as well as the ratio of the 95th and the 5th percentile were evaluated to represent the spread of the distributions. These summary statistics are used to compare the output distributions with the deterministic results and to compare the uncertainty of JP calculations with that of PP calculations. Also, some initial statements regarding the limits for distinction of single persistence values can be made on this basis.

To evaluate the contribution of the individual input parameters to the final output distributions, rank correlation coefficients were calculated. Rank correlation coeffi-
Table D.4: Parameters of triangular distributions for decay and formation of NPnEO and its transformation products. The fractions of formation entering the calculation are obtained as a combination of values sampled from the decay and formation distributions. LL: Lower limit, MLV: Most likely value, UL: Upper limit, TP: Transformation product.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Decay</th>
<th>Formation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LL</td>
<td>MLV</td>
</tr>
<tr>
<td>NPnEO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>0</td>
<td>0.99</td>
</tr>
<tr>
<td>w</td>
<td>0</td>
<td>0.99</td>
</tr>
<tr>
<td>a</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<tr>
<td>NP2EC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>0</td>
<td>0.99</td>
</tr>
<tr>
<td>w</td>
<td>0</td>
<td>0.99</td>
</tr>
<tr>
<td>a</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NP1EC</td>
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<tr>
<td>s</td>
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<td>0.01</td>
</tr>
<tr>
<td>w</td>
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<td>0.3</td>
</tr>
<tr>
<td>a</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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</tr>
<tr>
<td>s</td>
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<td>0.99</td>
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<tr>
<td>w</td>
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<td>0.99</td>
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<tr>
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<tr>
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</tr>
<tr>
<td>a</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>
Table D.5: Parameters of triangular distributions for decay and formation of perchloroethylene and its transformation products. The fractions of formation entering the calculation are obtained as a combination of values sampled from the decay and formation distributions. LL: Lower limit, MLV: Most likely value, UL: Upper limit, TP: Transformation product.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Decay</th>
<th>Formation</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>LL</td>
<td>MLV</td>
</tr>
<tr>
<td>PCE</td>
<td></td>
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</tr>
<tr>
<td>s</td>
<td>0</td>
<td>0.16</td>
</tr>
<tr>
<td>w</td>
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<td>0.45</td>
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<tr>
<td>a</td>
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<td>0.99</td>
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<tr>
<td>DCE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>s</td>
<td>0</td>
<td>0.05</td>
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<tr>
<td>w</td>
<td>0</td>
<td>0.34</td>
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<tr>
<td>a</td>
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<td>0.78</td>
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<tr>
<td>TCAC</td>
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<td></td>
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<tr>
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<td>0</td>
<td>0.01</td>
</tr>
<tr>
<td>w</td>
<td>0</td>
<td>0.3</td>
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<tr>
<td>a</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>TCA</td>
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<td></td>
</tr>
<tr>
<td>s</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>w</td>
<td>0</td>
<td>0.3</td>
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<tr>
<td>a</td>
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<td>-</td>
</tr>
<tr>
<td>DCA</td>
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<tr>
<td>s</td>
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<td>0.3</td>
</tr>
<tr>
<td>w</td>
<td>0</td>
<td>0.3</td>
</tr>
<tr>
<td>a</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table D.6: Parameters of triangular distributions for decay and formation of atrazine and its transformation products. The fractions of formation entering the calculation are obtained as a combination of values sampled from the decay and formation distributions. LL: Lower limit, MLV: Most likely value, UL: Upper limit. TP: Transformation product.

