Ecotoxicological Risk Profiles of Chemicals

Concept and Application to Antifouling Biocides

DISSERTATION

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...

Wenn wir jedoch das Wesen der Technik bedenken, dann erfahren wir das Ge-stell als ein Geschick der Entbergung. So halten wir uns schon im Freien des Geschickes auf, das uns keineswegs in einen dumpfen Zwang einspert, die Technik blindlings zu betreiben oder, was das Selbe bleibt, uns hilflos gegen sie aufzulehnen und als Teufelswerk zu verdammen. Im Gegenteil: wenn wir uns dem Wesen *der Technik eigens öffnen, finden wir uns unverhofft in einen befreienden Anspruch genommen.*

...

Waltet jedoch das Geschick in der Weise des Ge-stells, dann ist es die höchste Gefahr. Sie bezeugt sich uns nach zwei Hinsichten. Sobald das Unverborgene nicht einmal mehr als Gegenstand, sondern ausschließlich als Bestand den Menschen angeht und der Mensch innerhalb des Gegenstandlosen nur noch der Besteller des Bestandes ist, – geht der Mensch am äußersten Rand des Absturzes, dorthin nämlich, wo er selber nur noch als Bestand genommen werden soll.

...

Martin Heidegger "Die Technik und die Kehre"

Solange wir daran festhalten, daß, was Natur ist, ausschließlich durch die neuzeitliche Naturwissenschaft bestimmt wird, solange haben wir es mit einer Natur zu tun, die für uns nicht ethisch relevant ist; Natur, sei es nun die äußere Natur oder die Natur, die wir selbst sind, bleibt uns äußerlich, ein Objekt, eine Maschine, ein System, ein Körperding. Es bedarf deshalb der Entwicklung eines ethisch-relevanten Naturwissens. *Ein solches Wissen muß aber aus einer Haltung heraus entwickelt werden, die bereits implizit eine ethische ist. Eine solche Haltung ist mit Hans Jonas als Verantwortung, mit Herder als Anerkenntnis der Natur, mit Goethe als Bildung und mit Rehmann als Mitvollzug mit der Natur zu bezeichnen.*

Gernot Böhme "bios | ethos"

Preface to the final version

Since the defense of the dissertation on September 25, 2001, almost four months have gone by. Nevertheless, this publication is largely identical to the dissertation reviewed by the commission. I did not go back into the literature, but I did go through the indicator definition part (page 29ff) to get the definitions more precise and I cleaned up the layout. The article about the antifouling biocide fate model [1] (cp. mainly Chapter 5 and Section 6.2) finally was accepted by Environmental Science and Technology, which made me very happy. I do plan to set up an internet site about the risk analysis of the antifouling biocides, to be constantly updated and discussed by the UFT risk research team. I will put a link on my homepage[1] when the time has come.

Acknowledgements

I am very thankful that I could not only experience three years of true academic freedom during my PhD studies, but was – beyond that – strongly supported in the development of a fresh theoretical perspective on the comparative risk analysis of chemicals. For this, I am very much indebted to the University of Bremen and her joint faculty of biology and chemistry (!), but especially to Prof. Dr. B. Jastorff, whose support and enthusiasm for this transdisciplinary work were inspiring and who enhanced the sometimes dry research work by encouraging the attending of conferences and generally taking the "human factor" into account.

From the UFT staff, I would like to especially thank Tobias Frische and Frauke Stock, who were always there for discussions, even when concepts and thoughts were still only rudimentary. I don't know what I would have done without them. Within the department of bioorganic chemistry, I thank the group working on intracellular messengers for their support in various chemistry matters, and all the colleagues for the nice atmosphere at work. The virtuosity of Ruth Krummrey-Rosch, Antje Mathews and Ulrike Bottin-Weber in carrying out administrative tasks with constant kindness is gratefully acknowledged. I also thank Christoph Grimmer for his efforts in obtaining literature that was difficult to access and his help in setting up the database. Donald Molnar introduced me to Debian GNU/Linux, which opened up many perspectives, and Howard Arnold was not only supporting the operating systems of CPUs, but also the men-

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[1] `http://www.uft.uni-bremen.de/chemie/ranke`

tal health of the scientist entangled with the (im)possibilities of modern data processing.

I thank Oliver Lönker for the countless mensa excursions with manifold topics, Jens Dannenberg, Horst Hahn and Hendrik Laue for their support by, apart from being great fellows, conveying some of the style of work of physics, and Arend Mitwollen for the pleasure of discussing philosophical matters once in a while. Singing a-capella with the Terzattacke ensemble and the choir pro musica Bremen has been and is a most delightful way to regenerate body and soul.

Outside of Bremen, I am thankful to Simon Spycher, who kept up the ETH environmental chemistry connection, and to Dr. Dr. Thomas Schulte-Heerbrüggen for repeated merits in remote and in-situ coaching. PD Dr. Gertrude Hirsch shared her knowledge of philosophical ethics in general and of H. Jonas in particular. Dr. Stefan Böschen triggered the process of reflecting the uncertainties in risk science and discovering its relationship to the transdisciplinary character of risk research in a more systematic manner. The discussions with Prof. Dr. H.-J. Knackmuss, Dr. H.-P. Rieger and Dr. T. Hirth during the initialization phase of a project about the sustainable development of chemicals which is yet to be realized were very helpful. The continuing connection to the group of Prof. Dr. K. Hungerbühler, especially to Dr. Martin Scheringer is always a source of motivation, knowledge, as well as an incentive to strive for quality. Also, Prof. Dr. Müller-Herold was always there to share his vast knowledge and to give helpful advice. Thanks go to all of them, and especially to Prof. Hungerbühler for his willingness to be co-examiner.

I want to use the opportunity to also express my gratitude towards my parents, who made all this possible in the first place. They were deprived of a lot of due attention during this phase of my life. After all, and with special emphasis, I would like to thank my wife, Dr. Frauke Clotz, for her positive attitude, her patience and her invaluable support.

Summary

The scientific risk analysis of environmental chemicals was stimulated a lot by the requirements of the European regulatory activities during the last twenty years. Also, total bans of certain substances that are recognized to cause exceptional hazards are increasingly being discussed on the global level. In both cases, the risks of using such substances are not assessed explicitly comparing alternative substances, but in an absolute manner.

In the first part of this dissertation, a novel concept for the *comparative* risk evaluation of environmental effects of chemicals is presented. Starting with an overview of strenghts and weaknesses of published methods, the use of five indicators – *release, spatiotemporal range, bioaccumulation, biological activity* and *uncertainty* – is proposed. For every indicator, possibilities for its quantification are shown and discussed. The concept serves as a simple and flexible alternative to the methods of risk analysis that are used in the aforementioned evaluation contexts. The five indicators taken together constitute an ecotoxicological risk profile for each of the evaluated substances, which enables manufacturers, users and other interested groups to compare different substances regarding the risk of damaging the environment by their use.

The second part of the dissertation shows the application of the concept to a comparative evaluation of the ecotoxicological risks of using the five different antifouling biocides tributyltin, Irgarol® 1051, Sea-Nine® 211 and pyrithione in commercial shipping. Since the high biological activity is a desired property of the substances, and therefore leaves little room for optimization from the environmental viewpoint, the other four indicators gain special importance in this case.

The comparative evaluation of the relese indicator only resulted in small differences between the substances. The fact that copper is an ingredient of almost all modern biocidal coatings, was taken into account in the evaluation. A comparison of the estimated copper input from antifouling coatings of the commercial world fleet with todays total copper inputs into the oceans yielded a fraction of 5 % for the contribution of antifouling coatings.

For the evaluation of the spatiotemporal range of the substances, a newly developed Level III fate model is presented. The influence of the variability of biocide-specific input parameters on model results, which was investigated by Monte Carlo simulations, is discussed, and the model results are compared with concentrations of tributyltin and copper that have been measured in the environment.

The residence times that were estimated by means of the model are about five days for Sea-Nine, about 17 days for tributyltin, about 10 years for Irgarol and about 40 000 years for copper. The uncertainty of the evaluation of the spatiotomporal ranges based on these calculations is greatest for Sea-Nine, and least for copper. The comparison of the ecotoxicological risk profiles results in the impression that Sea-Nine and pyrithione bear smaller risks of damage to the marine biosphere than tributyltin, while Irgarol seems to be a more risky candidate for the substitution of TBT because of its longevity and its very high phytotoxicitiy.

An additional dynamic simualation (Level IV) of copper concentrations with the fate model suggested, that steady state with the copper input rates estimated for today is only to be expected for the deep sea sediments on a timescale of over ten thousands of years. Thus it seems likely that todays copper input levels into the marine biosphere will leed to a significant rise in copper concentrations in pelagic water and pelagic sediments of the oceans, with unforeseeable consequences for the pertaining flora and fauna.

The concept of ecotoxicological risk profiles is presented as a method suitable for prospective decision support. An integration of the concept into a strategy for a sustainable development of chemicals is outlined.

Zusammenfassung

Die wissenschaftliche Risikoanalyse von Umweltchemikalien hat durch die Erfordernisse des europäischen Chemikalienrechts in den letzten zwei Jahrzehnten erhebliche Impulse erhalten. Auf globaler Ebene werden ausserdem in zunehmendem Mass Totalverbote für bestimmte als besonders gefährlich erkannte Substanzen verhandelt. In beiden Fällen werden die Risiken nicht in Form eines direkten Vergleichs alternativer Stoffe, sondern weitgehend unabhängig von Alternativen bewertet.

Im ersten Teil der vorliegenden Dissertation wird ein neues Konzept zur *vergleichenden* Risikoanalyse von Chemikalien hinsichtlich ihrer Umweltauswirkungen vorgestellt. Ausgehend von einem Überblick über Stärken und Schwächen publizierter Methoden wird die Verwendung von fünf Risikoindikatoren – *Freisetzung, räumlich-zeitliche Reichweite, Bioakkumulation, biologische Aktivität* und *Unsicherheit* – begründet. Für jeden der Indikatoren werden Möglichkeiten der Beurteilung angegeben und diskutiert. Dieses Konzept bietet eine einfach und flexibel zu handhabende Alternative zu den üblicherweise verwendeten Methoden der Risikoanalyse. Zusammen ergeben die fünf Indikatoren ein ökotoxikologisches Risikoprofil für jeden der beurteilten Stoffe, das Produzenten, Anwendern und anderen Interessierten die Möglichkeit eines Vergleichs verschiedener Substanzen hinsichtlich des Risikos einer Umweltschädigung durch ihren Einsatz bietet.

Den zweiten Teil der Arbeit bildet die Umsetzung des Konzepts in Form einer vergleichenden Beurteilung der Risiken einer Umweltschädigung durch die Anwendung der fünf Antifouling-Biozide Kupfer, Tributylzinn, Irgarol® 1051, Sea-Nine® 211 und Pyrithion in der kommerziellen Seeschifffahrt. Da die hohe biologische Aktivität der Substanzen eine im Sinne der Anwendung gewünschte Eigenschaft ist und deshalb kaum im Sinne einer Risikominderung optimiert werden kann, haben die übrigen Indikatoren in diesem Fall eine besondere Bedeutung.

Die vergleichende Bewertung des Risikoindikators Freisetzung ergab nur geringe Unterschiede zwischen den beurteilten Substanzen. Die Tatsache, dass Kupfer in fast allen modernen biozidhaltigen Antifoulinganstrichen enthalten ist, wurde bei der Bewertung berücksichtigt. Ein Vergleich des abgeschätzten Eintrags von Kupfer aus Antifoulingfarben der Welthandelsflotte mit aktuellen Gesamteinträgen in die Ozeane ergab einen Anteil von ca. 5 % für die Antifoulinganwendung.

Für die Beurteilung der räumlich-zeitlichen Reichweite der oben genannten Substanzen wird ein neu entwickeltes Level III-Ausbreitungsmodell vorgestellt. Der Einfluss der Variabilität der biozidspezifischen Ein-

gangsparameter auf die Ergebnisse wird anhand von Monte-Carlo Simulationen diskutiert. Anhand von in der Umwelt gemessenen Konzentrationen von Tributylzinn und Kupfer wird das Modell evaluiert.

Die mit Hilfe des Modells abgeschätzten Aufenthaltszeiten der Biozide in der marinen Biosphäre reichen von ca. 5 Tagen für Sea-Nine über ca. 17 Tage für Tributylzinn und ca. 10 Jahre für Irgarol 1051 bis ca. 40 000 Jahre für Kupfer. Die Unsicherheit der daraus resultierenden Beurteilung der räumlich-zeitlichen Reichweite ist bei Sea-Nine am höchsten und bei Kupfer am geringsten. Der Vergleich der ökotoxikologischen Risikoprofile für die fünf Stoffe ergibt die Einschätzung, dass Sea-Nine und Pyrithion geringere Risiken für die marine Biosphäre bergen als TBT, während Irgarol aufgrund seiner Langlebigkeit und seiner sehr hohen Phytotoxiziät, die aus den verfügbaren Daten abgeleitet wurden, ein bedenklicherer Stoff für den Ersatz von TBT zu sein scheint.

Eine zusätzlich durchgeführte dynamische Simulation (Level IV) mit dem Ausbreitungsmodell für Kupfer ergab, dass eine Einstellung der Gleichgewichtskonzentrationen, die sich aus den heutigen Einträgen ableiten, für die Tiefseesedimente erst in weit über 10 000 Jahren zu erwarten ist. Damit erscheint es wahrscheinlich, dass die heutigen Kupfereinträge in die marine Biosphäre langfristig zu einem erheblichen Anstieg der Kupferkonzentrationen im Tiefenwasser und in den Tiefseesedimenten der Weltmeere führen, dessen Konsequenzen für die dortige Flora und Fauna nicht abzusehen sind.

Das Konzept der ökotoxikologischen Risikoanalyse wird als geeignete Methode für die prospektive Unterstützung von Entscheidungen präsentiert. Abschliessend wird eine mögliche Einbindung des Konzeptes in eine Strategie zur nachhaltigen Entwicklung von Chemikalien dargelegt.

Symbols and Acronyms

Indicator Symbols

R Release

S Spatiotemporal range

B Bioaccumulation

A Bioactivity

U Uncertainty

Acronyms[2]

BCF Bioconcentration Factor

BUA Beratergremium für Umweltrelevante Altstoffe

CAS Chemical Abstracts Service

CBB Critical Body Burden

CEPE European Paint Makers Association

ECDIN Environmental Chemicals Data and Information Network

EINECS European Inventory of Existing Chemical Substances

ELINCS European List of Notified Chemical Substances

ERM Entity Relationship Model → G

EU European Union

EURAM European Risk Ranking Method

EUSES European Uniform System for the Evaluation of Substances

GSH Glutathione

IPCS International Programme on Chemical Safety

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[2] Acronyms with the symbol → G are explained in the Glossary of Terms, page 131

KEMI Kemikalieninspektionen (Swedish National Chemicals Inspectorate)

LOEC Lowest Observed Effect Concentration

LRT Long Range Transport

NOEC No Observed Effect Concentration → G

PBT Persistent, Bioaccumulating and Toxic

PEC Predicted Environmental Concentration

POPs Persistent Organic Pollutants

PNEC Predicted No Effect Concentration

PPR Property-Property Relationships

QSAR Quantitative Structure-Activity Relationships

SAR Structure-Activity Relationships

SCRAM Scoring and ranking system for persistent, bioaccumulative and toxic substances for the North American Great Lakes

SETAC Society of Environmental Toxicology and Chemistry

SPC Self-Polishing Copolymers

SPR Structure-Property Relationships

SQL Structured Query Language

TBT Tributyltin compounds

TGD Technical Guidance Document

UK United Kingdom of Great Britain and Northern Ireland

US EPA United States Environmental Protection Agency

USES Uniform System for the Evaluation of Substances

Contents

Chapter 1

Introduction

1.1 Risk – hazard – danger

There have been many attempts to give general definitions of the term "risk" and other terms describing potential damage. Each of these definitions has its advantages and its blind spots. For the discussion of a risk assessment of chemicals it is important to be aware of the common distinction between the *hazard* that a substance represents by its mere identity or its inherent properties and the *risk* which is a result of a combination of exposure and effect characterization.

However, this distinction fails to directly address an important finding of the psychology of risk: The perceived risk of a dangerous activity depends, among other factors, on the degree of control the evaluator has on it [2]. This is one of the phenomena discrediting any attempt to define something like an "objective risk", which would simply mean that we abstract from the differences in judgements of individual subjects and ignore their different relationships to the dangerous activity.

As a consequence, in the present work the *influence of the observer* is a precondition for the applicability of the term "risk". The following definition, which will be used throughout the work, illustrates this:

> *Risk is an expression for the relevance of possible future damages that can be attributed to a decision.*

This means that every risk is related to a decision and it is this decision influencing the possibility of damages that makes the difference. If the possible damages would be independent of decisions, a risk management following the risk assessment would be senseless. Something that is beyond control and is not influenced by a conscious decision of the actor would be a danger, not a risk[1].

From this viewpoint it also makes a difference *who* is judging the risk. Ideally, the risk assessor should be identical with the decision-maker and at least they have to communicate in order to approximate this identity.

This definition of risk is also coherent with the initially mentioned distinction of hazard and risk for substances: The hazard of a chemical, resulting from its properties, is only related to its identity, but not to any decision on its use, its handling or its disposal. The substance can be more or less "hazardous". On the other hand, only the way of using the substance can entail a risk and only such handling can be influenced by decisions.

1.2 Decisions on the release of chemicals

From the viewpoint of ecotoxicology, the possible damages to organisms in the environment start with the release of the substance in question. Once this release has taken place, there is generally no control on the distribution and the effects of the substance any more[2]. Consequently, the release of the chemical is the most crucial point of a risk analysis. The quality of the ecotoxicological risk analysis can never be better than the quality of the release information.

The type of risk analysis depends on the type of decision that should be informed. For an ecotoxicological risk analysis of chemical substances, the relevant decisions are decisions with an impact on the release of chemicals. In this dissertation, I would like to refer to three different types of decisions affecting the release of chemicals from the technosphere to the environment (Table 1.1).

The main difference between the first decision type and the two others is that in the first case there is an absolute judgement if a certain use of a chemical is acceptable or not. In the two other cases, the risk of a damage to the environment — if taken into account at all — is judged in a relative way, comparing the different alternative chemical substances or products serving the intended purpose.

The information base for an absolute judgement of the first type must

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[1] This distinction between risk and danger according to the presence/absence of control on it was repeatedly and prominently advocated by the sociologist N. Luhmann [3, 4], but is also used by contemporary risk sociologists [5]

[2] If significantly contaminated parts of the environments are being decontaminated, these parts actually become part of the technosphere and do no longer belong to the environment.

Table 1.1: Scheme of decisions influencing the release of chemical substances to the environment

Decision	**Choices**	**Actor**
Limitation of production/use	Yes/No	Government
Choice during production of goods	Different Chemicals	Industry
Demand of products	Different products	Consumer

be very reliable. The magnitude of the costs of codifying and enforcing a governmental limitation of the production and/or the use of a substance illustrates this quite clearly. Unfortunately, experience has shown that it is quite difficult to gain a reliable or widely accepted information base for risk assessments. Another significant problem for the protection efficiency of this approach is that the alternatives that will be used might bear risks that have not even been looked at.

In the second and the third case, the question of substitutes for an objectionable substance is addressed from the very beginning and very directly. This could be very helpful in efficiently reducing ecotoxicological impacts of our society. However, tools for the comparative analysis of the ecotoxicological risks of using different chemicals are rare.

1.3 The role of science

We have stated that risk and decision are inseparable. In analogy, the risk assessor and the decision-maker have to be identical or they have to communicate effectively. The risk that our society is taking by releasing toxic chemicals to the environment affects all of us and therefore traditionally falls into the domain of politics. This would mean that the decisions regarding these releases should be made by political mechanisms.

Even if the necessity of this approach is not disputed, there are some reasons to assume that it is not the only way of societal risk management of ecotoxic chemicals.

- The mere number of chemical substances used in industrial countries is a severe obstacle for a centralistic evaluation of each of them by politics.[3]

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[3] Even if a single-substance assessment considering all relevant releases would be carried out for each relevant chemical, combinatorial effects would not be covered.

- On the other hand, there is a growing awareness of both consumers and industry of their influence on the environmental impacts of our industrial lifestyle.

If the awareness of our risk of producing ecosystem damage is to be put to work for an improvement of our handling of ecotoxic chemicals, actors and decision-makers must have means to determine, which one out of several alternative substances will likely produce the least environmental impact.

Science is especially suited for the generation of this kind of information since:

- There is a vast amount of freely accessible information in the scientific literature that can be used in comparative risk assessments.
- The scientific paradigm of a steady improvement of collective knowledge – as opposed to normative fixation of rules – allows for immediate incorporation of newly available information if necessary.
- Science disposes of an excellent international discourse structure, with congresses, scientific journals and the scientific internet as its most important elements.
- In science, the ideal of independence from particular commercial interests is still present.

Of course, scientists will not be able to carry out comparative risk assessments for society, if they don't get support from administrative bodies responsible for the regulatory risk assessments that might be carried out in parallel. Maybe even more important is the cooperation of industry, because the knowledge which alternative substances come into question from a technical point of view is almost exclusively present in industry. Also, the important first step, the release estimation, largely depends on on the cooperation of industry.

Science can be an independent consultant for the evaluation of chemical risks from an ecotoxicological point of view, but the decision-making does not belong to the tasks of scientists. An effective risk communication, including all necessary aspects of the evaluation in an easily accessible manner, is necessary in order to convey the findings of risk research to everybody deciding on the release of chemicals.

1.4 Structure of the dissertation

Based on these considerations, a theoretical framework for the comparative evaluation of chemical substances from the viewpoint of ecotoxicological risk research was set up, which consists of five indicators, each aggregating information from a defined area.

In Part I, Chapter 2, the concept and application of indicators in other disciplines is shown. Especially in attempts to generate a sustainable development of our society, indicators are being used to gain the possibility of success control. Also, many quantifications of risk can be regarded as indicators and will be discussed as such. A discussion of the state of science in the narrower field of comparative evaluation of chemicals forms the main part of the chapter. Special emphasis is placed on methods which are based on exposure modelling.

Then, in chapter 3, the method of generating ecotoxicological risk profiles is presented in general[4]. This entails the discussion of criteria for the selection of substances that should be compared, the theoretical description of the indicators and the underlying reasoning as well as suggestions for the scoring procedure. Different possibilities are compared to present the results graphically.

Part II is a detailed comparative risk analysis of five antifouling biocides. After a short introduction, a fate model which was constructed for a better evaluation of the spatiotemporal range is presented in chapter 5. The chapter deals with the quantification of residence times for the different biocides in the marine biosphere as an operationalization of the indicator spatiotemporal range. It was separated from the rest of the case study in the following chapter because it deals with the fate evaluation in a very detailed way and can be regarded as a preparatory work for their complete comparative risk analysis. The fate modelling study carried out for this purpose has previously been described in [1]. The description was adapted for the context and scope of the dissertation.

The generation of ecotoxicological risk profiles for five commonly used antifouling agents in chapter 6 is a completely revised and updated version of the study already published [8] which originated from a preliminary study about the present status of antifouling techniques [6]. Newly available data were incorporated for all categories and especially the results of fate modelling reported in the previous chapter were taken into

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[4] The basic idea for the method was developed during a study on account of the Senator for Women, Health, Youth, Social Affairs and Environmental Protection of the Freie Hansestadt Bremen [6]. Some advantages of the method from the viewpoint of theoretical ecology were added in a subsequent publication [7]

account.

Part III presents the final chapter dealing with the general applicability of the presented ecotoxicological risk profiles for the broader context of a sustainable development of chemicals. A combination with Life-Cycle Analysis for coverage of the ecological aspect of sustainable development is proposed and the integration of a screening level sustainability assessment into product development is advocated.

Appendix A is a description of structure and contents of the database UFT_SAR where all risk relevant data that were collected from scientific literature, administrative reports and from several databases was stored. Meanwhile, it does not only contain referenced literature data about the antifouling agents tracted in this dissertation, but also about vulcanization agents. The database is publicly accessible via internet[5].

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[5] `http://eckehaat.uft.uni-bremen.de/UFT_SAR`

Part I

Theory

Chapter 2

Indicators

In addition to well-established indicators on a national level like the Gross National Product for the economic growth of a country or the infant mortality as a wealth indicator, there is a growing use of indicators for management purposes in many areas.

In recent developments of environmental sciences, different methods for the Life-Cycle Analysis of products (e.g. [9]) provide the possibility to score their environmental impacts. These scores can also be regarded as indicators, although the systems which are evaluated are entirely different from the examples given above.

Before the discussion of the use of indicators in the special cases of sustainability assessments or risk assessments, a definition for the term "indicator" is given as it is used in the present dissertation:

> *An indicator is the representation of aggregated information about a defined entity from a defined viewpoint.*

This definition leaves open to what degree the method of aggregation is defined. However, it strictly requires that the entity to be evaluated is specified and that the type of information entering the aggregation process is documented.

2.1 Sustainability indicators

One application of indicators which has become prominent in the years after the United Nations Conference on Environment and Development (UNCED) held in Rio de Janerio, Brazil in 1992, is the evaluation of the sustainability of the development of our global human society [10]. In the Agenda 21 [11], adopted by more than 178 Governments, the scientific and technological community is intended to be enabled ″to make a more open and effective contribution to the decision-making processes concerning environment and development.″(chapter 31 of the agenda). In the final chapter of the Agenda, the role of information for decision-making is accentuated as well as the need to improve access and capability to use and interpret such information, especially for the developing countries. It is also in this chapter where the role of indicators is pointed out:

> Indicators of sustainable development need to be developed to provide solid bases for decision-making at all levels and to contribute to the self regulating sustainability of integrated environment and development systems [11].

Different institutions and organizations have provided lists of such sustainability indicators [12]. The discussion of their utility is still going on, on the level of townships or municipalities up to the level of countries or even the whole world. The interesting point for the risk analysis of chemicals is the general discussion of different types of indicators. This discussion also applies to indicators for the risk of releasing chemicals to the environment.