| Precursor | Decay | | Formation | |
|-----------|-------|---|---|---|---|
|           | No. r | TP | LL | MLV | UL |
| Atrazine  | 1+2   | DEA+DIA | 0 | 0.11 | 1 |
|           | 3     | HA | 0 | 0.1 | 1 |
|           | 1+2   | DEA+DIA | 0 | 0.15 | 1 |
|           | 3     | HA | 0 | 0.09 | 1 |
|           | 1+2   | DEA+DIA | 0 | 0.9 | 1 |
|           | 3     | HA | 0 | 0.1 | 1 |
| DEA       | 4     | DEHA | 0 | 0.16 | 1 |
|           | 5     | DAA | 0 | 0.29 | 1 |
|           | 4     | DEHA | 0 | 0.25 | 1 |
|           | 5     | DAA | 0 | 0.47 | 1 |
| DIA       | 6     | DIHA | 0 | 0.09 | 1 |
|           | 7     | DAA | 0 | 0.33 | 1 |
|           | 6     | DIHA | 0 | 0.12 | 1 |
|           | 7     | DAA | 0 | 0.46 | 1 |
| HA        | 8+9   | DIHA+DEHA | - | - | - |
|           | 8+9   | DIHA+DEHA | - | - | - |
| DIHA      | s     | 0.99 | 1 | - | - |
|           | w     | 0.99 | 1 | - | - |
|           | a     | 0.99 | 1 | - | - |
| DEHA      | s     | 0.99 | 1 | - | - |
|           | w     | 0.99 | 1 | - | - |
|           | a     | 0.99 | 1 | - | - |
| DAA       | s     | 0.99 | 1 | 12 | DAHA | 0 | 0.5 | 1 |
|           | w     | 0.99 | 1 | 12 | DAHA | 0 | 0.5 | 1 |
|           | a     | 0.99 | 1 | 12 | DAHA | 0 | 0.5 | 1 |
| DAHA      | s     | 0.99 | 1 | 15 | atral0 | 0 | 0.5 | 1 |
|           | w     | 0.99 | 1 | 15 | atral0 | 0 | 0.5 | 1 |
|           | a     | 0.99 | 1 | 15 | atral0 | 0 | 0.5 | 1 |
| atra9     | s     | 0.99 | 1 | 16 | atrall | 0 | 0.5 | 1 |
|           | w     | 0.99 | 1 | 16 | atrall | 0 | 0.5 | 1 |
|           | a     | 0.99 | 1 | 16 | atrall | 0 | 0.5 | 1 |
| atra10    | s     | 0.99 | 1 | - | - |
|           | w     | 0.99 | 1 | - | - |
|           | a     | 0.99 | 1 | - | - |
| atrall    | s     | 0.99 | 1 | - | - |
|           | w     | 0.99 | 1 | - | - |
|           | a     | 0.99 | 1 | - | - |
coefficients allow the identification of nonlinear (but monotonic) dependencies between input and output parameters, and they are sensitive to both (i) the strength of the relationship and (ii) the range of variation of the output relative to the range of variation of the input. They are calculated by storing the input and output parameter values of each shot in lists. These lists are then sorted and the values are replaced with ranks, starting with 1 for the lowest value in the list and ending with \( m \) for the highest value in the list, where \( m \) corresponds to the number of shots. A correlation \( RC_{X,Y} \) is then calculated for each pair of lists of input \( X \) and output \( Y \) according to Equation D.9, where \( r(x_k) \) stands for the rank of the input parameter, \( r(y_k) \) for the rank of the output parameter and \( \bar{r} = (m + 1)/2 \) for the median rank. One can thus obtain the strength of correlation between each input and output parameter which comprises both sensitivity to and uncertainty of the input parameter.

\[
RC_{X,Y} = \frac{\sum_{k=1}^{m}(r(x_k) - \bar{r})(r(y_k) - \bar{r})}{(\sum_{k=1}^{m}(r(x_k) - \bar{r})^2 \cdot \sum_{k=1}^{m}(r(y_k) - \bar{r})^2)^{1/2}}
\]

(D.9)

Additionally, rank correlation coefficients can be used to compute the relative contribution of each input parameter to the total variance (CTV) of the resulting output distribution (see Equation D.10).

\[
CTV_{X,Y} = \frac{RC_{X,Y}^2}{\sum_X RC_{X,Y}^2}
\]

(D.10)

Another question to be answered for the interpretation of the results, is how far apart two distributions lie and whether they are distinguishable at all given the uncertainty inherent in sampling a limited number of scenarios. For that purpose, the horizontal separation of the CDFs can be expressed by means of the S-Score (\( S \)) as suggested by Maddalena et al. (2001). The S-Score is calculated as the logtransformed Euclidean distance between the icosatiles, i.e. the persistence values corresponding to every 5th percentile of a CDF, of a distribution defined as baseline distribution, CDF(\( Y \))\(_b\) (\( p_{b,j} \)), and those of a distribution CDF(\( Y \))\(_i\) (\( p_{i,j} \)), which should be compared to the baseline distribution (see Equation D.11).