The functions of indicators in general have been defined as follows [13]:

- Analysis
- Communication
- Warning and Mobilization
- Coordination

This list illustrates that indicators do not only have to fulfill one function at a time. Rather, their generation has to be a compromise with respect to very different demands.

This point is further strengthened by Figure 2.1, which shows that a good indicator should on the one hand be robust, meaning that it is sound from a technical and scientific perspective, and that it is derived in a transparent and reproducible manner. On the other hand, for the purpose of effective communication, an indicator should be resonant, meaning that it is understood and accepted by the people who are to be informed for improved decision-making. Only if both targets are kept in mind, a meaningful and effective indicator will result.

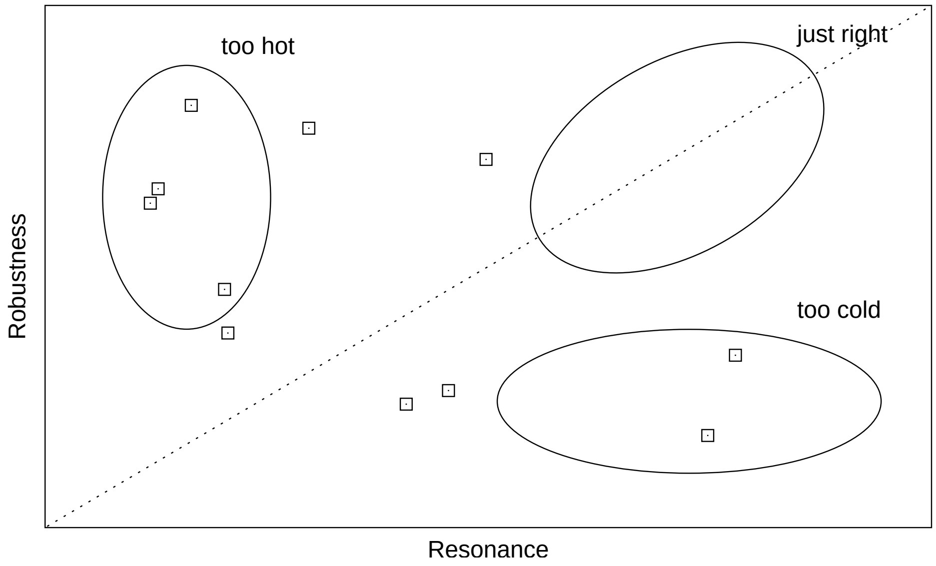

Figure 2.1: Two dimensions of indicator optimization. Adapted from [14]

2.2 Risk quantifications

If the potential damages that a risk quantification should describe can be expressed in a single dimension, then the formula for risk used in insurance mathematics can be applied:

$$r = \sum_i f_i D_i \tag{2.1}$$

In this equation, D_i are the different damage types that are taken into consideration. The symbol f_i stands for their probabilities, if nonrecurring incidents are analyzed, or their estimated frequencies of occurrence in the future for recurring incidents. The risk indicator r is an expression for the most likely average damage to be expected per time interval. The combination of damages measured on different scales, like fatal accidents and financial damage is of course problematic, because then a conversion factor has to be defined.

The risk of damaging the environment by using certain chemical substances is usually quantified in a different way. In analogy to the comparison of measured concentrations of chemicals with limiting values, Predicted Environmental Concentration (PEC) values are compared to Predicted No Effect Concentration (PNEC) values[1]. The quotient of these is

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[1] An excellent comprehensive introduction to this type of risk assessment of chemicals

called risk ratio. The risk ratio is a central concept in the regulation of chemicals dangerous to the environment in the European Union [16]. Every substance newly notified for a production of more than 100 metric tons per year undergoes a PEC/PNEC-risk analysis. Additionally, newly notified substances with a lower production volume that are classified hazardous to the environment and a priority selection of the so-called "existing substances" that have been on the market before 1981 have to be checked by the PEC/PNEC scheme [17].

The purpose of the comparison of PEC with PNEC in this context is to decide if the member states of the European Union have to take action and either request more risk-relevant information or enforce regulations of the production or use of the substance. Thus, it serves for informing decisions of the first type in Table 1.1. There are a couple of reasons, why the PEC/PNEC scheme is not ideal for informing decisions of the two other types – which are mainly addressed in the present study – namely choices made by industry, deciding which chemical substance to use in a certain product and choices by consumers, deciding which product to buy.

The biggest problem for the application of the PEC/PNEC scheme to decisions of the latter types is that it is very demanding in theory and practice. This is only natural, because it will have considerable consequences, if an international federation like the European Union makes a statement on the question if there is a risk or not.

One important reason why the PEC/PNEC-analysis can generally be regarded as pretentious, is that it is based on the assumption that it is possible for a substance to have "no effect"(Predicted No- Effect Concentration). As a consequence, if the Predicted Environmental Concentration is below the PNEC, this is interpreted as the complete absence of a risk. From a scientific point of view, it seems impossible to conclude that there is no risk of releasing a substance to the environment, the risks can only have different magnitudes.

Another point of criticism is that uncertainties that have occurred during the assessment process are not reflected in the final result. They are taken into account by different methods, e.g. the uncertainty factors [18], but in the end, the condensed risk communication only consists of the risk ratio, although the uncertainties of the evaluation can be very different, depending on the quality of the information e.g. for the release estimations, but also depending on the nature and chemistry of the substance.

A further point of critique regarding the method described in the TGD is that a wrong incentive for suppliers of effects data is given by the Eu-

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is the textbook by K. Van Leeuwen [15]

ropean System: If several biological species have been tested for a certain endpoint (EC$_{50}$or NOEC), the lowest value is selected as the basis for calculations. This discourages data suppliers from generating (or submitting) additional data instead of rewarding it in favor of an improvement of the quality of the risk assessment.

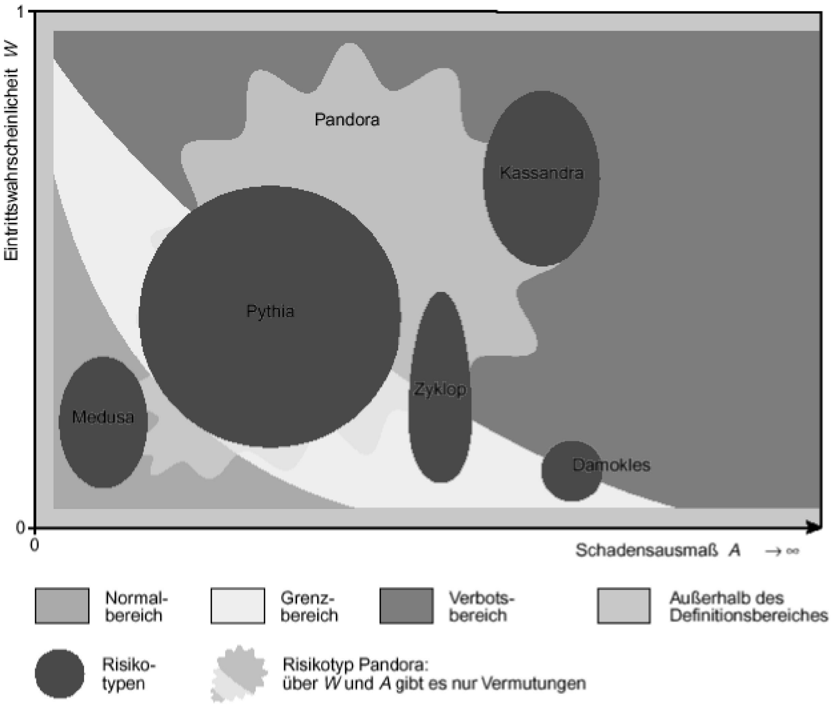

Figure 2.2: A graphical classification of risks according to probability of occurrence (Eintrittswahrscheinlichkeit W) and severity of damage (Schadensausmass A) [19], with kind permission of Springer-Verlag, (C) 2000. "Normalbereich" is the area where there is no special risk, "Grenzbereich" is the borderline area of risk, "Verbotsbereich" is the area of unacceptable risks, "Ausserhalb des Definitionsbereichs" means that risks in this area are not defined, "Risikotypen" are types of risk. "Risikotyp Pandora" means that there are only speculations about W and A.

The PEC/PNEC scheme according to the Technical Guidance Document (TGD) has been successfully in use in the EU for more than five years now. The points of criticism show, that even if the concept is good for the use by governmental institutions, it is not necessarily the best solution to a comparative risk quantification for chemical substances, carried out by non-governmental parties. These considerations have been important for the development of the ecotoxicological risk profiles that will be described in the next chapter.

The importance of a reflection of the uncertainties of the risk assessment mentioned above is also illustrated by Figure 2.2. It shows a classification of risks not only by the estimated probability of occurrence of damage W and its severity A, but also by their respective uncertainty [19]. According to the authors of this classification, the risk due to the use of Persistent Organic Pollutants (POPs) is characterized by the high uncertainty both of the probability and the severity of damage. In the PEC/PNEC-terminology, this means that both exposure and effects can only be estimated very roughly for these chemicals. This characterization means that the risk of using these substances is of the Pandora type, which was named after the ancient greek myth of Pandoras can.

2.3 Evaluation of substances

In the course of the collection of substances that were deemed on the European Market before 1981 in the European Inventory of Existing Chemical Substances (EINECS) it became clear that it was impossible to carry out a full risk assessment for all the 100 195 so-called existing substances in a reasonable timespan, especially considering the requirements of the later published TGD [16].

Since that time, a considerable number of methods for the screening of these substances with respect to hazards and/or risks to human health and the environment have been described, with some of them specifically aiming at selecting priority substances for carrying out a full risk assessment.

The following overview over a selection of these methods should give an impression of the different possibilities to construct such substance evaluation methods. Since this dissertation is mainly concerned with environmental risks, especially methods that address environmental effects were selected. They are presented in a systematic manner, so not all unique characteristics of the methods will be mentioned. Instead of a linear description of each of the methods, it is shown how they deal with the different tasks and problems that all evaluation methods have to handle.

The original publications tracted in this subchapter are the early German essay "Zur Bewertung von Umweltchemikalien" by F. Schmidt-Bleek and W. Haberland from 1979, describing a yardstick for chemical substances that uses substances with known hazard potential as reference substances [20], a second proposal by the same plus two other authors, describing the environmental hazard assessment of new chemicals as classification into three classes [21], an "Ecotoxicological Profile Analysis" by D. Freitag et al., describing mainly a set of laboratory methods for generation of relevant data for a comparative evaluation [22], a more conceptional paper by R. Frische et al. about the criteria for assessing the environmental behavior of chemicals [23], a unique paper by E. Halfon and M. Reggiani introducing the use of Hasse diagrams to the evaluation of substances [24], a system which was proposed both for environmental prioritiy setting (EPS) of existing chemicals [25] and for environmental hazard ranking (EHR) of new chemicals [26], the actual European Risk Ranking Method (EURAM), as it was used for selecting the chemicals for the second and third priority list of existing substances [27], and the recently published SCRAM "scoring and ranking system for persistent, bioaccumulative, and toxic substances for the North American Great Lakes"with a unique way to incorporate data availability into the evaluation [28, 29, 30, 31].[2]

Finally, the definitions of the *evaluative fate indicators* persistence [33, 34, 35, 36, 37], spatial range [37, 38], characteristic travel distance [39] and long-range transport potential [40] are included into the discussion.

Purposes and application contexts

The majority of the methods was devised with the purpose of rationally dealing with the unknown hazards and risks of the huge number of chemical substances that are being produced. The aim is either

- to give every one of the substances one or more index values,
- to order them with respect to risk or hazard (ranking), or
- to group them into different risk/hazard classes.

Some of the methods have a specific application context. For example, the purpose of the yardstick-method [20] was to carry out a relative assessment for new chemicals, using known properties of chemicals that are undisputedly hazardous to the environment as a reference. In this,

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[2] Many aspects of these methods have been and are discussed in parallel by other authors regarding pesticides. Some *pesticide indicators* treated in the European CAPER project with the title "Comparing environmental risk indicators for pesticides" [32] are already in practical use by farmers and their advisors, as a complement to Council Directive 91/414, which regulates the marketing of pesticides in the European Union.

as in the most cases, the consequences to be drawn from the evaluation results are not clearly addressed. Most of the methods primarily serve informational purposes, which means that the action which should follow the evaluation is not specified.

This openness for different application contexts is only consequent for the ecotoxicological profiles by Freitag et al. [22] and the graphical rankings by Halfon and Reggiani [24]. Their aim is to give a general impression of possible detrimental effects of the substances and their studies are *driven more by scientific interest* than by an interest to produce normative, binding evaluations. This is also true for some of the studies about evaluative fate indicators mentioned above. In the methods by Schmidt-Bleek [20, 21], Frische et al. [23] and the SCRAM system, on the other hand, the use by governmental authorities is specifically addressed, even if it is not always specified.

Some papers about evaluative indicators of only the global fate of chemicals mention a specific purpose. As they can generally be regarded as contributions to the discussions about *restricting or banning Persistent Organic Pollutants (POPs)* or Persistent, Bioaccumulating and Toxic (PBT) chemicals, carried out in international bodies like the United Nations Environmental Programme (UNEP) or the Oslo-Paris convention (OSPAR), the recent study about the Long Range Transport (LRT) of persistent organic pollutants [40] even states its purpose explicitly, being the establishment of LRT as a fourth criterion which should be considered when banning substances internationally.

The clearest purpose is stated for the methods devised in the context of the *European dangerous chemicals regulation*, EPS, EHR and the EURAM method [27]. The latter was actually used for setting up priority lists, designating the substances for which a full risk assessment according to the TGD has to be carried out by the member states of the European Union.

Protection goals and system boundaries

The question of the protection goals of the evaluation of potential environmental effects of chemicals can be answered in multiple ways. Most methods simply consider the "environment" in general as the protection goal of the evaluation [33, 20, 21, 23, 22, 24, 26, 25]. In many cases, "human health" is either additionally introduced at a later point or implicitly included by consideration of toxicological endpoints relevant to human health. A definition of the term "environment" is only given by Frische et al. [23], who use the term "technosphere" as its counterpart. Later, this has often been referred to as the ”functional definition” of the environment (cp. also the discussion about release to the environment in the next chapter).

Not a definition, but a further explication of the protection goal ”environment” is also given in the EPS/EHR, the EURAM and the SCRAM publications [25, 26, 27, 28]. In addition to the distinction of environment and human health, the environment is split up in different ways: In EPS and EHR, separate scores for air, water and soil are considered, citing the environment definition in the 6th amendment of council directive 67/548/EC. In EURAM, the spatial differentiation of the environment is initially defined by the compartments of the Level I exposure model by Mackay [41]. Later in the publication, only the aquatic and the terrestrial compartments are used, and the protection goals ”microorganisms in sewage treatment plants” and ”top predators” are added, for which additional exposure estimations are applied. In the SCRAM system [28], the environment is differentiated into biota, air, soil, sediment and water for the evaluation of the persistence score. In the effects characterization, an aquatic system, a terrestrial system and human health are distinguished. For the terrestrial toxicity score, effects to plants, mammals, herps (amphibians and reptiles), birds and invertebrates are considered, while the aquatic organisms are differentiated into plants, amphibians, warm water fish, cold water fish and invertebrates.

Naturally, the evaluative fate indicators use *spatial differentiations* of the environment for their approaches. Scheringer [37, 42, 43] uses seawater, air and soil for his global models[3], which are each further split into a variing number of segments, while he conceeds that freshwater, deep-sea water and sediments might also be important for the global budget of POPs. For the calculation of the characteristic travel distance by Bennett [39], the environment relevant for this metric is constituted by air, plants, surface soil and root zone soil. A typical Mackay-type differentiation into surface water, air, soil and sediment is used by Webster [36] for the calculation of the ”overall” persistence, and also in the TaPL model used in the paper by Beyer et al. about the generalization of the characteristic travel distance to the concept of long-range transport potential [40].

Generally, in these approaches the space itself is the protection goal, independent of the organisms living there and the effects on them. As these evaluative indicators are also independent of the amount of the substance released to the environment and of the bioaccumulation potential,

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[3] following Klein [44]. The same scheme was later also used e.g. by Müller-Herold and Nickel [38]

they can well be fit into a multicriterial evaluation scheme as is being established for example with the PBT concept [4]. The other concepts claim to be sufficient for the evaluation of endangerment of the protection goals in themselves, even if they can be viewed as lower-level methods in the higher-level framework of e.g. the body of European dangerous chemicals regulations.

Another issue concerning the borders and elements of the system evaluated (the chemical substance in the environment) is the consideration of *impurities and transformation products*. The potential importance of impurities is only mentioned in one study, but without really showing a method of dealing with them [26]. Concerning the transformation products, it should be noted that since the early discussions about degradability, a distinction between primary degradation, which does not contain any information about degradation products, and mineralization, which means degradation to carbon dioxide, water and other compounds considered anorganic, has been established. Nevertheless, this distinction is still sometimes ignored, usually in the form that primary degradation is called just degradation.

In the evaluation methods discussed here the significance of transformation products is generally ignored, except that in some cases data for mineralization, determined by measuring CO_2 evolution, are required [22, 27] and in the EHR description [26], the necessity of regarding each hydrolysis product as a further chemical to be assessed, if hydrolysis data is used at all. In the SCRAM system, metabolites should be scored if it is known that degradation products of a chemical are responsible for all or most of its toxic effects. This formulation has the large disadvantage that it already requires a lot of information that is usually not available.

Two recent publications [45, 46] have exemplified the possibility of the inclusion of transformation products into evaluative fate indicators. Unfortunately, only for very few substances appropriate data can be found in the scientific literature. Expert judgment and known structure-degradability relationships have to be applied in order to obtain a plausible set of conversion rates.

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[4] In contrast to the other authors working on evaluative fate indicators, Scheringer argues that the criteria persistence and spatial range are already a sufficient basis for taking consequences.

Data availability

Generally, there are three possibilities for an evaluation method to handle data availability:

- Exactly define the number and each type of required data
- Exactly define a minimum set of required data, but also define possibilities to consider additional data
- Define the types of data to be considered, but not a minimum set

Based on these specifications, there are different possibilities to deal with missing data, or generally with the different data availability for different substances.

The study by Freitag et al. [22] uses the first approach, defining even experimental details for the generation of data for their method. No compensation for unavailable data is mentioned. In the hazard ranking method by Schmidt-Bleek et al. [21], missing data simply lead to the worst-case score. In the criteria definition paper by Frische et al. [23], some required data types are specified, but the definitions are not very strict.[5]

While the EHR method can rely on the submission of the base set data for the new chemicals to be evaluated, the EPS system for prioritizing existing chemicals was constructed to be operable even with very limited types and amount of data. The minimum set required for priority setting includes only the production volume, the use type and an acute toxicity test, preferably rat LD_{50}. For every criterion, data are scaled on the same scale from 0 to 100 percent, even if there only semi-quantitative data are available. Low data availability is neither punished by the scoring system nor explicitly shown in the final result.

The SCRAM uses a different approach for dealing with data gaps: each data type required for the evaluation is associated with an uncertainty score, which depends on the number of data points available, but also on the significance of the data type for the aim of the evaluation. For example, in estimating the environmental persistence, the uncertainty score is a function of the number of values available for the five compartments. Acceptable data types are mentioned, but not further specified.

In the EURAM, data availability is dictated by the IUCLID database [48] for existing substances. As commonly applied in the calculation of

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[5] For later discussions it is interesting to note that the criterion "mobility" does not appear in the final evaluation formula, although the data for this criterion are relatively well-defined by reference [47].

PNEC values, assessment factors are used, taking the data availability for the effect scores into account. However, only a difference in the type of (aquatic) effect data is rated, rating the availability of chronic EC_{10} or NOEC values better than only the availability of EC_{50}values. For the data aggregated into the exposure score, no procedure for evaluating/handling different data availabilities for different chemicals is mentioned.

For the evaluative fate indicators, the first possibility of the above list is chosen, i.e. the set of data and the type of acceptable sources are generally exactly defined.

Uncertainties

Different data availabilities for different substances can result in different uncertainties of the evaluations. Since we just discussed the ways to handle *data availability differences*, and since we already mentioned the uncertainties that result from *uncertain system boundaries* (environmental compartments and transformation products and impurities considered), at this point, additional strategies of dealing with uncertainty are discussed[6].

One strategy, that is quite common in hazard ranking methods that are more oriented towards the requirements of science than towards the requirements of decision-making, is to carry out *own experiments*. While the exact definition of relevant experiments and the generation of the pertaining results as demonstrated by Freitag et al. [22] is a great contribution to understanding possible effects in the environment, this can not be regarded sufficient.

It should be kept in mind, that simple interpretation methods like the normalization of experimental results to a general scale, e.g. from 0 to 100, and the successive weighing of the different types of results can be quite arbitrary. A study about the sensitivity of different schemes of this type [51] did not find major differences between schemes, but this was mainly because most chemicals were classified as having ″uncertain likelihood of enviromental hazard″. Furthermore, one of the experimental results, the accumulation in sewage sludge, was rated negative in most schemes, as generally belonging to the properties showing accumulation potential, but it was rated positive in another scheme, since it leads to easier purification of aqueous phases, e.g. in a sewage treatment plant. This kind of conflict can not be resolved by the partial ordering methods using

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[6] This is only a very specific discussion of the ways to deal with uncertainties in the selected evaluation methods. For general perspectives on uncertainties, their handling and their communication, see the comprehensive works by Finkel [49] and Morgan and Henrion [50]

the Hasse-Diagram technique [24, 52]. Only clear declaration of protection goals (water only, water and/or sediment) in combination with simple fate models can resolve this issue, or in this case, the use of an approximation of the overall environmental persistence [33, 35, 37, 36].

This example illustrates the importance of a *clear conceptional background* for evaluation methods. This can be discussed without the technical details, and, if agreed upon, can serve to reduce the uncertainty of the evaluation method considerably. Among the publications discussed here, Scheringer [37, 53] put exceptional effort to a stringent theoretical foundation of his method, up to the mathematical definitions of his evaluation criteria.

A rather technical way to deal with uncertainties of the input data of the models is to attribute use *probability distributions* instead of single values for the input data. This generally requires not only knowledge of single data points, but also knowledge of the specific variance of each datum. This can be either gained by fitting distributions to a number of data points interpreted as belonging to a set of equally varying values. Another possibility, frequently used for probabilistic health risk assessments, is to look up typical variances in the literature [54]. This technique, oftentimes followed by a Monte Carlo Analysis used to determine the consequences of the variance of input data for the final result, has not been used in the studies cited above. However, especially since the broad availability of computers for statistical calculations and the accessibility of large databases over the internet or on comparatively cheap CD-ROM media, both in environmental exposure modelling as in environmental effects assessment, probabilistic methods are widely applied (e.g. [55, 56, 57]). The fact that this is usually in the general context of evaluations following the PEC/PNEC scheme does not mean that probabilistic methods can not be incorporated into alternative evaluation methods [1]. The consequence of this type of consideration of data uncertainty is that the results will only be of a probabilistic nature. Either they can be reduced afterwards by generation of mean values and separate metrics for the variance of the results, or the results can be presented as cumulative density or probability density representations.

Presentation of the results

As already mentioned in the subchapter about purposes and application contexts, some of the methods are constructed to produce one unequivocal final score for each chemical (sometimes called index). These are called "overall rank" [23], "aquatic score" [27] and "final composite score" [31]

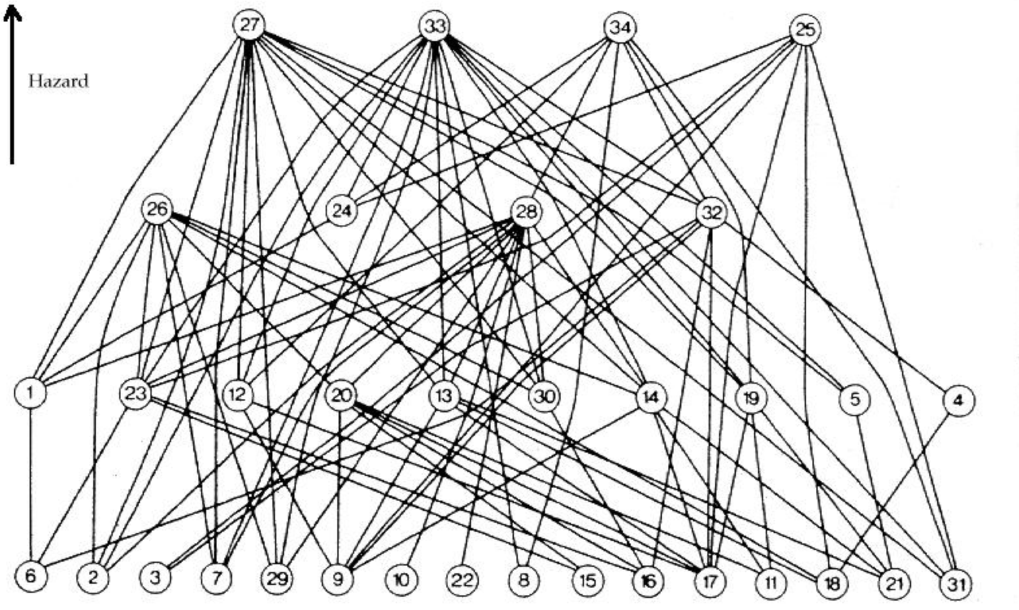

Figure 2.3: Hasse Diagram as used for the application in evaluating substances. Adapted from [24]

for the methods comprising fate and effects, and "overall persistence" [36], "characteristic travel distance" [39], "long-range transport potential" [40] or "characteristic spatial range" for the methods comprising only the fate of the chemical, respectively one aspect of the fate. They are each presented as the decisive, decision-supporting result of the method.[7]

The other methods do not aggregate the evaluation result up to a single value. Therefore, a graphical representation of the result in two or more dimensions is generally given. The Hasse-Diagram in Figure 2.3 shows the partial ordering of the thirty-four substances tested also in [22]. If a chemical is located on a higher level (more towards the top of the graph) than another chemical, and if there is a line connecting them, then the method claims that the hazard potential is unequivocally higher[8]. By the

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[7] For the "hazard ranking scheme" [21], there is also only one final result, namely a classification of all substances into three groups. If they get the attribute "black", then immediate further testing is called for, if they get "gray", they should be "kept under consideration" and specific earlier testing should be considered, and if they are classified "white", no immediate regulatory interest is stated.

[8] The mathematical rigor and consequence of the method, however, should not distract

use of levels in the graph, the method also produces a classification of the substances, but substances from the same "level"can not be further distinguished.

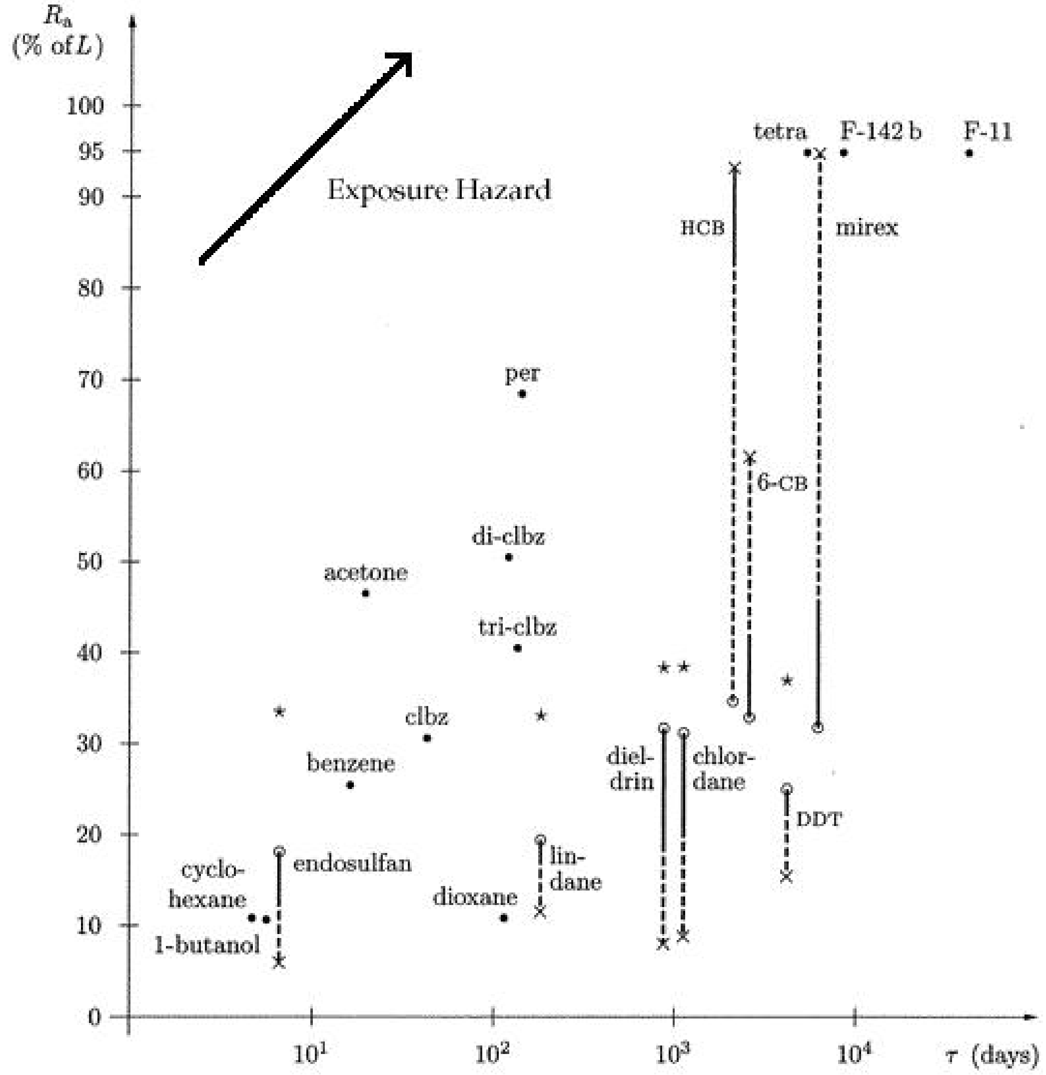

Figure 2.4: Persistence τ and spatial range in air R_a as two evaluative indicators differentiating the chemicals in two dimensions. Adapted from [42]

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from the fact that sometimes the problem lies more in the uncertainty about the precision of the underlying data, and, as has been illustrated in the subsection above, even about the question, if high values of a certain test result mean a relatively high or a relatively low hazard.

Two-dimensional representations of the final results are shown in Figures 2.4 and 2.5. Scheringers approach (Figure 2.4) displays persistence and spatial range as two separate aspects of an exposure-based assessment[9]. The EPS method (Figure 2.5) presents one scaled value for exposure and one for effects in each of their three two-dimensional graphs, each representing one of the protection goals air, water and soil.[10]

The "ecotoxicological profile" devised by Freitag et al. [22] is represented graphically by a simple bar chart, showing all six evaluation criteria for the tested chemicals, as shown in Figure 2.6. This kind of information is even harder to interpret in the context of decisions, which was probably the incentive to further interpret the data by means of the Hasse-diagram discussed above.

A real multi-dimensional representation of aggregated risk indicators is used on the website[11] of the US organization "Environmental Defense". Depending on the number of risk indicator evaluations available for a certain chemical, a variable number of indicator values is shown in a bar chart as shown in the example in Figure 2.7. In this example, the possible differences between the final results and the necessarity to understand the basis of the evaluation of such a method are quite obvious, even in the case of a substance as well-known as benzene. The common dimension "Hazard" which is suggested by the projection of the indexes on the scale from 0 to 100 % does not really exist.

Except for the sensitivity analysis resulting in a kind of error bar in Figure 2.4, no uncertainties are explicitly shown in the final results. However, refraining from aggregating the evaluation into a simple unequivocal resulting dimension can be regarded as an expression of uncertainty in itself. The sources of these uncertainties and the fact that some of these uncertainties are not reducible by scientific means, will be discussed in the next chapter, where the concept of a separate uncertainty indicator is introduced.

Expert judgement

Expert judgement is an important element of all evaluation procedures, at least in the construction of the method. Some methods explicitly try

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[9] Fate-based risk assessment would be more precise, since fate, contrary to an exposure, is independent of the amount entering the environment.

[10] An interesting three-dimensional characterization of textile chemicals has been given by Beck et al. [58], where the residence time in water, the negative logarithm of the PNEC, and an aggregated Life-Cycle Index are used as evaluative categories.

[11] `http://www.scorecard.org/chemical-profiles/`

to get rid of the necessity for expert judgment at least for some parts of the substance evaluation. For example Schmidt-Bleek et al. state that ”the evaluation of property-related environmental hazards by the application of standardized procedures can be carried out *without* any expert knowledge on the condition that the competent authority is sufficiently staffed, both in terms of quality of personnel and numbers.”[21]. In EURAM, expert judgment is needed for some very important and demanding tasks like selecting appropriate data for scoring effects on terrestrial organisms. However, this only takes place after the automated evaluation procedure based on the ”aquatic score”[27]. In the fate indicator publications, the importance of expert knowledge for the selection of appropriate data for mostly equilibrium partitioning constants and rate constants from the literature is obvious, and is in some cases mentioned by the authors. Generally, expert knowledge can fulfill a wide variety of functions in an evaluation system and it can be absolutely necessary to resolve conflicts in the data or deal with special cases. However, excessive use of expert knowledge requires very detailed additional documentation in order to keep the method transparent.

All these methods have their specific advantages and disadvantages. Since their purpose is different, they can not be directly compared. Nevertheless, their analysis, together with the discussions of the use of indicators in general and of different methods of risk quantification, provides a basic understanding, what elements scientific evaluation has and how the specific methods fit to the different requirements of decisions about the release of chemical substances to the environment.

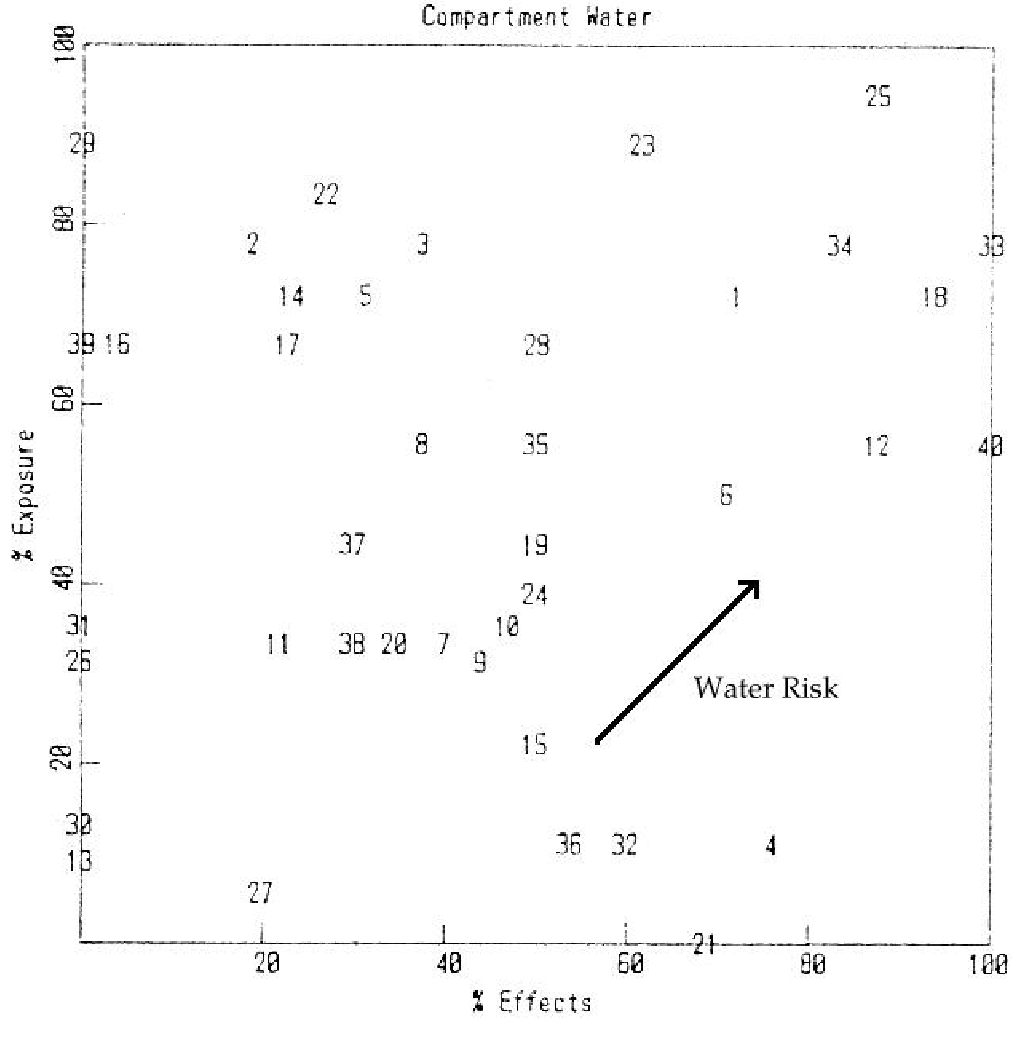

Figure 2.5: Separate exposure and effects scores for the water compartment. The same type of graph is used for soil and air, so the number of final evaluative dimensions is six. Adapted from [21]

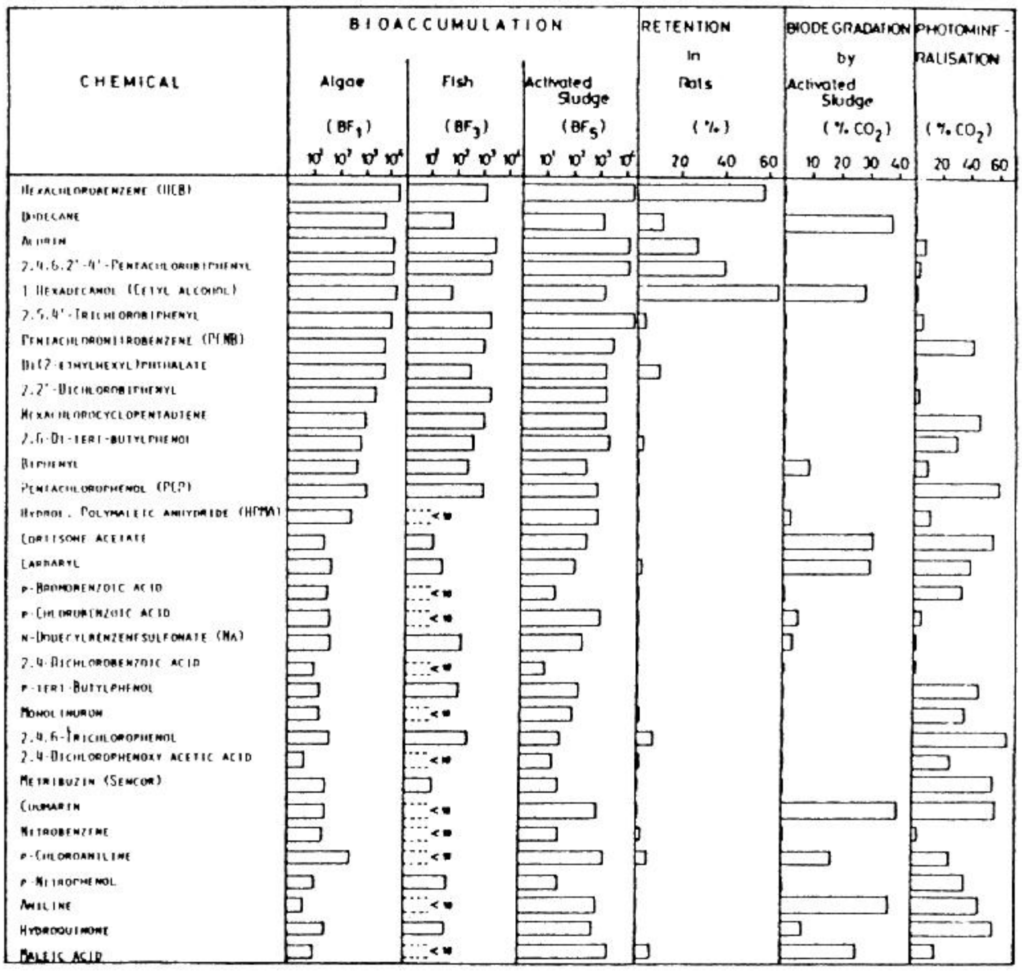

Figure 2.6: Bar chart of the results of six accumulation and degradation experiments for 32 substances. Each test result is presented as one evaluative indicator, so the final evaluation has six dimensions [22]. With friendly permission of Harcourt Academic Publishers (C)

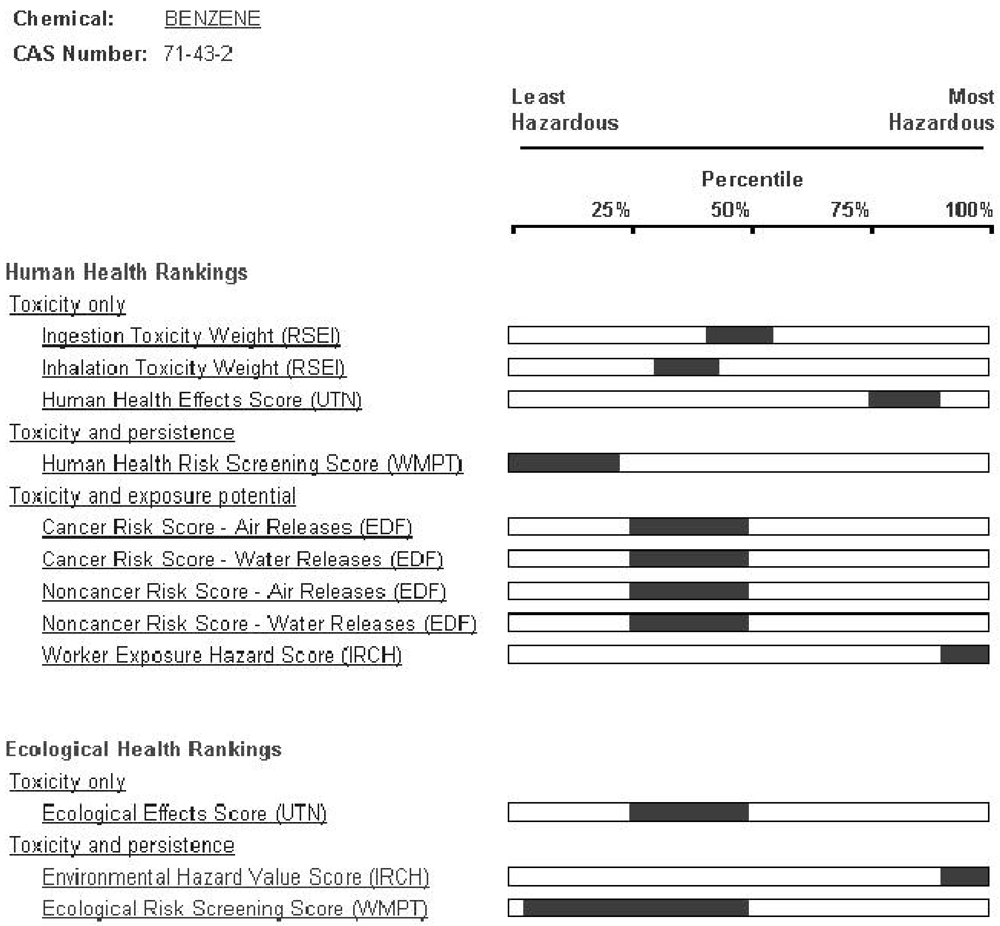

Figure 2.7: Bar charts of the results of 12 different hazard evaluation methods for benzene from the Scorecard website (see footnote)

Chapter 3

Ecotoxicological risk profiles

> *Science tells us what we know, but what we can know is little, and if we forget how much we cannot know we become insensitive to many things of great importance. [...] Uncertainty, in the presence of vivid hopes and fears, is painful, but must be endured if we wish to live without the support of comforting fairy tales.*
>
> Bertrand Russell "A History of Western Philosophy"

While the present method of generating ecotoxicological risk profiles of chemicals released to the environment was first developed in the specific context of a comparative evaluation of antifouling biocides [6, 8], the underlying considerations are presented here for the first time in detail as a general concept for the comparative analysis and communication of ecotoxicological risks of chemical substances. From this concept, operative methods can be derived for the comparison of substances, as exemplified in a later chapter in the case study of antifouling biocides.[1]

Figure 3.1 shows how ecotoxicological risk research draws information from different areas. Each arrow pointing towards risk research represents one of the five risk indicators that make up the ecotoxicological profile: Data about the *release* of substances to the environment originates from the technosphere. Additional knowledge about the behavior of the substance in the environmental compartments makes an assessment of the *spatiotemporal range* possible, observations of the uptake, metabolization

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[1] Further applications of the concept are the Diplomarbeit of F. Stock which is a comparison of vulcanization agents [59] and a comparison of tributyltin and its main metabolites, carried out in the context of a risk evaluation of the land deposition of tributyltin-contaminated sediment dredged from harbors [60].

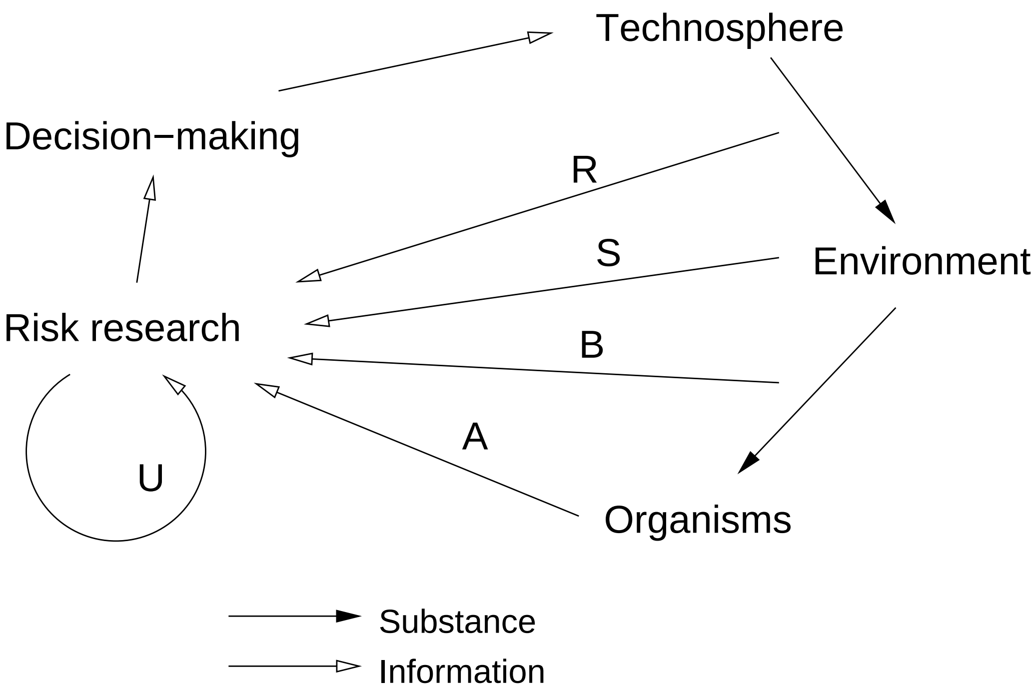

Figure 3.1: Scheme of the risk management cycle showing what kind of information ecotoxicological risk research mainly relies on and how the loop of self-referential regulation of society can be closed. R = Release, S = Spatiotemporal range, B = Bioaccumulation, A = Biological activity and U = Uncertainty

and depuration of the substance in organisms constitute the *bioaccumulation* indicator, observations of ecotoxicological endpoints on different levels of biological organization (cells, single organisms, populations communities) make up the indicator *biological activity* and finally, perceptions of the different capabilities of risk research itself to evaluate the different substances are aggregated into the fifth, reflexive indicator *uncertainty*.

The structure of this evaluation concept only allows for an unequivocal comparison of two substances, if one of them has lower indicator values in the first four indicators and if the uncertainty indicator for both is not exceedingly high. In mathematical terms, the substances and their indicator scores form a partially ordered set. Because of the relatively high number of five indicators, it will oftentimes not be possible to draw unequivocal conclusions about the substances. This, however is congruent with our reluctance to make unequivocal statements about something which we can not know. It seems that the evaluation of environmental effects of substances comprises so many aspects of such a high complexity that an unequivocal scientific statement is oftentimes not adequate [61]. Even if it is recognized that decisions about substances have to be taken and that methods for arriving at such decisions have to be derived with a sound scientific basis, it is argued here that if a method of substance evaluation is devised from the scientific point of view, it provides valuable risk-relevant information even without exactly defining how the decision should be taken.

Preconditions for a meaningful application of the concept, comprising its transformation into a specific evaluation method and the evaluation itself are

- a decision about the use of chemicals which is to be informed about the ecotoxicological risks,
- a defined set of chemicals which is to be compared in order to support the decision.
- a scientist or a team of scientists independent from commercial interests in particular substances to be evaluated, and skilled to perform the transformation of the concept into a specific method as well as to carry it out and
- a medium for the communication of the results.

The concept is related to the approach of M. Scheringer [37, 42], in defining indicators for the evaluation of chemicals released to the environment and providing some theoretical background, why these indicators are relevant (compare [62, 63, 53]). The two indicators used by Scheringer, persistence (temporal range) and spatial range, however, are combined here to a single indicator called ″spatiotemporal range″ and the concept is extended by four indicators, resulting in an evaluation with five dimensions.

The name of the concept ″ecotoxicological risk profile″ suggests some similarity to the ″ecotoxicological profile analysis″ by Freitag et al. [22], which was discussed in the previous chapter. However, there are two major differences: The main difference is marked by the word ″risk″ in ″ecotoxicological risk profile″[2]. It means that the concept presented here is concerned with decisions about the release of chemicals to the environment. While the amount actually entering the environment is not within the scope of Freitag et al., it is explicitly the very starting point for generating ecotoxicological *risk* profiles and at the same time the main target of the decision to be informed, which becomes a risk *managing* decision by taking the risk profile into account.

The area of usage as defined above is rather wide and the concept is of a very general nature. A disadvantage of this is that it has to be broken down to a usable method for every application. At the same time, this is an advantage, because it encourages to account for case-specific problems and solutions. Furthermore, the concept provides a general framework which can also be discussed independent from its specific implementations.

3.1 Preparatory work

The basic procedure of generating five indicator values for each substance is simple. In a first step, the type of decision which should be informed by the evaluation is to be addressed. If possible, even the specific actors, who might take the decision based on the analysis should be named. The method is meant to inform decisions of producers as well as of concerned institutions, which includes Non-Governmental Organizations like the World Wildlife Fund for Nature or Greenpeace. Producers naturally have to decide which substances to use/incorporate during production, while organizations concerned with the protection of the environment have to decide where to set the focus of their activities.

The set of substances to be put defined in the next step has to have something in common regarding the decision defined in the first step. The

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[2] Please refer to the remarks about the term ″risk″ stated in the Introduction

obvious case for the producers is that for a specific application, there is the possibility to choose between several substances fulfilling the same purpose. It is however also possible that the international discussion about the ban of certain substances, recently calling for attention through the UN meetings in Johannesburg and Stockholm, will lead to the adoption of a similar concept for the selection of candidates for global use restrictions.[3]

After it has been ascertained that time and resources are sufficient to carry out the evaluation in an independent manner, and after the medium or the media of communication of the results has been defined, the data for the evaluation of the substances have to be collected. Although own experimental expertise of the risk scientists and even more own laboratory experience concerning the substances is very valuable for the evaluation process, it is not a prerequisite. In the course of carrying out the risk evaluation, Structure-Activity Relationships (SAR) knowledge (cp. glossary of terms) will be very helpful in many places. Going back to the structure of the substance to be evaluated, to its transformation products and metabolites and considering their stereochemistry, their molecular interaction potentials and their inherent reactivity will provide invaluable resources for plausibility checks, improved interpretation of test protocols, but also for a reasonable handling of data gaps. This is especially necessary in cases where a lot of transformation products and metabolites will be formed, from which the relevant have to be selected. Oftentimes, they have to be evaluated on the base of almost no test data.