\[
S_i = \sqrt{\sum_j (\ln \frac{p_{i,j}}{p_{b,j}})^2}
\]

(D.11)

In order to quantify the noise of the baseline itself, i.e. the uncertainty from sampling a limited number of values, the baseline separation, \( \bar{S} \), is defined as the average of a set of \( S_i \) values for a number of \( n \) calculations of the distance \( S_i \) between the results of each of the \( n \) calculations and the average of the \( n \) calculations (baseline).
The stopping rule, indicating where the separation between two CDFs is no longer significant, is then defined as $S_{\text{stop}} = \bar{S} + 1.28 \text{se}(\bar{S})$ for a number of 9 Monte Carlo analyses with 2500 shots, where $\text{se}(\bar{S})$ is the standard error of the set of $S_i$s or $\sigma_S/\sqrt{n-1}$ (for derivation see Maddalena et al. (2001)). The $S$-Score was used for the quantitative analysis of the difference between JP and PP, and for the analysis of the contribution of generations of transformation products to the JP.
Appendix E

Symbols

E.1 Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.i.</td>
<td>active ingredient</td>
</tr>
<tr>
<td>B</td>
<td>Bioaccumulation Potential</td>
</tr>
<tr>
<td>BUA</td>
<td>Advisory Committee on Existing Chemicals of Environmental Relevance</td>
</tr>
<tr>
<td>CA</td>
<td>Concentration addition</td>
</tr>
<tr>
<td>CFC</td>
<td>Chlorofluorocarbons</td>
</tr>
<tr>
<td>CTB</td>
<td>College voor the toelating van bestrijdingsmiddelen</td>
</tr>
<tr>
<td>CTD</td>
<td>Characteristic Travel Distance</td>
</tr>
<tr>
<td>DDT</td>
<td>2,2-bis(chlorophenyl)-1,1,1-trichloroethane</td>
</tr>
<tr>
<td>DIA</td>
<td>Desisopropyl atrazine</td>
</tr>
<tr>
<td>DT50</td>
<td>Half-life time</td>
</tr>
<tr>
<td>DT90</td>
<td>Time until 90% of a compound are degraded</td>
</tr>
<tr>
<td>EF</td>
<td>Extrapolation Factor</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>EPCRA</td>
<td>Emergency Planning and Community Right-to-Know Act</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>HCFC</td>
<td>Hydrochlorofluorocarbons</td>
</tr>
<tr>
<td>HPV</td>
<td>High Production Volume</td>
</tr>
<tr>
<td>LDE</td>
<td>Linear Differential Equations</td>
</tr>
<tr>
<td>MTBE</td>
<td>Methyl tert-butyl ether</td>
</tr>
<tr>
<td>NGO</td>
<td>Non-Governmental Organization</td>
</tr>
<tr>
<td>NPE</td>
<td>Nonylphenol ethoxylates, nonylphenol ethoxy acids, and nonylphenol</td>
</tr>
<tr>
<td>NPEO</td>
<td>Nonylphenol ethoxylates</td>
</tr>
</tbody>
</table>
NPnEO  Nonylphenol polyethoxylates
OECD  Organisation for Economic Cooperation and Development
P  Persistence
PAH  Polycyclic Aromatic Hydrocarbons
PBT  Persistent, bioaccumulative and toxic chemicals
PCE  Perchloroethylene
POP  Persistent Organic Pollutant
QSAR  Quantitative Structure-Activity Relationship
QSPR  Quantitative Structure-Property Relationship
R  Spatial Range
SR  Spatial Range
T  Toxicity
TBA  Tert-butyl alcohol
TCDD  2,3,7,8-Tetrachlorodibenzo-p-dioxin
TGD  Technical Guidance Document
UNEP  United Nations Environment Program
VOC  Volatile Organic Compound

E.2  Symbols

E.2.1  Substance properties

\( BCF \)  Bioconcentration factor  [-]
\( k \)  Degradation rate constant  \([s^{-1}]\)
\( \kappa \)  Degradation rate constant  \([s^{-1}]\)
\( K_{ow} \)  Octanol-water partition coefficient  [-]
\( K_{oc} \)  Organic carbon-water partition coefficient  [-]
\( K_{om} \)  Organic matter-water partition coefficient  [-]
\( K_H \)  Henry’s law constant  \([\text{Pa} \cdot \text{m}^3/\text{mol}]\)
\( L(E)C_l \)  Lethal (Effect) Concentration for l % organisms  \([\mu g/l]\)
\( MW \)  Molecular Weight  \([g/\text{mol}]\)
\( NOEC \)  No Observed Effect Concentration  \([\mu g/l]\)
\( PNEC \)  Predicted No Effect Concentration  \([\mu g/l]\)
\( p_v \)  Vapor pressure  \([\text{Pa}]\)
\( S \)  Solubility  \([\text{mol/l}]\)
\( T_m \)  
Melting point  
[K]

\( T_b \)  
Boiling point  
[K]

\( t_{1/2} \)  
Half-life time  
[d]

\( \theta \)  
Fraction of formation  
[-]

### E.2.2 Model parameters

- **\( h \)**  
  Height of compartment  
  [m]

- **\( u \)**  
  Transfer process between compartments  
  [s\(^{-1}\)]

- **\( v \)**  
  Volume of compartment  
  [m\(^3\)]

- **\( c_0 \)**  
  Concentration at time \( t = 0 \)  
  [mol/m\(^3\)]

- **\( M_0 \)**  
  Overall mass at time \( t = 0 \)  
  [mol]

- **\( q \)**  
  Steady-state flux into model system  
  [mol/m\(^3\)-s]

- **\( Q \)**  
  Overall steady-state flux into model system  
  [mol/s]

- **\( S \)**  
  Matrix of degradation and interphase transfer processes  
  [s\(^{-1}\)]

- **\( K \)**  
  Matrix of formation processes  
  [s\(^{-1}\)]

### E.2.3 Model outputs

- **\( c(t) \)**  
  Concentration at time \( t \)  
  [mol/m\(^3\)]

- **\( c^{\text{stst}} \)**  
  Steady-state concentration  
  [mol/m\(^3\)]

- **\( e \)**  
  Exposure  
  [mol· s/m\(^3\)]

- **\( m(t) \)**  
  Mass at time \( t \)  
  [mol]

- **\( M(t) \)**  
  Overall mass in model system at time \( t \)  
  [mol]

- **\( M^{\text{stst}} \)**  
  Overall steady-state mass in model system  
  [mol]

- **\( \mu \)**  
  Mean time  
  [d]

- **\( \tau \)**  
  Persistence  
  [d]

- **\( \tau^{\text{stat}} \)**  
  Residence time  
  [d]

- **\( \tau^{\text{equiv}} \)**  
  Equivalence width  
  [d]

- **\( \tau^{\text{equiv,off}} \)**  
  Clearance time  
  [d]

- **\( \tau^{1/e} \)**  
  Time for decrease of initial mass to 37%  
  [d]

- **PEC**  
  Predicted Environmental Concentration  
  [\( \mu g/l \)]

- **PP**  
  Primary Persistence  
  [d]

- **SP**  
  Secondary Persistence  
  [d]
E.2.4 Statistical measures

\( \mu \)  \hspace{1cm} \text{Arithmetic mean}
\( \sigma \)  \hspace{1cm} \text{Arithmetic standard deviation}
\( CV \)  \hspace{1cm} \text{Coefficient of variation}
\( GM \)  \hspace{1cm} \text{Geometric mean}
\( GSD \)  \hspace{1cm} \text{Geometric standard deviation}
\( \mu_{ln} \)  \hspace{1cm} \text{Logarithmic mean}
\( \sigma_{ln} \)  \hspace{1cm} \text{Logarithmic standard deviation}
\( RC \)  \hspace{1cm} \text{Rank correlation coefficient}
\( CTV \)  \hspace{1cm} \text{Contribution to variance}
\( CDF \)  \hspace{1cm} \text{Cumulative distribution function}
\( PDF \)  \hspace{1cm} \text{Probability density function}
CURRICULUM VITAE

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