Especially for the likely case that the evaluation embraces also existing substances, a vast amount of data of highly differing quality and relevance have to be reviewed and ideally made accessible in a relational database. Details about the possibility of storing the data in a way that both browsing the database and specifically selecting data by means of the Structured Query Language (SQL) are discussed in Appendix A. For the sake of transparency, special attention should be given to careful inclusion of source references.

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[3] A concept also using five indicators, keeping the fate indicators persistence and long-range transport potential separate and not considering an uncertainty indicator, was proposed by D. Mackay during the Society of Environmental Toxicology and Chemistry (SETAC) world meeting in Brighton in May 2000 [64]. In this case the set of substances would be made up by the chemicals for which an extraordinarily high probability of serious detrimental effects in the environmental has already been shown.

3.2 Indicator evaluation

There are several possibilities to set up scales for the scoring of substances. Starting from the presupposition that scores for five indicators have to be constructed, the questions remaining are:

1. How many possible scores should be on each scale? This number is often as low as three (low, medium, high) and often 100 (percentage scale) or higher.
2. Should the scale be an absolute scale that is fixed independent of the specific set of substances to be evaluated or should it be relative to the specific set in that it its lowest value for each indicator is equivalent to the lowest value occuring in the specific set and its highest value is equivalent to the maximum value for the set?
3. Should the scale be equal for all indicators?

The answer to the first question will depend on the accuracy that the risk scientist will find appropriate for the evaluation. There is no use in differentiating between scores of 53.4 and 53.7, if this is only based on one numerical value, e.g. an 48 hour *Daphnia magna* EC_{50} value in the category biological activity, because of the variability of this parameter and because it only has a quite limited significance for the biological activity towards other organisms and on longer timescales. Since the indicators of the concept presented here each have a very wide scope, from which very different types of data have to be aggregated in a manner which will be disputable in many aspects, the number of scores should be accordingly low. Another point which should be taken into account is that for low numbers of possible scores, it is advantageous to use an even number, because this will prevent the loss of differentiating power by the common tendency to give medium scores.

Setting up an absolute scale for each indicator is feasible if this can be done in a widely accepted manner. For example, a scale for the first indicator, the amount released to the environment, can be derived independently from the specific set of substances, if common values for generally comparable substances are available. However, even if an absolute scale for e.g. the commonly cited production volumes in the EU is available, data about the release, taking into account the percentage which will actually enter the environment, will be much harder to find. If there is no feasible base for an *absolute* scale of an indicator, it is feasible to consider the range covered by all the substances from the set and possibly additionally take into account comparable data about other substances, so that a scale is made up which will fit the substances and therefore allows relative differentiation, and also gives some information about the position of the set of substances in relation to other, maybe more well-known substances. In any case, the reasoning for the scale construction should be explained before the discussion of any specific evaluation results.

An equal scale for all indicators will facilitate the interpretation of the results considerably. In graphical representations, this is commonly done whithout explicit reasoning, as can be seen e.g. in Figure 2.6, where the bar charts for very different experimental results are shown on a common graphical scale. An equal scale, however, might be interpreted as equal importance of the indicators, or even as equal function in the evaluation. In the case of the indicator system presented here, especially the uncertainty indicator does not have an equal function of the other indicators, because it aggregates the meta-information "uncertainty of the evaluation" for the four other indicators. This can be expressed by the use of e.g. an alphabetical scale for the uncertainty indicator (cp. [8]), or by some graphical separation from the other indicators. Based on the proposed mathematical definitions of the indicators which can be found in the following sections, a common logarithmic scale can be used. This is useful, because in this way, the differences of the chemicals regarding the different indicators can be compared. A mathematical quantification of the indicators bioaccumuation and biological activity according to the equations proposed is quite unrealistic, unfortunately.

Equal scales for the other four indicators does not mean equal weights. Especially if the uncertainty is high, the importance of the release indicator R is higher, followed by the spatiotemporal range indicator S. The indicator biological activity is only really meaningful, if it can be evaluated with sufficient data, which is often not the case, considering the importance of long-term effects, the number of species in the environment and the scarcity of effects data for species living in the terrestrial environment and the sediments.

Reading the description of the foundations of the next four indicators, it should always be kept in mind, that they will each be evaluated in a twofold manner: First, the indicator itself, for which the most realistic value should be chosen, and second, the uncertainty indicator, which should express the relative uncertainty in evaluating the indicator for the respective chemical, in comparison to the other substances. The uncertainties of the first four indicators are combined to the fifth indicator. This construction of the method makes it unnessecary to work with conservative assumptions or worst-case scenarios.[4]

Release

The crucial role of the release to the environment for an ecotoxicological *risk* evaluation of substances has already been pointed out in the Introduction (Section 1.2). The maximum constant release to the environment globally is the production volume. Examples for functions that the production volumes already has in the international risk management of chemicals are the definition of a global list of High Production Volume (HPV) substances for which a base set of data on their hazard potential is generated in a multilateral collaboration coordinated by the International Panel on Chemical Safety (IPCS) and the definition of data requirements for new notified substances in the European Union, which depends on the intended production volume. Furthermore, the production volume linearly enters into PEC/PNEC-based evaluation methods like EURAM [27] and (E)USES [66].

However, a fraction of the produced amount will never enter the environment.[5] For a more precise definition of the release of substances to the environment, the functional definition of the environment from [23] is quite useful. According to this concept, the environment is conceived as the counterpart of the technosphere. The borderline between them can be derived from their differences listed in Table 3.1.

Table 3.1: Differences between the technosphere and the environment. Adapted from [23]

	Technosphere	**Environment**
Spatial extension	limited	unlimited
Targets	defined	mostly undefined
Concentration levels	known, controlled	punctual knowledge
Functional principles	known	punctual knowledge

The main difference is the human control which is exerted on the tech-

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[4] The problems that arise from working with worst-case assumptions, even if they are "realistic worst-case assumptions" have been addressed by G.W. Suter II: (a) The worst case can always be worse, (b) Uncertainty and errors are hidden (c) Societal and environmental costs of regulating "false positives" (in this case substances whose detrimental effects are much lower than suggested by the worst-case scenario and low in comparison to the costs of regulating them) [65]

[5] The main causes for this are the combustion of the substance after use and the land deposition, if the land deposits are seen as part of the technosphere.

nosphere. Regarding substances, the control in question is the control on where the specific substance is located in which amount and in which form. In technical products, this control is generally exerted during the production process, and therefore substances which fulfill their original functions within the technical product, still belong to the technosphere. If the product is disassembled or the substance leaves the product in any other way, and the substance is not located in a defined new technical function, the substance has enterend ″the environment″. The question, if e.g. land deposits should be regarded as parts of the technosphere or of the envionment therefore mainly depends on the question, if the chemical content in the deposit is controlled.[6]

A common way to do a rough estimation of the amount released to the environment is to use the approximation (cp. [23, 27])

$$A \approx \sum_{\mathrm{u}} f_{\mathrm{u}} \cdot P_{\mathrm{u}} \tag{3.1}$$

where A is the calculated released amount, u is an index for the different use patterns, P_{u} is the respective production volume for use pattern u and f_{u} is the fraction of the respective production volume deemed to enter the environment during the life cycle of the substance. For example, the fraction f_{u} for the use pattern ″closed systems″ is 0.1 in the EURAM [27], meaning that it is estimated that 10 percent of the production volume designated for the use in closed systems will enter the environment. The release indicator R can then be defined as proportional to the released amount $\mathsf{R} \propto A$ or to its decadic logarithm $\mathsf{R} \propto \log_{10} A$. If the release indicator is not meant to represent the global release to the environment, import and export of the substance for the region or country have to be taken into account.

The latter definition of the release indicator R is useful for the comparison of risks caused by the use of different substances in a defined political area or in a company. The ecotoxicological risk profiles can then be used in order to select substances which are candidates for banning, which means substitution in most cases.

If the decision is a selection of substances for a defined function in a technical product, the release indicator can also be quantified in a different manner: the released amount can be expressed in relation to the functional unit. In other words, the less the amount that is required to fulfill the function of the substance, the lower the release indicator value. If, for example,

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[6] If it is in fact controlled, the substance can still enter the environment through dredge water or through released gases.

the functional unit is the sequestration of Ca^{2+} and Mg^{2+} ions from 1 litre hard water, the amount of sequestration agent released per litre treated hard water from the technosphere via untreated sewage, passage through the sewage treatment plants and transfer of sewage sludge to agricultural production makes up the release indicator. This way of defining the risk indicator, however, is only sensible, if the necessity of the function of the chemicals is not questioned, because in this case, the only purpose of the indicator system is to support the selection of a substance which entails the least risk of environmental damage.[7]

Regardless of the method of quantification, the amount of a substance released from technical systems to the environment is an indicator of the risk of causing or allowing damage in the environment by this release. Within the context of ecotoxicological risk profiles, it is regarded here as the most important risk indicator, since it is the one most independent from the other four indicators. Even if it is not possible to provide values for the other four indicators, the release indicator provides a first meaningful possibility for risk communication. The protection goal motivating this indicator as an independent risk indicator is the integrity of the environment in general.

Spatiotemporal range

From the functional definition of the environment given in the above explanations it follows that there is no control on the fate of substances once they have been released from the technosphere. If a decontamination of a certain segment of the environment should take place, this segment would become part of the technosphere by definition.[8] After the remediation process, or in the case of remediation by "natural attenuation", the segment

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[7] If one of the substances evaluated by means of such a function-specific ecotoxicological risk profile has become inacceptable by proof of inacceptable detrimental effects in the field, or by absolute risk analysis according to the PEC/PNEC approach, this substance might serve as a benchmark for the function-specific assessment. This seems to be the case for Tributyltin and will be further discussed in Chapter 6

[8] It can be argued, that the control exerted e.g. on the constitution of the atmosphere by prohibiting the use of certain halogenated hydrocarbons in the Montreal Protocol means that large parts of our global environment have already been turned into technosphere. However, since the control is mainly exerted on the technosphere and only indirectly on parts of the environment like the atmosphere, and since the concentrations of atmospheric trace gases are generally not under societal control, this argumentation is rejected here. A different case is e.g. the troposhere in large cities, which is increasingly turning into a technospheric compartment with respect to the concentrations of ozone, NO_x and SO_x.

will (again) be part of the environment.

Although no control of the fate of the released substances can be exerted, their fate in the environment can be approximatively predicted by means of fate models. It depends on the location(s) of the release, on their tendency to partition to the different static and mobile environmental media and on the kinetics of transformation reactions in these media.

The risk resulting from the release to the environment depends on likelihood and severity of effects that the substance might cause on objects of environmental protection. Without assumptions about the location of these objects and the quality and quantity of their interactions with the substance, it seems reasonable to assume that the total amount of a substance present in the environment at any given time is a better metric for the ecotoxicological risk than just the released amount. The latter is not only influenced by the amount released per time, but also by all processes which purge the substance from the environment. An indicator which describes the lack of such purging processes and which is therefore an ecotoxicological risk indicator is the overall persistence in the environment [36], which is defined as the total amount M_{env} of a certain substance in the environment divided by the steady release A by which it is caused. For the common case that degradation rates in a model are all of the first-order type, the overall persistence defined in this way is independent of the released amount.

This quantification of the spatiotemporal range of a substance is very much simplifying in that it does not discriminate, if the total amount M_{env} is evenly distributed in the environment or if it is concentrated in one or several environmental compartments or even segments[9]. It is, however, not necessarily worse to contaminate a large area to a low degree than to contaminate a small area to a high degree, if the total amount of contaminating substance is equal in both cases. The reason, why the indicator is called ″spatiotemporal range″ even though it does not include the calculation of a ″spatial range″ as proposed by Scheringer [37, 42] is that it describes the presence of the released substance in the environment *as space and time*. Neither the simple term ″persistence″, nor the more exact term ″overall persistence″ convey the very important spatial aspects of the fate of a substance. These spatial aspects are however directly incorporated into the calculation of an overall persistence by the spatial definition of the model environment.

There are several common spatial limitations to the usual fate models. Many times, they are not representing the whole global environment, but

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[9] See the glossary of terms for definitions of the terms ″compartment″ and ″segment″

only some region, which might be directly representing a geographical region or which might be generic. The problem with this type of limitation of the modeled area is that the substances can simply be exported e.g. in the air to another region, so that a residence time in such a fate model is not a good approximation for its range in the environment as a whole. A second important common spatial limitation is the negligence of the deep sea. Most models only consider water down to 200 m depth at the most. Even if this is the most biologically active zone, it can not be claimed that the marine environment is captured by such a model. The possibility of a slow build-up of huge reservoirs of contaminants in the waters of the deep sea is not in the scope of such models. A third, maybe less relevant limitation which applies to published global fate models [67, 68, 43], is that the special properties of the polar ice caps are not taken into account. A last example for unideal spatial limitations of fate models is the size of the sediment compartment. Many modelling approaches following D. Mackay assume a thickness of the sediment layer below water areas of only 1 cm [69]. However, the bioturbated layer in marine sediments is much larger (A standard textbook [70] gives 40 cm) and living organisms have been found hundreds of meters below the sediment surface. One important consequence of the common spatial limitations of current models is that there is not one global fate model fit to serve the purpose of estimating the spatiotemporal range of a substance. Rather, for every decision context the necessary and the reasonably operable scope and complexity have to be defined and the model best fit for this compromise has to be selected, if not newly created.[10]

Another, not directly space-related limitation of most present fate models as a base for the evaluation of the spatiotemporal range of a substance is their way of dealing with transformation reactions. Generally, if a substance is transformed, its transformation products do not show up in the model equations. It is, however, possible, that they are themselves not degraded any further, or that they are transported to a different part of the environment where they persist. If such transformation products cause detrimental effects, these have to be attributed to the release of their parent substance. Consequently, Fenner et al. [45] have defined a joint persistence as the total amount of the released substance plus a defined number of transformation products. Apart from the difficulties of finding the same partitioning data and rate constants for further reactions for the transformation products, it is not clearly defined what kind of transformation

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[10] As described for the evaluation of the spatiotemporal range of antifouling biocides in Chapter 5

products can be regarded as ecotoxicologically irrelevant. If all degradation reactions up to complete mineralization are taken into account, the complexity and the lack of adequate data become intractable for many substances. The consequence of this for the generation of comparative ecotoxicological risk profiles is that the aim is to express in the indicator ″spatiotemporal range″ S the joint persistence of the substance and all transformation products deemed to be environmentally relevant. Since even for the best-known environmental chemicals like atrazine [45], many parameters important for the calculation of a joint persistence have to be roughly estimated, there will be uncertainties, depending on the weight of the unidealities of the informations. These, however should not lead to a limitation of the scope of the analysis, but should rather be adequately reflected by means of the uncertainty indicator (see below).

These examples illustrate that the modeled environment used to calculate the overall persistence is not equivalent to the environment from the above functional definition. The model of the environment is necessarily limited to a complexity which can be technically dealt with and should be limited to a complexity which is reasonable facing the uncertainties in the substance-specific parameters. As a consequence it has to be realized that the information gained by the calculation of a fate parameter can only be gained by a limitation of the scope of the risk analysis. Although it would be possible to combine the indicators release and spatiotemporal range into a single indicator ″total amount present in the environment″, the accuracy of risk communication is argued here to be better, if they stay separate. The goal of protection leading to this second risk indicator S is the integrity of the environment within the spatial and temporal scope of the model used to quantify it.

Bioaccumulation

A further step towards an overall analysis of the effects that released substances have on organisms in the environment and their interrelations is to observe, how much of the released substance and its relevant transformation products is actually present within the living organisms. In analogy to the total amount of a substance in the environment in steady-state M_{env}, a total amount of a technically released substance present in living organisms M_{bio}, including relevant transformation products and metabolites, can be regarded as an even more relevant indicator of the risk of ecotoxicological effects. This measure would be dependent among other factors on the released amount and on the spatiotemporal range of the substance, but it would have, by error propagation, an even lower accuracy than these.

A general metric for bioaccumulation which would be independent of the first two indicators is the fraction of the total amount of the released substance and its relevant transformation products in the environment, which is present within organisms

$$F = \frac{M_{\mathrm{bio}}}{M_{\mathrm{env}}} \tag{3.2}$$

In the same manner that the known dependencies of laboratory observations and properties of the environment are expressed in fate models for the evaluation of the spatiotemporal range S, a model can be built approximating F for the evaluation of the bioaccumulation indicator B. This approach to the quantification of bioaccumulation encompasses the uptake from the medium the organisms live in and the uptake from food and is in this respect consistent with one of the common definitions of bioaccumulation [15, 71], but not consistent with others, which only count the uptake from the surrounding medium among bioaccumulation processes [72].

The simplest reasonable model for the approximation from equation 3.2 seems to be the assumptions (a) that the environment is made up of water, (b) the substance is not transformed in the environment, so that no transformation products have to be taken into account (c) uptake into and clearance from the organisms is dominated by equilibrium partitioning into the lipid content of the organism i.e. there are no active uptake and depuration mechanisms and (d) 1-octanol is sufficiently similar to lipids regarding its properties as a matrix for physicochemical partitioning. If these assumptions are valid, the fraction F proposed as an indicator for bioaccumulation is proportional to the 1-octanol-water partitioning coefficient K_{ow}, the proportionality coefficient being the ratio of the compartment sizes of the living organisms (lipid) and the environment (water). The plausibility of this approach is documented by the importance of measured and even estimated K_{ow} values as a trigger for further studies, usually of bioconcentration or biomagnification, but also for risk communication and risk management in the different national and international regulations of dangerous chemicals [72].

A way of approximating bioaccumulation which is usually preferred over the former approach is the determination of a Bioconcentration Factor (BCF). Commonly this is done by exposing a certain fish species to a low concentration of the candidate substance in the surrounding water, which is preferably held constant by water exchange (flow-through systems) and controlled by analytical chemistry. If the result of such a test is taken to be an approximation to the fraction F defined above, only assumptions (a) and (b) are necessary from the above list, but assumptions (c) and (d) are replaced by the assumptions, that (e) there is no additional uptake via contaminated food organisms and (f) that the uptake and depuration processes taking place in the testing species are qualitatively and quantitatively representative for all the organisms living in the environment.

Obviously, both methods have their severe limitations and it can not even be said that a bioaccumulation indicator based on a BCF is much more realistic than one based on a K_{ow}, since e.g. the depuration processes taking place in the testing species can be absent in other, even aquatic, species or even in large and relevant taxonomic groups.[11] The general focus on the aquatic environment is only recently addressed by suggestions for OECD testing methods for BCF values for species living in soils (earthworms) or sediments (tubificids, e.g. *Tubifex tubifex* [74, 75]). Especially for substances which will be released or transported to soils respectively sediments in significant amounts, this is an important extension of the possibilities to carry out risk assessments.

The problem of assumption (e) which makes the BCF unrealistic or, – more precisely – which limits its relevance for an ecotoxicological risk assessment, is addressed by observations of biomagnification. Biomagnification describes the enrichment of a substance in a consumer organism as compared to its food organisms. It is generally observed by sampling their populations in the field. For aquatic food chains, it can not only be caused by the uptake of contaminated food by the consumer, but also simply by less efficient depuration processes in the consumer organism.

Generally, the assessment of bioaccumulation might be considerably improved if the organism which are tested would be selected according to the results from a fate assessment. In the case that a substance will be sorbed to sediments in great quantities, a bioconcentration test for sediment-dwelling organisms might even be more important than the common BCF for fish. Also, the possibility of an accumulation in plants should be taken into consideration.

There are several possibilities to improve the evaluation of the bioaccumulation indicator even without testing the substance in the laboratory or even carrying out field observations. Qualitative and quantitative SAR, Structure-Property Relationships (SPR) and Property-Property Relation-

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[11] An interesting example for this given by Beek [72] (citing [73]), is the lower depuration efficiency of lungs of marine mammals like dolphins as compared to fish gills for moderately lipophilic contaminants like γ- Hexachlorocyclohexane (γ-HCH).

ships (PPR) that have been established by comprehensive scientific experience with substance released to the environment since decades and studied in multiple ways, serve as an important means of (a) judging the relevance of certain tests for the evaluation of bioaccumulation according to the above reasonings and (b) provide risk relevant information independent from tests.

An example for case (a) would be that the relevance of the K_{ow} for the evaluation of the bioaccumulation of substances with similar structural features as parathione should be regarded very skeptical, since parathione shows significant bioaccumulation, although it has a very low K_{ow} [72]. An example for case (b) would be the evaluation of metabolites of substances, which have not been tested for bioaccumulation themselves. Oftentimes, it can simply be seen from their chemical structure that they are hydrophilic enough to be swiftly eliminated from organisms.

These reasonings show that the evaluation of the accumulation of substances released to the environment in organisms, although generally well correlated to (eco-)toxic effects, is not easily done, if the complexity of the task, encompassing also the accumulation of transformation products and the lack of depuration of metabolites which can be passed on along the food web is taken into account. If substances with different surface activities or different charges, maybe even depending on the pH in the environmentally relevant range, are to be compared, it is possible that the data are so scarce, that only a rough qualitative impression can be used for chosing the adequate bioaccumulation indicator value. Nevertheless, the relevance of the indicator should not be underestimated, especially in the context of the increasing tendency to define the biological activity of a substance by means of a Critical Body Burden (CBB), which show that in many cases, the type of interaction of the substance with biomolecules is much less important than the internal exposure of the organism to it. The further reduction of the scope of the risk evaluation from the release to the environment with the integrity of the environment as a whole as the protection goal, via the spatiotemporal range of the substance with the integrity of space and time as the protection goal, leads to the possibility of an additional assessment of the tendency of a substance to bioaccumulate, with the protection goal being the integrity of organisms with respect to their material constitution.

Biological Activity

An ideal metric for an ecotoxicological risk assessment for the release of substances from the technosphere to the environment would be a metric of the effects that the substance, its transformation products and metabolites have on the organisms in the environment and on the ecosystems that they are part of. The severity of these effects is a function of the released amount, the spatiotemporal range, bioaccumulation and the biological activity of the substance. Obviously, a calculation of this severity for all organisms is impossible, not only because of a lack of data about substances, organisms and environment, but also because of the complex interrelations between them.[12]

The role of the indicator biological activity A is to express the relation between the substances accumulated in the organisms and their effects. Therefore, the most accurate type of data for its assessment is the internal effect concentration [76], which should be considered for the substance and its transformation products and metabolites which have been proven relevant in the preceeding assessment parts. An average of these internal effect concentrations weighted according to the distribution of the bioaccumulated substances over the different organisms would be ideal.

Data about biological activity in such organisms, in which the greatest part of the substance and its transformation products will be accumulated, should be preferred. This is influenced on the one hand by the fate of the substance in the different environmental compartments, and on the other hand by specific accumulation processes in certain taxonomic groups.

Usually, internal effect concentrations will not be available for the substances to be evaluated. Also, the bioaccumulation will not be known for many relevant taxonomic groups, as algae or plants. Therefore, generally it will be necessary to rely on external effect concentrations, although they aggregate information on bioaccumulation and biological activity of the substance [76]. Additional information, that can influence the indicator biological acitivity A would be information about biochemical mechanisms of observed noxious effects. Even if it is not easy to differentiate the relevance of e.g the photosynthesis system PS II and the reproduction system of mud snails, it seems that the former will have larger relevance for the biozoenosis from a functional point of view.

At this stage of the assessment, the information from the previous steps might have made the situation rather complex, e.g. if many transforma-

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[12] The conventional risk assessment, following the PEC/PNEC-paradigm does not estimate such a severity, but rather assesses the probability that relevant effects will occur or are occurring at all

tion products have to be taken into account, or if the predicted distribution in the environment is very different for the different substances. In the latter case, given that the overall persistence is similar for two substances to be compared, but they partition into different compartments, it is not very sensible to simply compare e.g. EC_{50} values for a certain fish species, since their relevance might be very different for the different substances. Even if a substance is much more biologically active in the water compartment, if it will partition mainly to the sediment, the accumulation and activity towards sediment-dwelling organisms is much more relevant. A direct comparison of *internal* effect concentrations would of course be possible in a much more straightforward manner than the comparison of external effect concentrations in two different media.

According to these considerations, the evaluation of the indicators S, B and A takes information gained in the evaluation of the respective previous indicators R, R and S, or R, S and B into account, although the assessment metric for these indicators is independent of the assessment metrics of the previous indicators, as has been demonstrated in the above indicator derivations.

Uncertainty

A risk evaluation can only be a scientific risk evaluation, if not only the facts are reported which are relevant for the risk evaluation, but if also knowledge about the relevance of these facts is communicated, and if knowledge about the size of gaps in knowledge and interpretation is conveyed. In the case of ecotoxicological risk profiles, this means that the uncertainties in the evaluation of each of the four indicators R, S, B and A are evaluated and combined with a fifth indicator, thus constituting the complete risk profile.

In evaluating each indicator, the following sources of uncertainties can be relevant for the risk profile:

- Strongly varying data
- Open questions about the reliability of data
- Comparatively little data, which produces a comparatively high uncertainty for the respective substance
- Comparatively low adequacy of the available data to the evaluation method

- Contradictory data

Of these uncertainty factors, only the first point, the variance of the data, can be quantified by mathematical calculations. Even more than in the cases of the other indicators, the evaluation of the uncertainty indicator therefore requires a sense for the relative importance of the different evaluation factors to be aggregated in the final indicator value.

3.3 Comparison of substances

An example for the interpretation of the ecotoxicological risk profiles made up of five indicators is given in Chapter 6. At this point, only a few general comments shall be given.

As a consequence of the many estimations and subjective evaluations that have to be carried out in order to obtain an ecotoxicological risk profile, the authors should always be mentioned together with the presentation of the risk profiles. The interpretation of the profiles and the consequences for risk management will depend on the priorities of the interpreter, and of his interests. Even an aggregation of the indicator values to one single indicator of ecotoxicological risk might be done, although this is not recommended here.

Once the indicator values have been collected in a table, they should speak for themselves and interpretation should be straightforward. If the number of chemicals is too high to simply compare the substances and interpret the indicator values in an ad-hoc way, the following procedure is recommended: First, the ranking of the substances according to the release indicator R only is looked at. Then, the spatiotemporal range indicator S is additionally considered, and the change in the evaluation is noted. In the next steps, the bioaccumulation indicator B, the biological activity indicator A and the uncertainty indicator U are additionally considered, with an intermediate evaluation stop after each indicator. Then, a Hasse-Diagram (cp. the example given in Section 2.3, Figure 2.3) can be generated[13], showing the unequivocal ordering relations, resulting from the generated risk profiles. Finally, a radial plot for the five indicators should be prepared, which is the most condensed form of risk communication of the ecotoxicological risk profiles recommended here.

This procedure will generally not lead to an unequivocal result, determining the substance which entails the least risk of ecotoxicological dam-

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[13] For this purpose, the dynamic website at `http://eckehaat.uft.uni-bremen.de/hasse/` can be used.

age upon usage. It does, however, provide a subjective impression of the pros and cons of the different substances, and it will hopefully help to inform the choices of decision-makers in a realistic way, whithout neglecting the risk of ecotoxicological damage, but also without overestimating our capacity to perceive it.

Part II

Case study:
Antifouling biocides

Chapter 4

Background

The use of antifouling agents for ship hulls has a history [77] that can be traced back as far as 700 b.C.. From this time, a phoenizian galley with planks plated with lead has been found. In the 16th century, the use of boards plated with lead for the fight against the ship worm *Teredo navalis* was started again, until plating of wooden ships with copper became predominant during the 18th century, which also prevented settlement of organisms on the outside. In the same period, plating of commercial ships with zink came up.[1]

The possibilities to use iron hulls in marine waters, where fouling is much heavier than in fresh water, was improved considerably, when the use of red lead (*minium*) for the coating of iron hulls was superseded by the use of patented paints during the second half of the 19th century. These paints contained copper, copper oxides, lead, lead oxides, sulfur, arsenic, mercury iodides and other iodides.

In 1860, John Rahtjen from Bremerhaven produced the first antifouling coating based on shellac, containing iron or mercury oxydes and arsenic. The short drying times of these coatings were the reason for their market leadership up to the beginning of world war one. Other variants of these coatings also contained antimonium sulfide and lead oxides.

Later, copper oxides, mercury oxides and organomercury compounds, but also zink oxides and substances already in use as fungicides as thiram, zineb, maneb and ziram (for structures, please refer to Table 4.1) gained primary importance. The use of organotin compounds was tested in the 1960ies, but since they do not form insoluble pigments, their use only became predominant after the introduction of tributyltin and triphenyltin

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[1] Later, in order to prevent the erosion of the metal at higher speeds, alloys were introduced. Copper/Nickel 90/10 alloys are still used for the hulls of smaller ships today.

copolymers, also referred to as Self-Polishing Copolymers (SPC).

Various national and international actions of risk management have taken place so far. The use of mercury and arsenic was prohibited in Europe among other uses specifically for the use in antifouling paints by Council Directive 89/677/EEC [78] in 1989. In the same Directive, the use of organotin compounds was restricted to ships with an overall length greater than 25 m, which had alredy been anticipated by France in 1982, and by the UK in 1987. The United States enacted the Organotin Antifouling Paint Control Act in 1988, where the restriction to a leaching rate of 4 μg per cm^2 per day, anticipated by many coastal states, was introduced to the Federal level. The combined restriction according to ship size and leaching rate was also adopted by South Africa, Canada, Sweden, but no restrictions on organotin were passed so far by e.g. Brazil, China, Korea, Russia and the United Arab Emirates. Total bans of organotin in antifoulings were so far only enacted in New Zealand, Switzerland and Austria, which either have no marine harbors at all, or no drydock facilities [79].

Organotin-free antifouling coatings are generally based on copper which is also widely used in organotin-containing coatings[2]. Instead of the predominant tributyltin compounds, organic "booster biocides" are used, because some fouling organisms like green ribbon grass *Enteromorpha sp.* are quite tolerant to copper.

Out of these booster biocides, Denmark has banned the use of Diuron and Irgarol®1051 starting in 2000 for pleasure boats and small commercial vessels. Very recently, the UK resolved to ban the use of Diuron totally, and the use of Irgarol 1051 for ships smaller than 25 m. The Netherlands have even banned the use of copper for pleasure boats.

These recent regulations were based on monitoring results, where mainly the waters of marinas were sampled and levels toxic to marine life were encountered. For the future of fouling control on ships, several questions remain open:

1. Is the use of copper in antifouling coatings sustainable in the way it is currently practiced?
2. Which biocide combinations entail the least risk of damage to the environment?
3. Is the use of biocides in antifouling coatings sustainable?

Neither the first nor the last question will be fully addressed in the present case study, since the ecotoxicological risk profiles present a *relative sub-*

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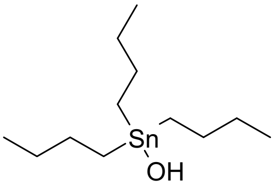
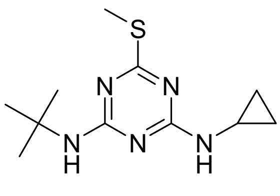
[2] This fact will be important in the discussion of the comparative risk analysis results

stance assessment. Nevertheless, some conclusions concerning the last question will be drawn from the result of an assessment of the first two indicators for copper. Even the second question is not discussed directly. However, the informations aggregated in the ecotoxicological risk profiles are a prerequisite for a comparative assessment of antifouling coatings with their respective biocide combinations.

From the substances listed in Table 4.1, five substances were selected for the first application of the risk profiles [8]. With this selection shown in Table 4.2, it was intended to cover the most widely used substances (Copper and Tributyltin) for which a lot of ecotoxicological data exist, and the most important candidates for a replacement of Tributyltin compounds, namely Irgarol®1051, Sea-Nine®211 and Zinc Omadine®[3]. While the ecotoxicological profiles of the substances had to be updated due to newly available data and a refined methodology, the selection of substances still seems to be a good choice.

Table 4.1: Antifouling biocides in use today, as they will occur in the environment, ordered according to the frequency (listed in parentheses) of their occurrence in the antifouling coatings listed by the UK authorities [80], augmented by a list from [81]

Name (Freqency)	**Structure in water**	**CAS-Nr**
Cu (654)	Cu^{2+}	
TBTOH (355)		1067-97-6
Irgarol (124)		28159-98-0
Zn (106)	Zn^{2+}	

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[3] Irgarol is a trademark of Ciba Specialty Chemicals, Sea-Nine is a trademark of Rohm & Haas and Omadine is a trademark of Arch Biocides (former Olin corporation)

Table 4.1: (continued)

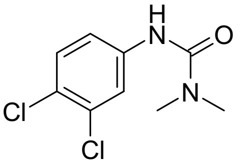
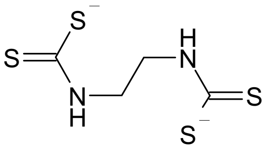
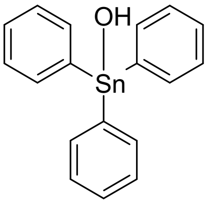
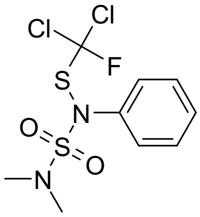
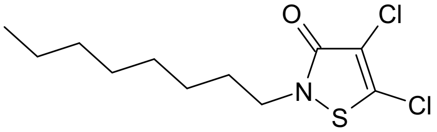
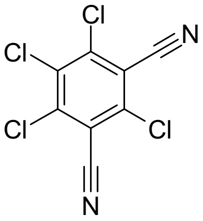
Name (Freqency)	Structure	CAS-Nr
Diuron (94)		330-54-1
Ethylenebisdithiocarbamate (57)		
TPTOH (31)		
Pyrithionate (27)		45529-38-2
Dichlofluanid (26)		1085-98-9
Sea-Nine (20)		64359-81-5
Chlorothalonil (20)		1897-45-6

Table 4.1: (continued)

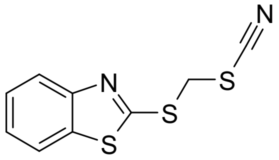
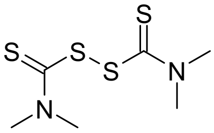
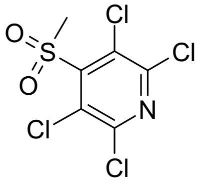
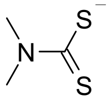
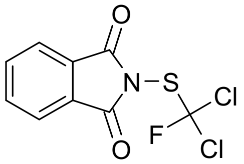
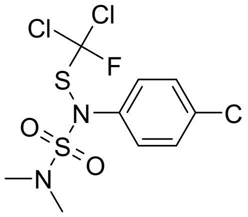
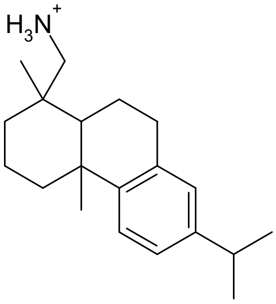
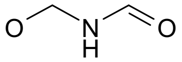
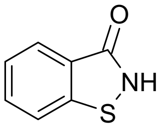
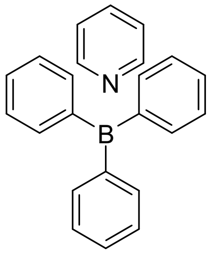
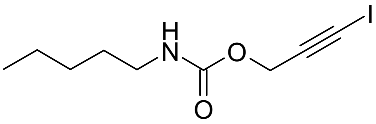
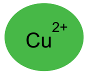
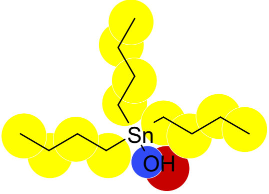
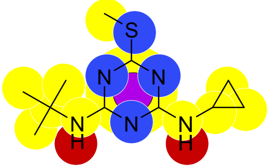
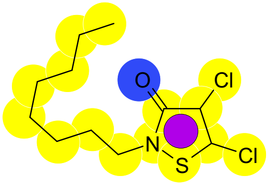
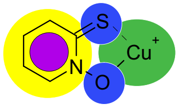
Name (Freqency)	**Structure**	**CAS-Nr**
TCMTB (10)		21564-17-0
Thiram (9)		137-26-8
Tetrachloromethylsulphonylpyridine (8)		13108-52-6
Dimethyldithiocarbamate (3)		
Fluorofolpet (0)		719-96-0
Tolyfluanid (0)		731-27-1
Dehydroabietylamine (0)		1446-61-3

Table 4.1: (continued)

Name (Freqency)	Structure	CAS-Nr
Hydroxymethylformamide (0)		13052-19-2
Benzisothiazolone (0)		2634-33-5
Pyridinetriphenylborane (0)		971-66-4
Iodopropynylbutylcarbamate (0)		55406-53-6

The identity of the substances is defined as the chemical species released to seawater, not the biocide product used for paint production. The names from the first row of Table 4.2 refer to this definition. This means, that with the substance copper, the copper content of all copper-releasing biocides is addressed, which are mainly the red copper oxydul (copper(I)-oxide Cu_2O) and, to a lesser amount, copper metal Cu(0), but also the white copper(I)-thiocyanate CuSCN and the black copper(I)-sulfide Cu_2S [80, 82]. All these substances will lead to a release of copper ions, i.e. Cu(II) in oxic surface waters. The mainly used compounds which will lead to the release of tributyltin (TBT) are tributyltin acrylate and methacrylate copolymers, bis(tributyltin)oxide, tributyltin chloride and tributyltin fluoride. Irgarol will be released, if the biocide product Irgarol®1051 is used, Sea-Nine will be released from Sea-Nine®211 and Pyrithionate from Zinc Omadine®, but also from other Pyrithionate salts, like Copper Omadine®, which is also listed in the EINECS and sold as an antifouling biocide, although it is not registered with the US EPA yet. An adaption as compared to the first evaluation [8] is the focus on the pyrithionate copper complex which is expected to be the dominating species of pyrithionate salts released to seawater.

Table 4.2: Names and Structures of the five biocides selected for the case study, as well as their molecular interaction potentials according to Jastorff [83]. Yellow: lipophilic interaction potential, red: hydrogen donor potential, blue: hydrogen acceptor potential, purple: $\pi - \pi$ interaction potential, green: cationic interaction potential.

				
Chemical name of the species predominant in seawater				
$Cu^{2+}_{(aq)}$	Tributyltin hydroxide	2-Tert-(butylamino)-4-(cyclopropylamino)-6-(methylthio)-1,3,5,-triazine	4,5-Dichloro-2-n-octyl-4-isothiazoline-3-one	[1-Hydroxy-2-pyridinethionate copper]$^{+}_{aq}$
Elemental composition				
Cu	$C_{12}H_{28}OSn$	$C_{11}H_{19}N_5S$	$C_{11}H_{17}Cl_2NOS$	C_5H_4NOSCu
Short names used throughout this dissertation				
copper	TBT	Irgarol	Sea-Nine	Pyrithionate
Trade names of the most important antifouling biocide product				
cuprous oxide	Tributyltin oxide	Irgarol®1051	Sea-Nine®211	Zinc Omadine®

The data sources that were used for the evaluation can be classified into different types. *Monographs* on TBT or organotin in general where the International Programme on Chemical Safety (IPCS) Environmental Health Criteria [84], the collections of Champ and Seligman [85] and de Mora [86], the review articles of K. Fent [87], R.J. Maguire [88] and J.P. Meador [89] as well as the risk analysis by L.W. Hall et al. [90] and the literature survey by S. Karlsson [91] and the report of the GDCh-Advisory Committee on Existing Chemicals of Environmental Relevance (BUA) [92]. A wealth of information could also be found in the Proceedings of the Organotin Symposia of the "Oceans" 1986 and 1987, and of the ACS Symposium "Tributyltin Compounds in the Aquatic Environment" from 1998. Monographs on Copper were the IPCS Environmental Health Criteria [93], the Criteria Document Copper of the Netherlands [94, 95], the evaluation of the Swedish National Chemicals Inspectorate KEMI [96, 97], the chapter about copper in [98], the risk analysis by L.W. Hall [56] and the assessment of the Danish Environmental Protection Agency [99]. Monographs on Irgarol were the "Information on active components" from Ciba Specialty Chemicals [100] and – containing almost the same information – the KEMI evaluation [101, 102, 103, 104]. A review [105] supported by Ciba Specialty Chemicals gave additional information. On Sea-Nine, the KEMI evaluation [106, 107] and the risk assessment of the Danish EPA [99] were the most important monographs, complemented by an ASTM (American Society for Testing and Materials) publication [108]. All of the above substances except for copper were also covered by a risk estimation on behalf of the German Federal Environmental Agency (UBA) [109]. On Pyrithione, the only comprehensive literature was the Danish risk assessment [99] and a risk assessment by the manufacturers [110].

A great number of *original scientific papers* where accessed for updated informations on the substances and for aspects which were not or not sufficiently covered by the above monographs. Several bibliographic databases were used for this purpose (Biological Abstracts, Chemical Abstracts, Science Citation Index, Toxline) and ChemID plus [4], the integrated search interface to the Medline, MeSH, Toxline, HSDB and Cancerlit databases of the Department of Health and Human Services and the National Cancer Institute of the United States of America.

Finally, some additional data, but mostly on TBT and mostly on mammal toxicity, was available through on-line fact databases like Environ-

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[4] http://chem.sis.nlm.nih.gov/chemidplus/

mental Chemicals Data and Information Network (ECDIN) [5], OEKOPRO[6] and the EXTension TOXicology NETwork[7].

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[5] http://ecdin.etomep.net

[6] http://www.oekopro.de

[7] http://ace.ace.orst.edu/info/extoxnet/ghindex.html

Chapter 5

A global fate model for antifouling biocides

In the following, the global distribution model that was used to evaluate the spatiotemporal range of the biocides in chapter 6, is described. The model parameters necessary for calculations are derived and the biocide data used as an input for the model are presented. Additionally, an evaluation of the model comparing wich discusses the comparison of result distributions generated with Monte Carlo simulations with concentrations measured in the environment. Special attention is given to copper, because of its natural occurrence in the environment. The results are presented and discussed in Chapter 6.

5.1 Model description

The evaluative antifouling-agent fate model AFM is a linear 9-box model (Level III [111]) and can be understood as an extension of the two-box model of the oceans first described by Broecker [112]. It is based on nine mass balance equations for the nine model compartments (boxes) given in Figure 5.1.3. The processes that are modeled are presently

1. Input from ship hulls into the surface water compartments
2. Dilution by water exchange between the compartments
3. Transport from water to underlying sediments by adsorption to particles and subsequent sedimentation
4. Export from the system by burial of sediments with new sediment

5. Export from the system by degradation according to first order kinetics. Degradation rates for water and sediment are different

The main purpose of the model is analyse the fate of different antifouling biocides. The evaluative parameter, the residence time τ is calculated from the amount estimated to be in the model system in steady state M_{ss} and the steady input into the model S_{ss}.

$$\tau = \frac{M_{\mathrm{ss}}}{S_{\mathrm{ss}}} \tag{5.1}$$

The layout of the five global water compartments and the four global sediment compartments as well as input and transport fluxes taken into account are shown in Figure 5.1. Compartment abbreviations, volumes, surface areas and particle concentrations are given in Table 5.1.

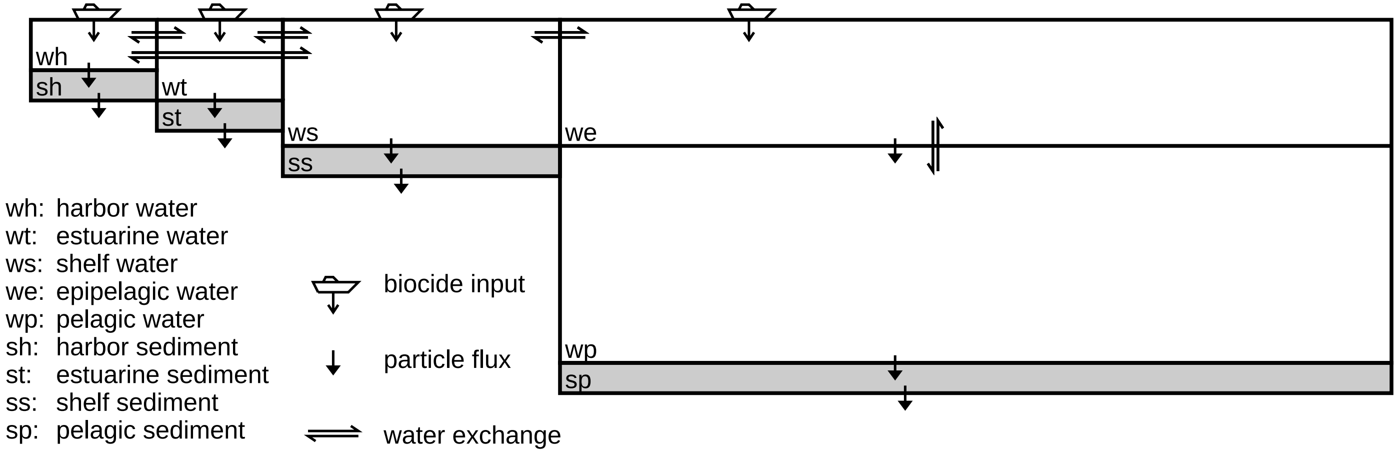


Figure 5.1: Layout of the compartments in the evaluative fate model. Water input by river water and water evaporation is not shown.

The compartments representing the biotope referred to as "marine biosphere" were derived according to the following reasoning: Epipelagic water (0-200 m) and pelagic water (>200 m) of the sea are distinguished as commonly found in the literature because of their large differences in elimination, transport and sedimentation of biocides. Water and sediment on the continental shelf are separated from the main ocean compartment because biocide input into shelf water and sedimentation rates are much higher on the shelf than in the deeper parts of the ocean. The sediment compartments are confined to a depth of 40 cm below the seafloor, considered as comprising the majority of the bioturbated layer [70]. Estuaries in which harbors are located are also separated due to the difference of biocide input, volume and water exchange as compared to shelf water. Commercial harbor basins have an even higher ratio of biocide input per volume, and are therefore represented separately by water and a sediment compartment.

The mass loss due to photolytical, biological and chemical degradation is described by kinetic rate constants k_{w} and k_{s} in water and sediment, respectively. Neither temperature dependence nor other spatial or temporal differences in degradation processes are included in the present fate model because of a lack of suitable degradation data.

In the following, compartment abbreviations from Table 5.1 will be used as superscript indices for mathematical symbols. The first letter of each compartment abbreviation indicates if it is a water (w) or a sediment (s) compartment, the second letter gives the geographical characterization. In the subscript indices, w stands for water and p for particles. For example, $F_{\mathrm{p}}^{\mathrm{ws,ss}}$ signifies the flux of particles from the shelf water compartment to the shelf sediment compartment.

5.1.1 Input estimations

The magnitude of the estimated total release rate S_{tot} from ship coatings to the marine environment does not affect the calculated residence times of the biocides, since the steady state quantity M_{ss} in equation 5.1 is directly proportional to S_{ss}. Nevertheless, realistic approximations for release rates from ships were used in order to be able to compare calculated concentrations with concentrations measured in the environment (Section 5.2).

Antifouling biocides are released to the marine biosphere from biocide factories, during transport of biocides, during application of antifouling paints and in the process of removal of antifouling paints from ships in drydocks. Not all of these release pathways are negligible, but they can

Table 5.1: Volumes V, surface areas A [113, 114] and particle-water ratios r_{pw} [115, 70] of the compartments, summed water exchange rates $F_{\mathrm{w}}^{\mathrm{wx,wy}}$ and sediment burial rates B as well as turnover τ_{t} times (d = days, y = years) of water in the water compartments and of solid matter in the sediment compartments. The abbreviations wh, wt, ws, we and wp stand for harbor water, estuary water, shelf water, epipelagic water and pelagic water, respectively. The abbreviations sh, st, ss and sp stand for harbor sediment, estuarine sediment, shelf sediment and pelagic sediment, respectively

Comp.	V (m^3)	A (m^2)	r_{pw} (g L^{-1})	$\sum_y F_{\mathrm{w}}^{\mathrm{wx,wy}}$ (m^3 s^{-1})	B (m y^{-1})	τ_{t}
wh	$1.2 \cdot 10^{10}$	$1.2 \cdot 10^{9}$	0.01	$5.5 \cdot 10^{3}$		2.5 d
wt	$3.0 \cdot 10^{10}$	$1.2 \cdot 10^{9}$	0.01	$1 \cdot 10^{5}$		3.3 d
ws	$2.2 \cdot 10^{15}$	$2.7 \cdot 10^{13}$	$1 \cdot 10^{-3}$	$7.5 \cdot 10^{8}$		34 d
we	$6.7 \cdot 10^{16}$	$3.3 \cdot 10^{14}$	$7 \cdot 10^{-5}$	$7.8 \cdot 10^{8}$		2.7 y
wp	$1.3 \cdot 10^{18}$	$3.3 \cdot 10^{14}$	$2 \cdot 10^{-6}$	$3.4 \cdot 10^{7}$		1200 y
sh	$4.8 \cdot 10^{8}$	$1.2 \cdot 10^{9}$	600		$2 \cdot 10^{-3}$	200 y
st	$4.8 \cdot 10^{8}$	$1.2 \cdot 10^{9}$	600		$2 \cdot 10^{-3}$	200 y
ss	$1.1 \cdot 10^{13}$	$2.7 \cdot 10^{13}$	800		$3 \cdot 10^{-5}$	13300 y
sp	$1.3 \cdot 10^{14}$	$3.3 \cdot 10^{14}$	800		$1.2 \cdot 10^{-5}$	33400 y

be technically controlled to a high degree. On the contrary, release from coatings of ships in service is desired for the purpose of fouling control. Because of its essential role in fouling protection of ships, only this release is being considered in the present residence time study. This must be kept in mind for the model evaluation described below.

For TBT and the organic biocides, a mean release rate of 3.5 μg per cm^2 per day was assumed for travelling vessels, as was estimated for the release of TBT from state-of-the-art self-polishing copolymer coatings [116]. For copper, the value 50 μg cm^{-2} d^{-1} used by experts from an European Community project [81] was adopted. For stationary vessels in harbors, a reducing factor of 10 was applied to all release rates, as reported in [116] (compare section 6.1).

For the calculation of the total release rates, a total surface area of the world commercial fleet of $3 \cdot 10^7$ m^2 was estimated from the ships with gross tonnage > 300 in 1998 [117] and average wetted hull areas of 8 types of ships [118] as shown in table 5.2. It was assumed that at any time 10 % of this wetted hull surface area is stationary in harbors, 1 % is travelling

Table 5.2: Wetted surface area s of the world fleet by ship types

Ship type	n^a	$\bar{s}^b/\mathrm{m}^2$	$ws_{\mathrm{tot}}/10^6\mathrm{m}^2$
Oil tankers	6885	6518.33	44.9
Chemical tankers	1329	2169.19	2.9
Liquid gas tankers	1009	3372.24	3.4
Bulk carriers	5903	7907.99	46.7
OBO carriers	236	14857.14	3.5
Container ships	2170	6048.05	13.1
General cargo ships	17438	2548.11	44.4
Passenger and cargo passenger ships	3530	968.43	3.4
Total	38500	4216.31[c]	162.3

[a]from [117] [b]average values from [118] [c]weighted average

in estuaries with harbors, 64 % is travelling above the continental shelf and 25 % is travelling in the open sea. For the case of all ships using TBT, the global release estimation from antifouling paints results to 1900 metric tons per year. If all ships use copper, a release from their hulls of $27 \cdot 10^3$ t y^{-1} is estimated.

Because of the large non-antifouling inputs of copper into the marine environment, these were estimated from literature values. On this basis, the potential contribution of copper antifouling paints on ships to the total copper input was additionally evaluated (Section 5.2). These background inputs where only used for the model evaluation. The residence times (Table 6.2 and Figure 6.2) used for the comparison of the biocides where calculated with the release pattern only from ship hulls.

For the total copper flux from rivers into the oceans, a geometric mean of a value from a recent study [119] and three older values [120, 121, 122] gave $5 \cdot 10^5$ t y^{-1}. One percent of this amount was apportioned as input into the wt compartment, since the river water $F_{\mathrm{w}}^{\mathrm{wr,wt}}$ of the model estuaries according to equation 5.2 amounts to about 1 percent of the total riverine water. 99 percent of the copper flux from rivers were apportioned as input into the shelf water compartment.

The total atmospheric input into the oceans is estimated by a geometric mean of values from [123, 122] to be $51 \cdot 10^3$ t y^{-1}. This amount was split as input into the surface water compartments according to their surface areas (Table 5.1). All modeled copper fluxes into the system are given in Table 5.4.

5.1.2 Water exchange

Water exchange from harbors is estimated on the basis of an approximative typical water exchange for commercial harbor basins every 60 hours. This exchange flow is split in the proportion 1:9 in estuary and shelf water, since every tenth harbor is assumed to be located in an estuary.

For estuarine water exchange fluxes $F_{\mathrm{w}}^{\mathrm{wt,ws}}$ into the shelf sea and from the shelf sea $F_{\mathrm{w}}^{\mathrm{ws,wt}}$ in relation to river discharge $F_{\mathrm{w}}^{\mathrm{wr,wt}}$, the following approximations are used [124]

$$F_{\mathrm{w}}^{\mathrm{wt,ws}} = 10 \cdot F_{\mathrm{w}}^{\mathrm{wr,wt}} \; ; \; F_{\mathrm{w}}^{\mathrm{ws,wt}} = 9 \cdot F_{\mathrm{w}}^{\mathrm{wr,wt}} \tag{5.2}$$

For the global model, the discharge from rivers into estuaries under influence of harbors $F_{\mathrm{w}}^{\mathrm{wr,wt}}$ was estimated to 10^4 cubic meters per second.

An average water exchange rate between shelf water and the open ocean of 3 $\mathrm{m}^2\ \mathrm{s}^{-1}$ ([125] p. 407, Table 5) multiplied with an approximate global shelf shoreline of $250 \cdot 10^6$ m gives $F_{\mathrm{w}}^{\mathrm{ws,we}} = F_{\mathrm{w}}^{\mathrm{we,ws}} = 7.5 \cdot 10^8\ \mathrm{m}^3\ \mathrm{s}^{-1}$. The cited exchange rate is only representative of continental margins with relatively straight edges. Enclosed shelf areas or even brackish water bodies like the Baltic Sea are therefore not represented by the shelf water compartment.

The vertical exchange rate of 3 m per year for epipelagic water with the underlying pelagic water is taken from Broecker [120], p. 253, corresponding to an overall mixing rate of $3.4 \cdot 10^7\ \mathrm{m}^3\ \mathrm{s}^{-1}$ (cp. also [121] and [113] p. 7).

5.1.3 Particle sedimentation and sediment burial

Harbor sediment accumulation is in a first approximation supposed to be similar to estuarine accumulation in terms of depth/time. 20 cm per 100 years from [126] multiplied with the total harbor area convert to $F_{\mathrm{p}}^{\mathrm{wt,st}} = F_{\mathrm{p}}^{\mathrm{wh,sh}} = 45\ \mathrm{kg\ s}^{-1}$.

Shelf sediment accumulations rates are taken from [127], p. 49, namely the terrigeneous sedimentation, averaging to approximately 30 m per million years. With 0.6 as porosity and $2 \cdot 10^3\ \mathrm{kg\ m}^{-3}$ as density of particles, the total sedimentation above the shelf was estimated to be $F_{\mathrm{p}}^{\mathrm{ws,ss}} = 2.1 \cdot 10^4\ \mathrm{kg\ s}^{-1}$.

For the particle flow from the epipelagial to the pelagial, Romankevich [128] gives sedimentation rates of organic carbon in dependence of the depth and primary production (p. 68). At 200 m, with a primary production of 50 g C m^{-2} per year [70], an average annual carbon flux of

$8.3 \cdot 10^{-7}$ mol cm^{-2} y^{-1} is calculated, in good agreement with Collier [121]. For the total oceanic area we get about $1 \cdot 10^5$ kg s^{-1} in good consistency with values given by Romankevich [128], p. 26. Assuming this to be ten weight percent of the total particle flux ([128], p. 66) from epipelagic water to pelagic water, we get $F_{\mathrm{p}}^{\mathrm{we,wp}} = 1 \cdot 10^6$ kg s^{-1}.

Benthic sedimentation rates are taken from Neshyba [114], p. 90 and Ricken [127], p. 49. The approximate mean of 12 mm per 1000 years, assuming an average porosity of 60 percent ([113], p. 994) and a mean particle density of 2 kg/L, gives a particle mass export from pelagic water to pelagic sediment of roughly $1 \cdot 10^5$ kg s^{-1}. Sedimentation rates and the corresponding residence times of settled sediment are collected in Table 5.1.

The molar quantity M of a biocide in each compartment is split in a fraction α_{w} in the water phase and a particulate fraction α_{p}. The water phase fraction is described in terms of the particle-water ratio r_{pw} and the particle-water partitioning constant K_{pw} by

$$\alpha_{\mathrm{w}} = \frac{c_{\mathrm{d}}V}{c_{\mathrm{p}}M_{\mathrm{p}} + c_{\mathrm{d}}V} = \frac{1}{1 + \frac{M_{\mathrm{p}}}{V}\frac{c_{\mathrm{p}}}{c_{\mathrm{d}}}} = \frac{1}{1 + r_{\mathrm{pw}}K_{\mathrm{pw}}} \tag{5.3}$$

where c_{d} [mol m^{-3}] is the concentration of the substance in solution, c_{p} [mol kg^{-1}] is the concentration in the particles > 0.45 μm, and M_{p} [kg] is the particulate mass and the Volume V [m^3] refers to the volume of the liquid phase.

Molar flows of biocide F_{B} due to particle scavenging from water compartment x to the compartment y below are thus expressed by

$$F_{\mathrm{B}}^{\mathrm{x,y}}(\text{scavenging}) = c_{\mathrm{p}}^{\mathrm{x}}F_{\mathrm{p}}^{\mathrm{x,y}} = \frac{\alpha_{\mathrm{w}}M}{V}K_{\mathrm{pw}}^{\mathrm{w}}F_{\mathrm{p}}^{\mathrm{x,y}} \tag{5.4}$$

Biocide loss from each sediment compartment by sediment burial can be described in dependence of the sediment burial rate B (Table 5.1) and the sediment depth z by

$$\dot{M} = \frac{B}{z}M \tag{5.5}$$

The resulting system of nine coupled linear differential equations is given explicitly in Figure 5.1.3. The water residence time as the average time a biocide molecule spends in the water compartments only is given by its total quantity in steady state ($\dot{\vec{M}} = 0$) in the water compartments divided by the biocide flux into the system. Total residence times, also derived from steady state, were calculated according to equation 5.1.

$$\begin{aligned}\dot{M}^{\mathrm{wh}} &= -\left(\frac{F_{\mathrm{w}}^{\mathrm{wh,wt}} + F_{\mathrm{w}}^{\mathrm{wh,ws}} + \alpha_{\mathrm{w}} K_{\mathrm{pw}} F_{\mathrm{p}}^{\mathrm{wh,sh}}}{V^{\mathrm{wh}}} + k_{\mathrm{w}}\right) M^{\mathrm{wh}} \\ &\quad + \frac{F_{\mathrm{w}}^{\mathrm{wt,wh}}}{V^{\mathrm{wt}}} M^{\mathrm{wt}} + \frac{F_{\mathrm{w}}^{\mathrm{ws,wh}}}{V^{\mathrm{ws}}} M^{\mathrm{ws}} + S^{\mathrm{wh}}\end{aligned} \tag{5.6}$$

$$\begin{aligned}\dot{M}^{\mathrm{wt}} &= \frac{F_{\mathrm{w}}^{\mathrm{wh,wt}}}{V^{\mathrm{wh}}} M^{\mathrm{wh}} - \left(\frac{F_{\mathrm{w}}^{\mathrm{wt,wh}} + F_{\mathrm{w}}^{\mathrm{wt,ws}} + \alpha_{\mathrm{w}} K_{\mathrm{pw}} F_{\mathrm{p}}^{\mathrm{wt,st}}}{V^{\mathrm{wt}}} + k_{\mathrm{w}}\right) M^{\mathrm{wt}} \\ &\quad + \frac{F_{\mathrm{w}}^{\mathrm{ws,wt}}}{V^{\mathrm{ws}}} M^{\mathrm{ws}} + S^{\mathrm{wt}}\end{aligned} \tag{5.7}$$

$$\begin{aligned}\dot{M}^{\mathrm{ws}} &= -\left(\frac{F_{\mathrm{w}}^{\mathrm{ws,wh}} + F_{\mathrm{w}}^{\mathrm{ws,wt}} + \alpha_{\mathrm{w}} K_{\mathrm{pw}} F_{\mathrm{p}}^{\mathrm{ws,ss}} + F_{\mathrm{w}}^{\mathrm{ws,we}}}{V^{\mathrm{wt}}} + k_{\mathrm{w}}\right) M^{\mathrm{ws}} \\ &\quad + \frac{F_{\mathrm{w}}^{\mathrm{wh,ws}}}{V^{\mathrm{wh}}} M^{\mathrm{wh}} + \frac{F_{\mathrm{w}}^{\mathrm{wt,ws}}}{V^{\mathrm{wt}}} M^{\mathrm{wt}} + \frac{F_{\mathrm{w}}^{\mathrm{ws,we}}}{V^{\mathrm{we}}} M^{\mathrm{we}} + S^{\mathrm{ws}}\end{aligned} \tag{5.8}$$

$$\begin{aligned}\dot{M}^{\mathrm{we}} &= \frac{F_{\mathrm{w}}^{\mathrm{ws,we}}}{V^{\mathrm{ws}}} M^{\mathrm{ws}} - \left(\frac{F_{\mathrm{w}}^{\mathrm{we,ws}} + F_{\mathrm{w}}^{\mathrm{we,wp}} + \alpha_{\mathrm{w}} K_{\mathrm{pw}} F_{\mathrm{p}}^{\mathrm{we,wp}}}{V^{\mathrm{we}}} + k_{\mathrm{w}}\right) M^{\mathrm{we}} \\ &\quad + \frac{F_{\mathrm{w}}^{\mathrm{wp,we}}}{V^{\mathrm{wp}}} M^{\mathrm{wp}} + S^{\mathrm{we}}\end{aligned} \tag{5.9}$$

$$\begin{aligned}\dot{M}^{\mathrm{wp}} &= \frac{F_{\mathrm{w}}^{\mathrm{we,wp}} + \alpha_{\mathrm{w}} K_{\mathrm{pw}} F_{\mathrm{p}}^{\mathrm{we,wp}}}{V^{\mathrm{we}}} M^{\mathrm{we}} \\ &\quad - \left(\frac{F_{\mathrm{w}}^{\mathrm{wp,we}} + \alpha_{\mathrm{w}} K_{\mathrm{pw}} F_{\mathrm{p}}^{\mathrm{wp,sp}}}{V^{\mathrm{wp}}} + k_{\mathrm{w}}\right) M^{\mathrm{wp}}\end{aligned} \tag{5.10}$$

$$\dot{M}^{\mathrm{sh}} = \frac{\alpha_{\mathrm{w}} K_{\mathrm{pw}} F_{\mathrm{p}}^{\mathrm{wh,sh}}}{V^{\mathrm{wh}}} M^{\mathrm{wh}} - \left(\frac{B^{\mathrm{sh}}}{z} + k_{\mathrm{s}}\right) M^{\mathrm{sh}} \tag{5.11}$$

$$\dot{M}^{\mathrm{st}} = \frac{\alpha_{\mathrm{w}} K_{\mathrm{pw}} F_{\mathrm{p}}^{\mathrm{wt,st}}}{V^{\mathrm{wt}}} M^{\mathrm{wt}} - \left(\frac{B^{\mathrm{st}}}{z} + k_{\mathrm{s}}\right) M^{\mathrm{st}} \tag{5.12}$$

$$\dot{M}^{\mathrm{ss}} = \frac{\alpha_{\mathrm{w}} K_{\mathrm{pw}} F_{\mathrm{p}}^{\mathrm{ws,ss}}}{V^{\mathrm{ws}}} M^{\mathrm{ws}} - \left(\frac{B^{\mathrm{ss}}}{z} + k_{\mathrm{s}}\right) M^{\mathrm{ss}} \tag{5.13}$$

$$\dot{M}^{\mathrm{sp}} = \frac{\alpha_{\mathrm{w}} K_{\mathrm{pw}} F_{\mathrm{p}}^{\mathrm{wp,sp}}}{V^{\mathrm{wp}}} M^{\mathrm{wp}} - \left(\frac{B^{\mathrm{sp}}}{z} + k_{\mathrm{s}}\right) M^{\mathrm{sp}} \tag{5.14}$$

Figure 5.2: Mass balance equations used in the model AFM. Superscript indices indicate compartments

5.1.4 Degradation and partitioning data for the biocides

For the biocide specific parameters k_{w} (degradation rate constant in water), k_{s} (degradation rate constant in sediment) and K_{pw} (partitioning constant between suspended particulate matter and water), strongly varying data were encountered in the literature. These parameters were described probabilistically using lognormal distributions (Table 5.3). From K_{pw}, k_{w} and k_{s} values for tributyltin and K_{pw} values for copper from literature data it was possible to do Maximum Likelihood estimations of lognormal distributions [50]. The variation was attributed mainly to variability of the observing systems, which corresponds to, but is not equivalent to the variability in the environment. For the degradation of tributyltin in sediments, rate constants estimated from depth profiles were used as well as rate constants from sediment microcosms.

Table 5.3: Geometric mean of particle-water sorption constants in water (K_{pw}) and degradation rates in water (k_{w}) as well as in sediment (k_{s}) with the number of data points n used for distribution estimations, the 5th percentile $q_{0.05}$ and the 95th percentile $q_{0.95}$ of the estimated lognormal distributions

Substance	Parameter	n	Mean	$q_{0.05}$	$q_{0.95}$	Unit	Source(s)
TBT^+/TBTOH	K_{pw}	13	$4.7 \cdot 10^3$	$0.28 \cdot 10^3$	$79 \cdot 10^3$	(L kg^{-1})	[129, 130, 131, 132, 133]
	k_{w}	13	0.061	0.042	0.088	(d^{-1})	[134, 135, 136, 137]
	k_{s}	4	0.24	0.062	0.90	(y^{-1})	[138, 139, 140, 141]
Cu^{2+}	K_{pw}	4	$45.7 \cdot 10^3$	$10.3 \cdot 10^3$	$204 \cdot 10^3$	(L kg^{-1})	[142, 143, 144, 145]
Irgarol	K_{pw}	1[d]	$3.1 \cdot 10^3$	$0.36 \cdot 10^3$	$26 \cdot 10^3$	(L kg^{-1})	[146]
	k_{w}	1[d]	0.0054[a]	0.0024	0.012	(d^{-1})	calc. from [147], as in [101]
	k_{s}	1[d]	0.086	0.038	0.19	(y^{-1})	[148], as in [102]
DCOI	K_{pw}	2[d]	$1.1 \cdot 10^3$[c]	$0.13 \cdot 10^3$	$9.3 \cdot 10^3$	(L kg^{-1})	[149, 150], as in [106, 107]
	k_{w}	5	0.44	0.07	2.7	(d^{-1})	[151], as in [99]
	k_{s}	1[d]	$6.1 \cdot 10^3$[b]	$2.7 \cdot 10^3$	$14 \cdot 10^3$	(d^{-1})	[152], as in [106, 153]

[a] only used for surface water compartments [b] In [152], 4.8 % to 0.7 % of the applied radioactivity as DCOI in aerobic water from days 15 to 30 was not identified and around 60 % was not extractable from the sediment. Despite the high degradation rate claimed by the manufacturers in [154], 4.8 and 2.6 % of radioactivity was found extractable as DCOI from anaerobic sediments on days 14 and 61, respectively [c] Geometric mean of the two values was used as estimator [d] No maximum likelihood estimates were carried out.

For Irgarol and DCOI, mainly values from commercially performed studies as cited in administrative reports [101, 102, 106, 107, 99, 108] were used as estimators of geometric means of the corresponding lognormal distributions. Except for the degradation of DCOI in water, where a maximum likelihood estimate could be performed, the geometric standard deviations expressing the parameter variability for these two organic biocides were estimated as intermediate between the geometric standard deviations for tributyltin (K_{pw}, k_{w} and k_{s}) and Cu (only K_{pw}) as shown in Table 5.3.

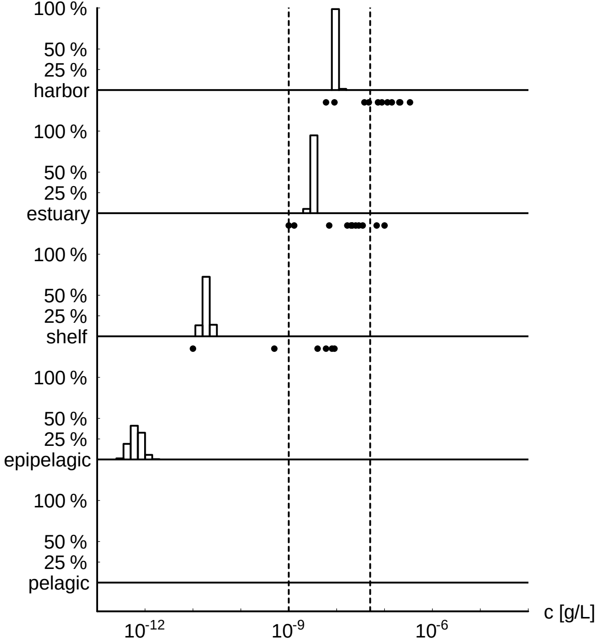
The predominant species of TBT in seawater will be the neutral TBTOH, since its acidity constant $\mathrm{p}K_{\mathrm{a(TBT^{+})}}$ is 6.25 at standard conditions [155]. The vapor pressure of TBTOH was estimated with the MPBP software v1.30 of Syracuse Research Center to be $2 \cdot 10^{-3}$Pa but it is not included in the group of volatile organotin compounds given in a recent study [156]. The vapor pressures of the two other organic biocides are even lower. Thus, except for copper, none of the substances meet the criterion for being involatile given by Mackay et al. [111] (vapor pressure $< 10^{-7}$ Pa). The inclusion of the process of volatilization of the biocides from the seawater would therefore possibly increase the accuracy of the model.

With the lognormal distributions for the model parameters k_{w}, k_{s} and $K_{\mathrm{pw}}^{\mathrm{w}}$ in Table 5.3, Monte Carlo simulations were carried through in order to analyze the uncertainty of the model output due to the uncertainty of these model parameters. For every calculation, 10000 parameter combinations were generated according to the estimated lognormal distributions of the input parameters. The use of random arrays larger than this did not noticeably change the resulting probability distributions of the output parameters. Generation of random arrays and all calculations were carried out using the Mathematica® software, version 4.0 by Wolfram Research, Inc. All degradation and partitioning data are publicly accessible in the database UFT_SAR [157] (see Appendix A).

5.2 Model evaluation

Tributyltin. TBT concentrations measured in water since 1990 and in sediment since 1985 (Tables A.3 and A.2 in the Appendix) where collected. In many cases, the geographic characterization of sampling sites only allowed tentative attribution to the idealized compartments of the model. The reported limit of detection given for the measurements of tributyltin in seawater was generally between 1 and 50 ng/L, for sediments it was between 0.2 and 250 μg/kg dry weight.

a) Tributyltin - water concentrations



a) Copper - water concentrations

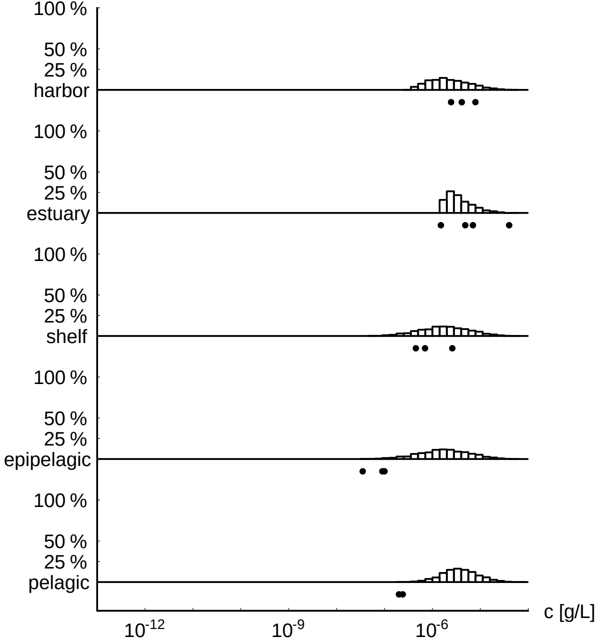


Figure 5.3: Comparison of histograms of calculated result distributions with measured concentrations (●) for a) TBT in water compartments, and b) dissolved fraction of Cu in the water compartments. Experimental values and their sources are given in Appendix A. Dotted lines in a) depict the typical range of TBT detection limits

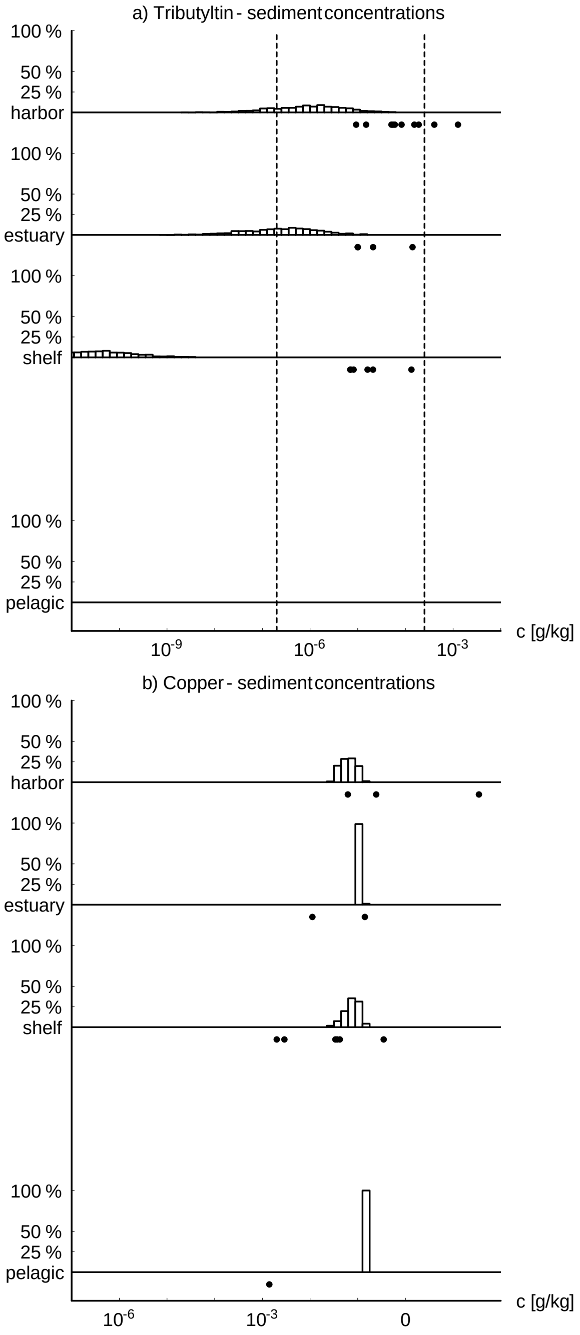


Figure 5.4: Comparison of histograms of calculated result distributions with measured concentrations (•) for a) TBT in sediment compartments and b) Cu in sediment compartments. Experimental values and their sources are given in Appendix A. Dotted lines in a) depict the typical range of TBT detection limits

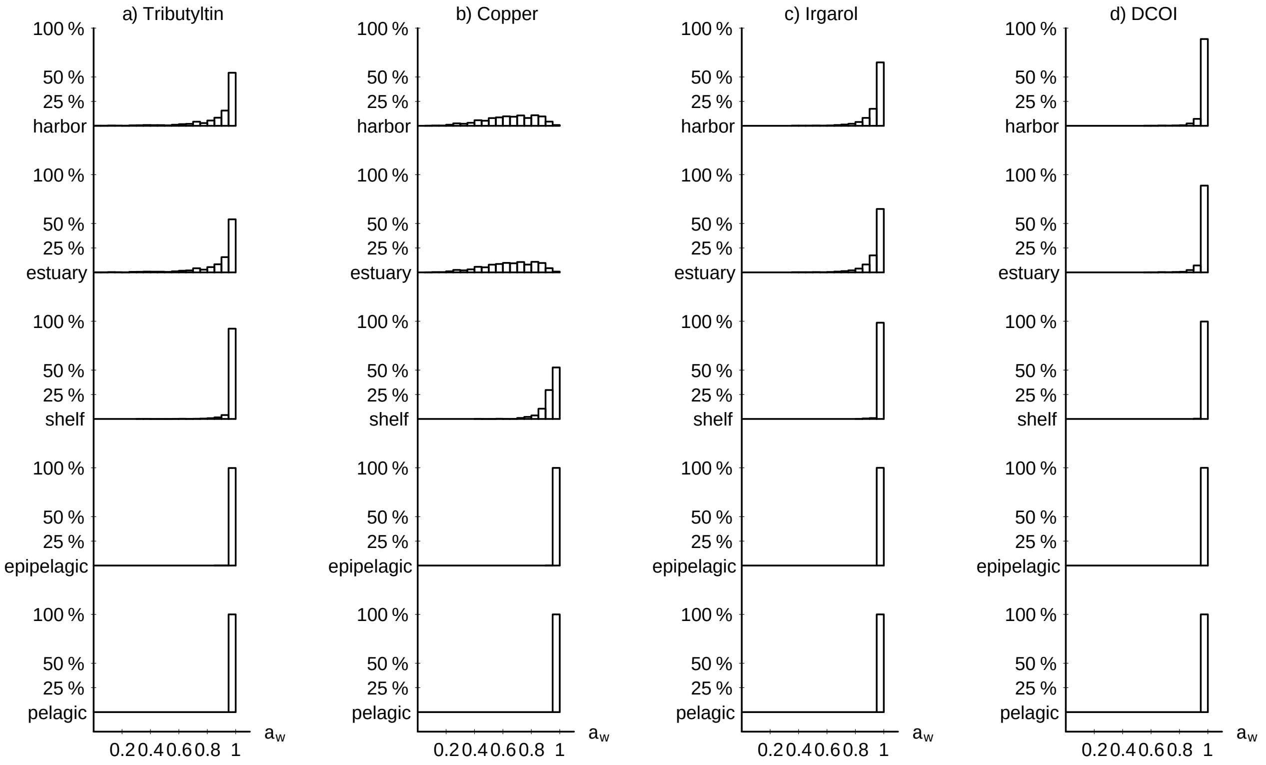


Figure 5.5: Histograms of the calculated dissolved fractions α_w for a) Tributyltin, b) Copper, c) Irgarol and d) Sea-Nine (DCOI) in the water compartments according to the model calculations

Figures 5.3 a) and 5.4 a) show a comparison of these measured concentrations with histograms of concentration data for total tributyltin from a Monte Carlo simulation for all model compartments. The most probable concentration values in water range from 10 ng/L in the harbor compartment down to $0.6 \cdot 10^{-12}$ g/L in the epipelagic water compartment and $3 \cdot 10^{-17}$ g/L for the pelagic compartment (not shown).

For shelf water, epipelagic and pelagic water, the sorption constants suggest that TBT will practically completely be present in the dissolved phase. In harbor and estuarine water, the dissolved fraction of TBT will most probably be greater than 90 % (Figure 5.5 a).

Because of strong geographic variability of harbor basins and estuaries as well as variations in the release over time, the measured TBT water concentrations, indicated by dots in Figure 5.3 a), show much more variability than the simulated values. Especially harbor and estuarine water concentrations of TBT are controlled by relatively fast water exchange process with water residence times in the model of 2.5 and 3.3 days, respectively. Considering the possibility of additional TBT inputs from drydock facilites into these compartments, resulting in higher TBT levels in real harbors and harbor-influenced estuaries, the validity of the estimated concentrations is not contradictory to the monitoring values. The monitoring data for shelf water are partly biased, because the values above 1 ng/L are from coastal areas close to very busy harbors. The reliability of the two values below 1 ng/L is unclear, since they are below the common range for the determination limit.

In the first two sediment compartments, the overlap of estimated and measured TBT concentrations supports the validity of the model. Again, a complete agreement can not be expected, since TBT input from drydock facilities is not represented in the model. However, the recent monitoring data from the Iberian coast (Spain) put the model results into question, since sites with a low shipping density were sampled as well.

The variability of the calculated concentrations in harbors and estuaries results from the combined variabilities of the adsorption constant to settling particles K_{pw} and the degradation rate in sediments k_{s}. The broad distributions indicate that a spatially resolved modelling approach would have to be based on more precise knowledge about the causes of this variability in the biocide-specific parameters.

Copper. Table 5.4 gives the estimated copper inputs into the surface water compartments. Figures 5.3 b) and 5.4 b) show calculated histograms of dissolved copper concentrations as compared to concentrations measured in filtered water and in sediments (Supporting information). The steady state mass of copper is mainly present in the pelagic sediment

Table 5.4: Estimated copper fluxes into the surface water compartments of the model in tons per year and contribution of antifouling paints f_{AF}

Compartment	**Abbr.**	S_{riv}	S_{atm}	S_{AF}	S_{tot}	f_{AF}
Harbor Water	wh	0	0.17	300	300	0.999
Estuary Water	wt	5000	0.17	150	5150	0.029
Shelf Water	ws	498000	3880	19100	520980	0.037
Epipelagic Water	we	0	47110	7400	54510	0.136
Total		503000	50990	26950	580940	0.05

(most probable value about 70 %) and pelagic water (most probable value about 20 %, data not shown).

Copper is sorbed by particulate matter > 0.45 μm to a significant degree in the particulate-rich harbor, estuary and shelf compartments (Figure 5.5b). As a consequence, scavenging is significant and the uncertainty in sorption to particles leads to a much higher variation of modeled concentrations than for TBT. Nonetheless, the estimated concentration ranges in the generic harbor, harbor estuary and shelf compartments are in reasonable agreement with data from the literature.

The comparison of measured and calculated copper concentrations for harbor, estuarine and shelf water shows that the uncertainty in the sorption parameter K_{pw} results in similar variation in concentration values as the temporal and spatial variability of the real world (Figure 5.3b). The model deviation in epipelagic and pelagic water could be caused by several reasons: a) particle export to bottom sediments could be underestimated, since the particle flows are quite uncertain, b) the sorption constant for deep sea particle sorption might be too low, since it has been derived for surface water and the chemistry of the particles changes through their degradation and through redissolution of calcium carbonate during passage down the water column [127]. Finally, c) the oceans might not have reached steady state concentrations with the increased copper inputs [158] since industrialization (compare section 7.2).

The overestimation of copper concentrations in pelagic sediments amounts to almost two orders of magnitude while it is only about one order of magnitude for pelagic water. This might indicate, contrary to hypothesis b) given above, that copper sorption to deep sea particles is lower than to surface water particles.

Except for the TBT concentrations on the continental shelf, the deviations are small considering the low spatial and temporal resolution of the model.

5.3 Remaining uncertainties

Model parameters and model structure. The size of the global harbor basin compartment is plausible, but it was impossible to come up with a reliable estimation. Similarly, the apportionment of the underwater hull area of the world commercial fleet to the different surface water compartments is only a rough approximation.

Uncertainties due to the structure of the model primarily concern the steady-state character of the model. The periodical tidal flow in estuaries is generally represented in the model by the water exchange rates of the estuary compartment with the shelf sea. Again, this will be quite different for each individual estuary, so no conclusion about the concentration in a single estuary can be drawn. Fluctuations in biocide input will take place on the time scale of years. The input fluctuations are relevant for the biocides with residence times of the same order of magnitude or longer. Especially for these biocides (e.g. Cu in the chosen subset), a dynamic model would be preferable.

Another deficiency inherent in the model structure is that only substance-specific parameters were modeled with probability distributions. A probability distribution for water residence times in harbor basins and for the particle settlement rates in all water compartments would lead to a much more realistic depiction of variability in the model output.

Biocide parameters. The dependency of degradation rates on temperature, redox potential, and on the concentration and activity of biomass could not be included in the model, because the available experimental data was not sufficiently detailed. Concerning the sorption constants to particles K_{pw}, the difference between terrigeneous particles (predominant in estuaries and shelf) and biogenic particles (predominant in epipelagic and pelagic water) was neglected, because no appropriate data were available.

If the model structure is reasonable, as suggested by the satisfying simulation of the copper concentrations, the tributyltin degradation rates must largely overestimate the real degradation taking place in the environment. Possible reasons could be the lack of correcting the degradation rates for temperature, the much lower metabolic activity of plankton in the shelf compartment, or even a systematic error of previous degradation observations due to uptake of TBT into algae during the experiments [60]. Recent measurements suggest that the total degradation of TBT in

North Sea water is slower by a factor 7 than the value from Table 5.3. This would partly explain the model deviation. Another source of errors is the assumption that the sediment compartment is well-mixed. Samples are likely to be taken from the uppermost part of the sediment profile, whereas the modeled concentration represents all the sediment up to a depth of 40 cm where it has aged considerably.

The fast disappearance of DCOI and other isothiazolones from aqueous biotic systems seems to be caused by its reaction with thiol groups of intracellular nucleophiles like glutathione or of proteins [159]. The high amount of inextractable residues in DCOI degradation studies, where organic matter is present, supports the hypothesis of covalent binding. However, reactions of isothiazolones with thioles and other nucleophiles have been shown to be reversible [160] and the presence of DCOI found in an anaerobic sediment-seawater system after 61 days [154] suggests that DCOI could also be remobilized from sediments.

Photodegradation of Irgarol is slow, the suggested decay rates in surface water [147] and sediment [102] have been extrapolated from observation times of 15 and 30 days, respectively. In the sediment, 99.3 % of the radioactivity was still found as Irgarol after the observation time, which illustrates the uncertainty of this degradation rate. Biological degradation studies of TBT and DCOI [161, 162] have shown that in filtered seawater (1.6 μm), the biological activity decreases much slower than would be expected from the cited chemical studies.

Chapter 6

Indicator evaluation

The scale chosen for the indicator evaluation in this case study spans from one to six. In comparison to the first evaluation of the substances, [8], the possibilities to differentiate between the substances have improved on the on hand, on the other hand the enlarged scale gave the opportunity to display the uncertainty of the evaluation for each indicator in a bar chart, as exemplified in the Figures 6.1, 6.7, 6.8 and 6.11 below. The indicator values 1 to 6 correlate to the expressions very low to very high, as listed in Table 6.1.

Table 6.1: Verbal expressions for the indicator values for the five ecotoxicological risk indicators.

Value	Expression
1	Very low
2	Low
3	Medium low
4	Medium high
5	High
6	Very high

6.1 Release

As already mentioned in the general chapter about risk profiles (page 36), the evaluation of the release can occur either based on the total release currently taking place, resulting from the present production and use patterns of the substances, or based on the release per functional unit.

The question that is being addressed here is not so much an evaluation of the acceptability of the current use pattern, but rather a relative evaluation of the different alternative substances. Consequently, what is being judged should be the release necessary for the functional unit, not the total release to the environment currently taking place. The functional unit in this case is the fouling protection of a certain ship hull area under defined conditons. These conditions would define the fouling pressure, which is dependent mainly on the water speed across the hull surface [163] and the abundance and growth conditions of the fouling organisms.

Unfortunately, there are almost no indications in the scientific literature, how high the release rates of the different biocides have to be in order to protect e.g. one sqare meter of a ship hull. What weighs more, is that it is not very reasonable to compare the amount of a single substance necessary for fouling protection, if in fact they are being applied in combinations [80]. The synergism of these combinations does not even have to be a synergistic effect on a single species. Rather, it might result from an advantageous overlap of effectiveness towards the different relevant fouling species. This will lead to the reduction of the necessary release of one biocidal substance by the use of a second (or even more) different biocide(s).

Instead of totally refraining from the evaluation of the release indicator for single substances, the evaluation is modified according to the following reasoning: First, it can be observed that a vast majority of antifouling coatings contains copper [80]. Second, the copper ($\mathrm{Cu}^{2+}_{\mathrm{aq}}$) which is being relesed from the coatings is also distinct from the other substances because is present in marine seawater in significant background concentrations[1], because (a) it is being released from various technical systems including copper mining facilities and (b) it is a product of natural rock erosion.

As a consequence, copper can not be compared to the other antifouling biocides on a one to one basis. This is the reason why it does not appear in Figure 6.1. In the synopsis of all indicators on page 112, the special situation for copper is only reflected by the missing release indicator values, but the above comparability restrictions should be kept in mind. Since it seems that it is not easily dispensible in modern biocidal coating technology, the risk of damaging the environment by using copper in antifoulings is closely correlated to the question, if the use of biocidal antifouling coatings is sustainable at all. A contribution to this discussion can be found in section 7.2.

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[1] about 0.1 to 0.15 μg/L [120]

The evaluation of the release rate of the biocides other than copper is quite simple. In the open literature, only detailed data about TBT (e.g. [116, 163]) and copper [164, 163] were encountered. For the evaluation of release rates of the other substances, the percentages used in antifouling coatings served as first indications [81, 164]. While copper (cuprous oxide or copper metal) is being incorporated into the paints up to a percentage of 65 %, Irgarol, Sea-Nine and pyrithione zinc only seem to be used at levels up to 15 % (the less soluble pyrithione copper up to 30 %). Tributyltin copolymers (whith unknown TBT content) are used with up to 60 %, and Tributyltin fluoride up to 6.5 %.

The high control of Tributyltin release in SPC coatings and the low maximum percentage of Tributyltin fluoride would suggest, that the release rates for Tributyltin necessary for fouling protection are lower than for the other biocides. This is also confounded by the very high biological activity of TBT. Release rate measurements from a very recently preprint [165] partially corroborate this, namely regarding the measurements with the custom flume system. The TBT release rates measured with the test system according to ISO/DIS 15181-1 are not significantly lower than the release rates of the other evaluated substances. Unfortunately, the use conditions for which the respective coatings were manufactured where not reported with the values, which means that the efficacy of the reported release rates in yielding the functional unit could only be assumed. Because of this, and since the ranges encountered for the single biocides overlap, and the only comparable data that were available for all the biocides are of limited significance, since they were each derived from only one coating type, no unequivocal differences in the biocide release rate necessary for fouling protection could be established between Pyrithione, Irgarol and Sea-Nine.

The values for biocide release for all coating types, all vessel velocities and all biocides except copper encountered in the literature ranged from 0.1 $\mu\mathrm{g\,cm^{-2}}$ per day to 18 $\mu\mathrm{g\,cm^{-2}}$ per day[2]. This range was split into 5 harmonic intervals, yielding six approximate marking points used for the evaluation: 0.1, 0.28, 0.79, 2.25, 6.37 and 18 $\mu\mathrm{g\,cm^{-2}}$ per day. The bars in Figure 6.1 show the relase indicator values that seem to best represent the release rates necessary for fouling control in combination with copper, under conditions representative for commercial marine shipping. The width of the grey bars is at the same time an indicator for the uncertainty of the release rate evaluation, which can also be expressed in words according to

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[2] Copper release rates of coatings that were registered for use on vessels longer than 25 m in Sweden range up to 101 $\mu\mathrm{g\,cm^{-2}}$ per day [164]

Compound	1	2	3	4	5	6
TBT	☐	▨	▨	▨	☐	☐
Irgarol	☐	☐	▨	▨	▨	☐
Sea-Nine	☐	☐	▨	▨	☐	☐
Pyrithionate	☐	☐	▨	▨	▨	☐
Approx. scale ($\mu g\,cm^{-2}\,day^{-1}$)	0.1	0.3	0.8	2.3	6.4	18

Figure 6.1: Indicator values of the four biocides selected for the release rate evaluation. The bar charts show the range of the indicator values, where 1 means the lowest release and 6 means the highest release necessary for fouling control in combination with copper

Table 6.1.

The release of TBT necessary to obtain the functional unit could be rated from low to medium high, which means an uncertainty of three units (medium low). Release of Irgarol could be rated medium low to high, also showing medium low uncertainty. Sea-Nine justifies release indicator values from medium low to medium high (low uncertainty), and Pyritionate causes medium low uncertainty, ranging from medium low to high.

6.2 Spatiotemporal range

The spatiotemporal range of the substances was evaluated by means of a simple global fate model, considering water exchange, sedimentation, degradation and sediment burial as the main fate affecting processes. This model has been described and evaluated before [1]. A detailed description, together with a model evaluation, is given in the previous chapter. For the comparative evaluation of the spatiotemporal range indicator S it is only important to consider some basic properties of the model.

The model defines ”the environment” as consisting of commercial harbors, their sediments, adjacent estuaries, the pertaining sediments, the sea and the sediment above the continental shelves, the epipelagic sea, the pelagic sea and the pelagic sediments (compare Figure 5.1, page 63).

As already pointed out in the previous chapter, there are several reasons why the concentrations calculated with the model are not directly comparable with concentrations measured in the real world. These reasons are (1) The fate of the antifouling biocide input resulting from ship repair facilities is not considered. Such inputs will include paint chips settling in the sediments close to drydock facilities. The biocides in these paint chips can still be released over long periods and will lead to increased biocide concentrations close to such facilities and possibly also in more remote areas, if these inputs are quantitatively significant. Background inputs from other technological and natural processes are neglected, with the exception of copper, where background inputs, especially from rivers, are much larger than inputs from ship hulls. (2) The assumption of complete mixing is relevant (a) for the comparison with measured concentrations in the real world and (b) for the accuracy of the modeled transport due to water exchange and sediment burial (see below). If the input of biocides into the surface water compartments is homogeneous over the surface area, only vertical mixing is required for equal distribution, which is much more realistic, for the disjunct harbor and estuary compartments as well as for the large epipelagic compartment. (3) The mobility of the sediments is not considered which might lead to dilution of biocides in the sediments along the path harbors - estuaries - shelf - pelagic. (4) Transport by diffusion according to disequilibria between water and sediments is not considered. This will be more significant in the water compartments with lower depths, for biocides that have very different degradation rates in water and sediment.[3] (5) Differences in degradation rates according to different temperatures, different sunlight intensity, different abundance and activity of degrading organisms are not modeled. The degradation rates are taken as a geographical mean over the globe. Therefore, local conditions will deviate from the modeled conditions in most cases also for this reason. (6) Other export processes like volatilization into the air or dredging of sediments from harbors, which generally results in the conversion of environment (harbor sediment) into technosphere (subsurface deposits like e.g. in Rotterdam or land deposition as currently tested in Bremerhaven) are not considered. This partially alleviates restriction (1a), but it will can lead to overestimation of biocide concentrations in harbor sediments after dredging, depending on the underlying, newly exposed sediment.

Since the model is an evaluative model, and not meant to exactly represent biocide concentrations in the environment, these restrictions are acceptable, as long as the concentrations calculated for the different compartments are not compared with Predicted No Effect Concentrations (PNEC) concentrations.

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[3] If the degradation rates in water and sediments would be the same, and the partitioning constants for suspended sediments and settled sediments would also be equal, this factor would be neglectable.

The appoach taken here is to take the residence time as an approximate metric for the spatiotemporal range of each substance. Recalling the requirements for a spatiotemporal range indicator postulated in the previous chapter, subsection 3.2, there is still an important deficit of this procedure, apart from the uncertainty in the input parameters of the model and the model layout itself: Primary degradation is modeled as an export of the biocide from the system which means that the fate of the transformation products is not described in the model at present.

Therefore, the results from the calculation of residence times have to be modified (a) considering transformation products that are known or postulated from Structure-Activity Relationships (SAR) knowledge and (b) completed by the consideration of substances with incomplete degradation data, in order to obtain meaningful indicator values for the spatiotemporal range indicator S.

Table 6.2 shows the results from residence time calculations with the fate model. With the exception of copper, the residence times in water are almost the same as the residence times in sediment, which corresponds to the fact, that the sum of the amounts estimated to be in water compartments in steady state is much larger than the sum of the steady state amounts in sediment compartments. For Pyrithionate, no measurements of the partitioning constants between water and sediment were available, so it was not included in the fate modelling study. The variability of the calculated total residence times due to the variability in the input parameters is additionally shown in Figure 6.2.

Figures 6.3 to 6.6 show schemes of transformation products that have been reported in the literature, complemented by structures, that could be expected according to SAR. For the literature sources, please refer to Table 6.3. Transformation products that have been positively identified in the literature are given in bold letters. The conditions of their occurrence and information about their further degradability are also given in Table 6.3. In this table, transformation products that could additionally be expected are included, in case they could be of importance for the risk evaluation.

As illustrated in Figure 6.3, there is only one major pathway for the degradation of TBT, the sequential debutylation by photolysis and biodegradation in water and sediments.[4] The possible contribution of DBT and MBT impurities in commercial TBT preparations is widely ignored in the literature. While the speciation of the TBT cation has been investigated and described in detail [167, 155], the chemical nature of the DBT and MBT

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[4] Hydroxylated intermediates that have been found in studies of the metabolism of TBT in various organisms, are not shown, because they do not appear to be stable [166].

Table 6.2: Geometric mean values for water residence times τ^{w} and overall residence times τ in the system. Pyrithionate was not modeled

Substance	τ^{w}	τ	**Unit**
Sea-Nine	4.55	4.76	days
TBT^{+}/TBTOH	16.5	16.9	days
Irgarol	10.2	10.2	years
Cu^{2+}	8350	42700	years

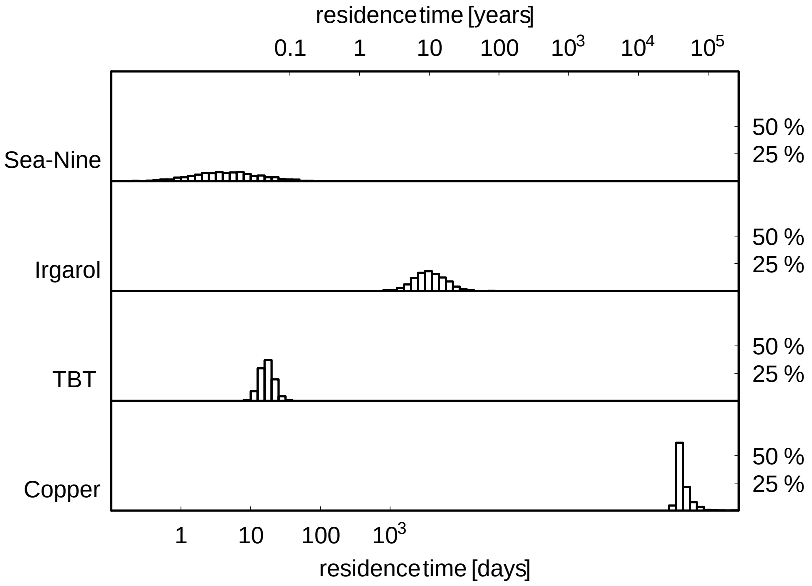

Figure 6.2: Histograms of total residence times in the system according to Monte Carlo simulations

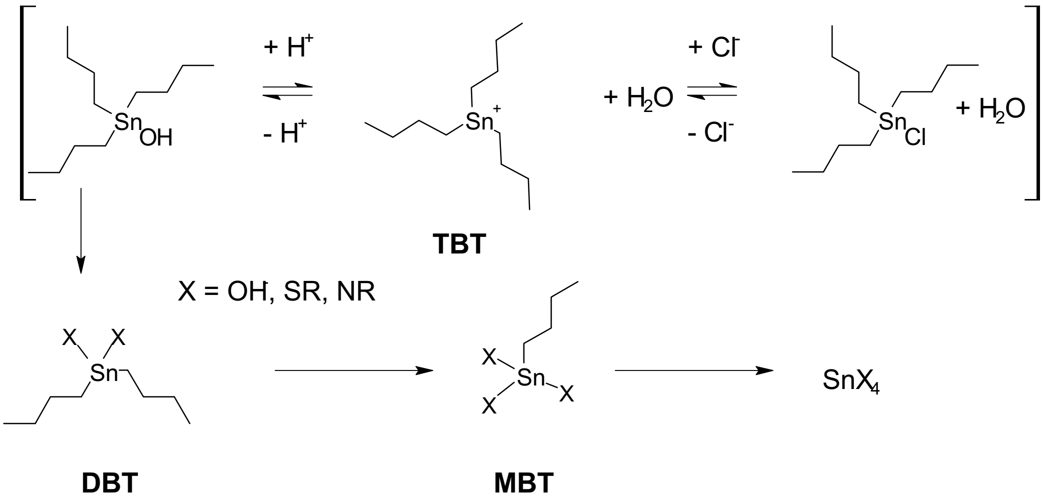

Figure 6.3: Scheme for the speciation of TBT in seawater and a commonly accepted way of degradation by sequential debutylation. Hydroxylated intermediates are generally thought to be unstable and are not shown

compounds is largely unknown. In the common analytical procedures, the groups X in $DBTX_2$ and $MBTX_3$ from Figure 6.3 are removed during alkylation to the tetraalkyl derivatives. The kinetics of further degradation of DBT and MBT is controversially discussed in the literature, if at all, although there is some evidence that their degradation rates are lower than for TBT. This especially seems to be the case for MBT in deeper, anaerobic sediment cores (compare Table 6.3). The fact that DBT and MBT are found in lower concentrations than TBT in most cases can still be explained, if TBT, DBT and MBT concentrations are controlled by dilution (turnover rates from Table 5.1) more than by degradation. Dilution rates are in fact generally higher than the primary degradation of TBT, especially in water.[5]

For Irgarol, the major primary degradation reaction seems to be the loss of the cyclopropylamino group. Oxydation and loss of the methylthio group, as well as subsequent hydroxylation have been observed. The kinetics of these reactions as well as the further degradation are not known, but they could be similar or slower than of Irgarol itself. Under anaerobic conditions, de-cyclopropylamino-Irgarol can be postulated to be even more stable than Irgarol. No evidence of the formation of ring-opened

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[5] Compare the argumentation in [136]. This also means, that in areas remote from TBT input, the DBT/TBT and MBT/TBT ratios should increase.

transformation products, nor mineralization has been reported (compare Table 6.3).

As the most important primary degradation product of Sea-Nine, N-octyl-malonamic acid is often cited. However, there is also evidence of reductive dechlorination, leading to 4COI, 5COI and OI as intermediate degradation products under reducing conditions (compare Table 6.3 for short names and sources of information). Since Sea-Nine is inert against hydrolysis at neutral pH values, and no other abiotic degradation processes have been described, it can be assumed that the aerobic degradation of Sea-Nine depends on intracellular, reducing nucleophiles like Glutathione (GSH), which open the ring by a reductive, nucleophilic attack at the sulfur atom [160, 159]. After the two-electron-reduction, either the isothiazolone ring can be re-established, loosing a chloride anion, or the ring-opened intermediate can be freed (Figure 6.5), which is expected to be very reactive, if there is a Cl atom at position 5 (formation of a thiacyl chloride). In this light, abiotic reductive degradation to N-octyl-malonamic acid (OMA) also appears plausible. Further degradation of OMA would probably involve N-dealkylation at some point and is not expected to be problematic.

The formation of Pyrithione sulfonic acid (PTSA) as one main degradation product of Pyrithionate compounds is well established (compare Table 6.3). The formation of PTSA, 2-mercaptopyridine (MP) and pyridine-2-sulfonic acid (PSA) has been shown in sediment/water systems, the latter two only under reducing conditions. While it is generally accepted that zinc pyrithione will transchelate to copper pyrithione, if copper is present even in lower concentrations than zinc, the nature of the environmental pyrithione copper species (1:1) or (2:1) has not been discussed in the literature. Because of the high copper loadings of ZnPT-containing antifouling paints, the formation of CuPT (1:1) species is expected.[6]. The excess of Cu would also explain the activity of Copper Omadine®($CuPT_2$) which is almost insoluble in water [168], in antifouling paints. Some ring-containing metabolites have been reported in the Pyrithione risk analysis, prepared for the Danish EPA, which are degraded at similar or lower rates than Pyrithione, but the disclosure of their structures has been prevented by Arch Chemicals, Inc., who generated the data in their laboratories.

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[6] The transchelation of PT compounds is also used for their analysis, where Cu^{2+} is added in excess [163]

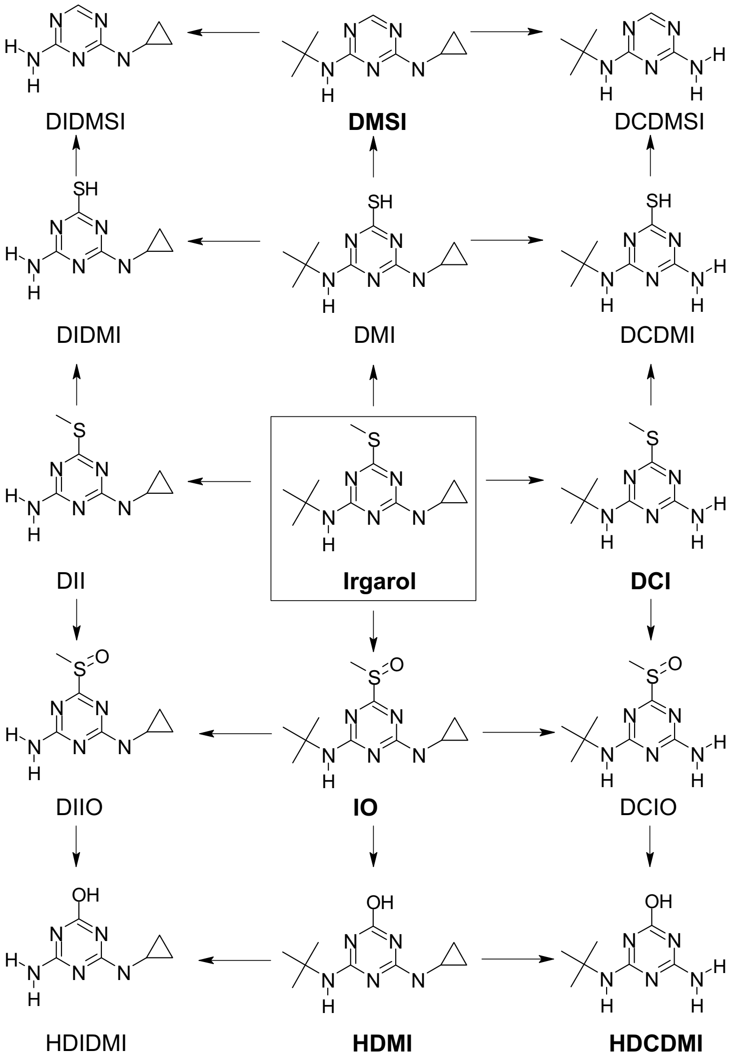

Figure 6.4: Theoretical scheme of possible transformation products of Irgarol. Compounds that have been identified in laboratory tests or the environment (Table 6.3) are in bold letters.

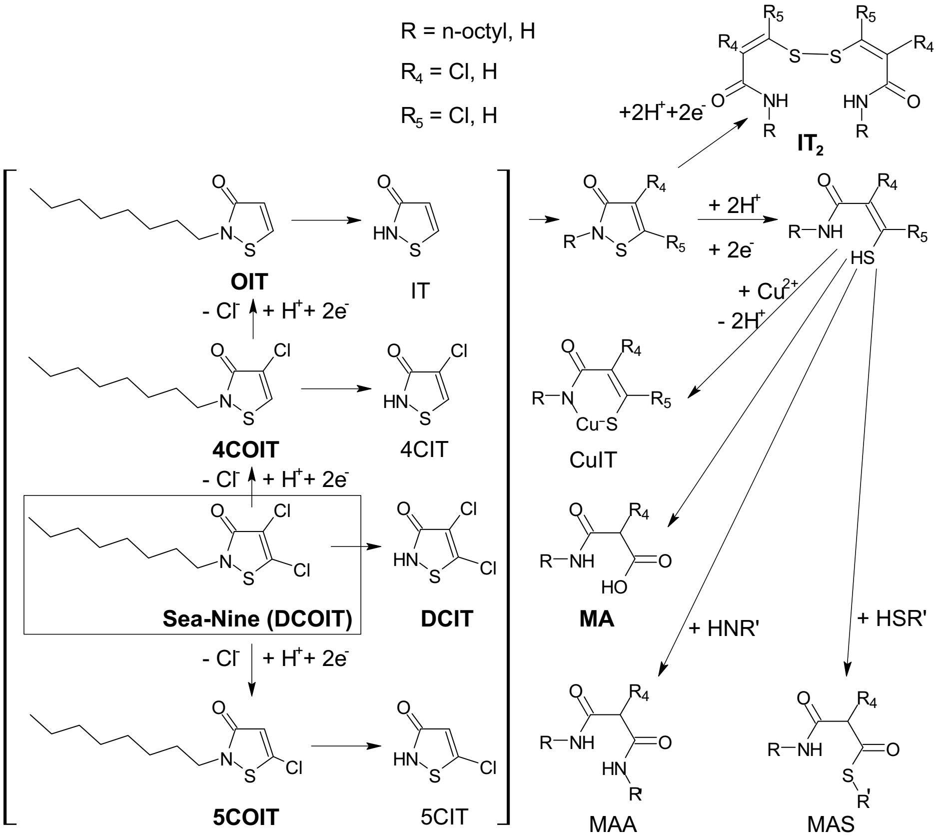

Figure 6.5: Proposed scheme of reductive dechlorination, N-deoctylation and reductive ring-opening for Sea-Nine. Compounds that have been found in laboratory degradation tests (Table 6.3) are in bold letters

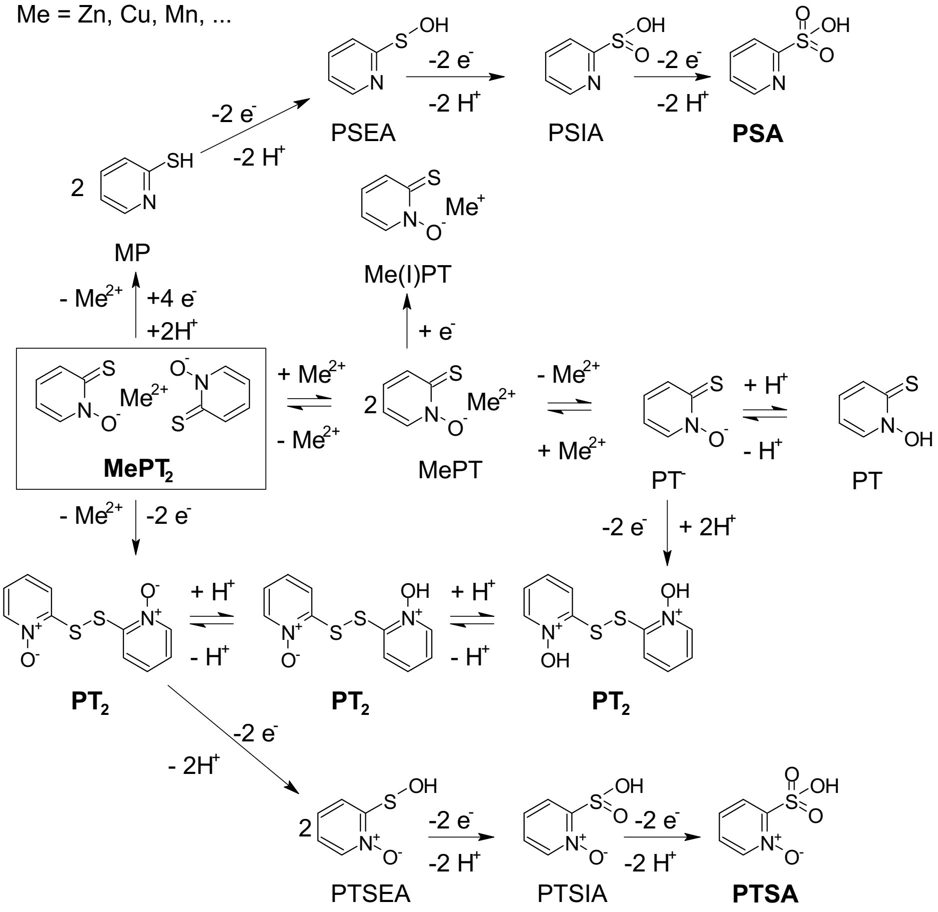

Figure 6.6: Proposed scheme of the speciation and degradation of Pyrithionate. Transchelation reactions, where Me is substituted by a different metal ion are not shown explicitly. Compounds that have been identified in laboratory degradation tests (Table 6.3) are in bold letters

Table 6.3: List of identified and some proposed transformation products of the evaluated substances, together with information about their further degradation

Short	**Chemical Name**	**Occurrence**	**Further Degradation**
Mother compound TBT			
DBT	Dibutyltin	Water, e.g. [169, 170, 171, 132] and Sediments, e.g. [169, 172, 140]	Similar [129], slower [136, 173] or faster [60] than TBT Tends to repartition from sediments to overlying water [140, 174]
MBT	Monobutyltin	Water, e.g. [169, 170, 132] and Sediments, e.g. [169, 172]	Similar [129], slower than TBT, especially in water [133] and estuarine sediments [175], as in [176], or faster [60]. Tends to repartition from sediments to overlying water [137, 177]
Mother compound Irgarol			
DCI	Decyclopropylirgarol	Marinas [178], aerobic water/sediment system [148], as in [102], fungus growth medium [179], Marina sediments [171]	Similar to Irgarol [180, 181] as in [105, 171], none [179]
IO	Irgarolmonoxid	aerobic water/sediment system [148], as in [102]	unknown
DMSI	Demethylsulfidirgarol	aerobic water/sediment system [148], as in [102]	unknown

Table 6.3: (continued)

Short	**Chemical Name**	**Occurrence**	**Further Degradation**
HDMSDCI	Hydroxy-demethyl-sulfiddecyclopropylirgarol	aerobic soil system [182], as in [102]	unknown
Mother compound Sea-Nine			
MCOIT	Monochloro-2-n-octyl-isothiazolone	anaerobic sand/seawater test system [183], as in [106]	similar to Sea-Nine
OIT	n-octyl-isothiazolone	anaerobic sand/seawater test system [183], as in [106]	unknown
IT_2	Isothiazolone dimers	OIT dimer found in anaerobic sand/seawater test system [183], as in [106]	unknown
DCIT	Dichloroisothiazolone		
MA	Malonamic acids	N-octyl-malonamic acid was identified in the sediment of an aerobic sediment/water system, after extraction with 1 M NaOH [154], as in [107] and in an anaerobic sand/seawater test system [183], as in [106]	decarboxylation to the acetamide
MAA	Malonamic acid amides	Possible thioacyl chloride adduct of amines [159]	unknown

Table 6.3: (continued)

Short	**Chemical Name**	**Occurrence**	**Further Degradation**
Mother compound Pyrithione			
$CuPT_2$	copper pyrithione (1:2)	Antifouling paints and other products	Similar to $ZnPT_2$ [99]
CuPT	Pyrithione metal complexes (1:1)	Most stable MePT complex in water [184] (Me/PT-ratio greater than 100 in solution)	unknown
PTSA	Pyrithione sulfonic acid	Aerobic photolysis [185], aerobic seawater/sediment test system [186, 187, 188], as in [99]	unknown
PT_2	Pyrithione disulfide	unknown	unknown
MP	2-Mercaptopyridine	unknown	unknown
PSA	Pyridine-2-sulfonic acid	aerobic and anaerobic seawater/sediment test system [186, 187, 189, 188, 190], as in [99]	unknown

Unfortunately, no data about the particle-water partitioning of Pyrithione compounds were available. Therefore, the input data for the model (Table 5.3) was not sufficient for Pyrithionate. However, dissipation half-lives in sediment/seawater systems have been reported to be in the order of 4 days (aerobic) and 19 hours (anaerobic) ([186], as in [99]). Degradation tests in seawater without sediment in the dark have not been reported to the knowledge of the author.

At this point of the evaluation, it has to be decided, which metabolites are included in the assessment of the spatiotemporal range. Structures, that are not included into the range will also not be included into the assessment of bioaccumulation and biological acitivity. On the other hand, inclusion of substances that are not harmful to organisms can cause the spatiotemporal range to be unreasonably high.

In this case, it was decided to include the following transformation products into the evaluation:

- None for Cu^{2+}_{aq}
- **DBT** and **MBT** for TBT
- Irgaroloxides (**IOs**), comprising the monoxide and the dioxide, and Desalkylirgarol (**DAI**), comprising Decyclopropyl-irgarol (DCI) Desisobutyl-irgarol (DII) and Decyclopropyl-desisobutyl-irgarol (DCDII) for Irgarol
- **MCOIT**, comprising the 4- and 5- substituted monochloro-N-n-octyl-isothiazolones, **OIT**, and **IT**, comprising the chlorinated derivatives of isothiazolone for Sea-Nine and
- **MePT** (1:1), Pyrithione oxides (**PTOs**), comprising Pyrithione sulfenic acid (PTSEA), Pyrithione sulfinic acid (PTSIA) and Pyrithione sulfonic acid (PTSA), Mercaptopyridine (**MP**), and Mercaptopyridine oxides (**MPOs**), comprising Mercaptopyridine sulfenic (MPSEA), sulfinic (MPSIA) and sulfonic acids (MPSA) (compare Figure 6.6) for Pyrithionate.

The inclusion of these transformation products means, that the residence times from Table 6.2 and Figure 6.2 have to be enlarged by the contribution of the transformation products. The evaluation of the spatiotemporal range therefore aims at the evaluation of a joint residence time. The following factors used in order to roughly estimate the spatiotemporal ranges: Factor 1 for copper, since no transformation is expected; Factor 4 for TBT, assuming that every TBT molecule will stay in the environment a little longer as a DBT molecule, and subsequently as a MBT molecule; Factor 3 for Irgarol, assuming that degradation of Irgarol either takes the route via IO or via DAI but these are further degraded with slower kinetics than Irgarol; Factor 2.5 for Sea-Nine, assuming that further dechlorination of MCOIT and ring-opening of OIT will be rapid, once the substance has reached a place with suitable conditions for reaction, and that initial N-dealkylation to IT is a minor pathway.

For Pyrithonate, in default of modelling data, 1 day served as a point estimate for the overall residence time, and Factor 100 was applied for inclusion of transformation products, considering that the metabolites included in the assessment seem to comprise all major degradation products with the intact mercaptopyridine structure, and that this ring is hardly cleaved, as proven by the mineralisation experiments with [2,6-^{14}C-pyridine] pyrithione cited in [99]. The resulting scale for the joint residence times ranges from about 10 days to about $15 \cdot 10^6$ days. The resulting approximate scale is shown in Figure 6.7, together with the indicator values resulting from the above considerations. The point estimates for the joint residence times of the substances, resulting from multiplication of the total residence times from Table 6.2 and the above factors are: 43 000 years for copper ($10^{4.6}$ years), 70 days for TBT ($10^{-0.73}$ years), 30 years for Irgarol ($10^{1.5}$ years), 10 days for Sea-Nine ($10^{-1.6}$ years) and 100 days for Pyrithionate ($10^{-0.56}$).

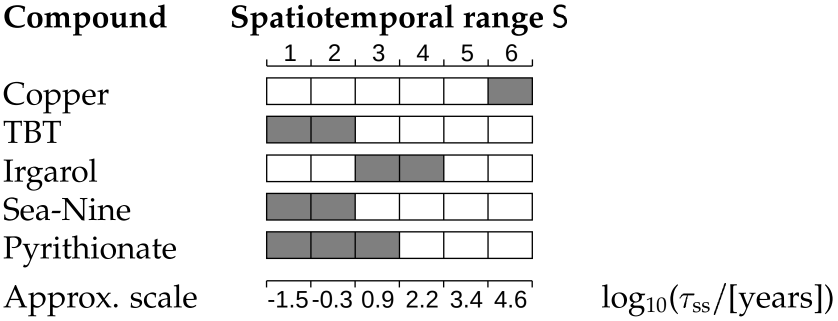

Figure 6.7: Indicator values resulting from the evaluation of the spatiotemporal range. The bar charts show the range of the indicator values, where 1 means the lowest and 6 means the highest spatiotemporal range.

The indicator values given in Figure 6.7 express a very high spatiotemporal range for copper, with a very low uncertainty, a very low or low spatiotemporal range for TBT, with low uncertainty, a medium low or medium high spatiotemporal range for Irgarol, with low uncertainty, a very low or low spatiotemporal range for Sea-Nine, with low uncertainty, and a very low to medium low spatiotemporal range for Pyrithionate, corresponding to a medium low uncertainty.

6.3 Bioaccumulation

The transformation products that have been included in the evaluation of the spatiotemporal range should also be included in the bioaccumulation assessment according to their contribution to the spatiotemporal range. If the compounds have a contribution to the joint persistence which is comparable to the mother compound and are significantly less bioaccumulating, their contribution to the overall bioaccumulated fraction (Subsection 3.2) will be low, since bioaccumulation differences easily span orders of magnitudes, while the joint persistence is of an additive nature.

Considering the idealized metric for bioaccumulation, the fraction of the amount in the environment, which is present within organisms (Equation 3.2), and drawing the knowledge from the residence time studies presented in chapter 5, that except for copper, by far the major portion of the substances is present in the water compartments, the evaluation can be simplified to an evaluation of the bioaccumulation of the substances from the water phase. Using this simplification, one should be aware of the fact, that no informaion about the relative amount of the biomass in the marine environment located in water, respectively sediment is used. However, considering that bioconcentration from sediments is generally much smaller than from water [72],[7] the simplification is plausible.

Copper bioconcentration factors for accumulation from water vary in an unknown relationship with the chemical composition of water and particles, as well as with other factors. In algae, animal plankton, molluscs and crustaceans, BCF values greater than 1000 have been reported. For some algae, macroalgae and bivalves (e.g. *Crassostrea virginica*: 28000) and crustaceans greater than 10000 [94]. The lower values for fish (150-700) can be rationalised by the fact that fish and higher invertebrates are able to regulate copper by active excretion [191]. Correspondingly, a biomagnification of copper along the food chain was generally not found [96, 94].

The bioconcentration of TBT is highly dependent on the type of organism. BCFs for fish and algae have been reported with values above 100 and sometimes even above 1000. For filtrating molluscs, bioaccumulation factors of above 100000 have been reported [192]. The ability to metabolise

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[7] This can be rationalised, considering the large concentration of organic matter in the sediments, which competes with the living biomass in the partitioning processes.

TBT has been stated to be the greatest in higher animals, particularly in vertebrates [87]. Biomagnification of TBT along the food chain has been considered to be insignificant [91]. Bioconcentration of DBT and MBT is generally assumed to be lower, because of the more hydrophilic nature of such compounds.

For Irgarol, determinations of the K_{ow} by contract laboratories have resulted in values from 2.8 (GLP study) to ≥ 3.95. A recalculation of the raw data carried through in KEMI, Sweden, even gave a value of 4.93. BCFs around 200 [101, 102] for fish indicate a high affinity to organisms. BCFs of at least 1000 seem realistic for macrophytes, while values of up to 30000 have been given in [193].[8] While bioaccumulation data about metabolites were not available, SAR estimations for log K_{ow} values result in reductions in lipophilicity by at least one logarithmic unit for the dealkylated substances, while the influence of oxydation of the methylthio group is less unequivocal [194].

Experimental values for log K_{ow} of Sea-Nine span from 2.3 to 6.4. Estimations carried out with quantitative structure-activity relationships published by Meylan et al. and Hansch and Leo (as in [195] indicate a log K_{ow} above 6. The assessment of BCFs indicate an associating reaction of Sea-Nine with body tissues. The lipophilicity, which is assumed to be high, is consistent with the high BCFs for fish of about 660 [106]. The uptake of the substance is presumably accompanied with metabolic transformations (compare Figure 6.5). However, MCOIT and OIT are still very lipophilic substances, to some extent amphiphilic, and possibly less reactive, which would favor their enrichment in biological membranes.

The very low lipophilicity of free pyrithione suggests a correspondingly low bioaccumulation. However, pyrithione is used in biochemistry as a vector for introducing zink ions into the cell.[9] Therefore, it can be assumed that MePT complexes will easily bioaccumulate, as has been shown with other lipophilic metal complexes as well, e.g. Cu-oxine complexes [196]. No measurements regarding bioaccumulation of MePT complexes were available.

The construction of a scale according to equation 3.2 in subsection 3.2 would imply the estimation of the total biomass in the system and the subsequent estimation of bioaccumulation according to the different taxonomic groups. On the other hand, only the data for copper and TBT would be sufficient to differentially judge the bioaccumulation of the main taxo-

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[8] These values have been put to question because of the very low detection limits (0.3 ng/L) claimed for aqueous concentrations in this study (personal communication P. Dollenmeier, Ciba Specialty Chemicals).

[9] personal communication by H. Haase.

nomic groups. Therefore, a lack of data is mainly shown in Figure 6.8 by a wider range of the indicator values, e.g. for Pyrithione.

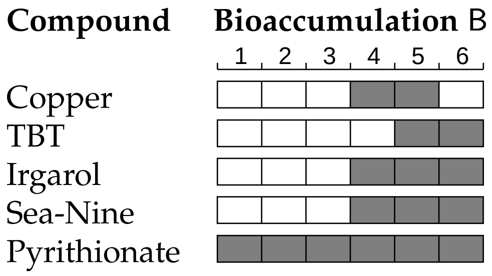

Figure 6.8: Indicator values resulting from the evaluation of bioaccumulation. The bar charts show the range of the indicator values, where 1 means the lowest and 6 means the highest accumulation.

The bioaccumulation indicator is medium high or high for copper (low uncertainty), high or very high for TBT (low uncertainty), medium high to very high for Irgarol (medium low uncertainty), medium high to very high for Sea-Nine (medium low uncertainty), and very low to very high for Pyrithionate, resulting from the very high uncertainty.

6.4 Biological activity

An assessment of the biological activity of the five antifouling biocides to be compared can only depend on the assessment of internal effect concentrations, as postulated in section 3.2, if both bioaccumulation and internal effect concentrations are known for the same taxonomic groups. In this case, knowledge of internal effect concentrations can help estimate effects on other taxonomic groups just by extrapolating from their respective bioaccumulation.

In the present case study, only very little data about internal effect concentrations were encountered for TBT and copper, while none was available for the other biocides. Therefore, the biological activity was almost exclusively evaluated according to external effect concentrations like EC_{50} or NOEC values. Since the amount of toxicity data for TBT is so abundant, and its extreme toxicity is well agreed on, external effect concentrations for TBT were used as a benchmark in the evaluation of the biological activity. Effect data on the five biocides that have been published were collected in the database `UFT_SAR`. The different activity towards different taxonomic groups can be seen in Tables 6.4 to 6.11.[10]

Of the metal ions naturally occurring in seawater, copper(II) is toxic at the lowest concentrations. Its toxicity is greatest towards molluscs and algae, while fish toxicity if quite a lot lower, since fish are able to regulate copper. Complex formation with different chelate ligands has been shown to lower the effect concentrations for bacteria, planktic algae and *Daphnia* [197]. Some antifouling biocides like thiram or pyrithione are known or suspected to increase the uptake and the toxicity of copper(II) in seawater. The persistence of such complexes is hardly discussed in the literature as yet.

A similar toxicity pattern can be observed for TBT, towards which molluscs are much more sensitive than the average species.[11] An increase in the percentage of mud snails with male reproductive organs was shown to be probable at chronic exposure with 2 ng/L TBT [198]. Trace concentrations of TBT compounds cause significant detrimental effects on the level of populations in a variety of mussels and snails. Biochemical modes of action include membrane toxicity in fish hepatoma cells, disturbance of Ca^{2+}-homeostasis and induction of apoptosis in thymocytes (immunotoxicity), inhibition of oxidative phosphorylation and photophosphorylation (ATP synthesis in mitochondria and chloroplasts), inhibition of ion pumps including the Na^+/K^+-ATPase and inhibition of the cytochrome P_{450} system. The combination of a positive charge with high lipophilicity seems to be responsible for the strong effects on different ion channels of membranes [87].

Like the structurally related triazine-herbizides, Irgarol has a very specific inhibitory effect on the photosystem II. This can also be seen in the external effect concentrations towards the different taxonomic groups presented here. According to Hall [105], the effects on photosynthesis rates of algae populations were shown for concentrations as low as 0.1 μg/L, while the 10th percentile of EC_{50} values for plant growth was 136 ng/L. Effects on organisms not photosynthetically active are generally around 1 mg/L (Tables 6.4 to 6.8). NOECs for some organisms are slightly lower, in the case of the rainbow trout about 4 μg/L [105].

Tests of the biological activity of Sea-Nine resulted in critical effects for almost all tested organisms at concentrations between 1 and 30 μg/L. A significant exception was the fiddler crab *Buca pugilator*, which showed an

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[10] The SQL queries that were used in order to extract the information in these tables from the database are given in the Appendix

[11] Concentrations of TBT at which approximatively 10% of the tested saltwater species of several taxonomic groups reveal acute toxic effects, range from 5 ng/L for zooplankton up to 1 μg/L for fish [90].

96 h LC_{50} value of a little more than 1 mg/L (one of the outliers in Figures 6.9 and 6.10. Since Sea-Nine is being used as a fungicide and since a high activity against a broad spectrum of bacteria was found for 3(2H)-isothiazolones, it is to be regarded as a broad-range biocide with high toxic activity. Effect concentrations for algae are comparable to the respective values for Irgarol, whereas in one publication an even lower effect concentration was found for Sea-Nine [199].

Related to the use of zinc pyrithione in anti-dandruff shampoos, some studies about skin sensitization, possible teratogenic or cytostatic effects and similar endpoints have been reported in the literature. ZnPT as well as the free pyrithione are active. ZnPT is accumulated in cell membranes and free pyritione is mainly found in the cytoplasm [200]. Except for algae, it seems to have effects at similarly low concentrations like Sea-Nine.

Starting with the crustacean species, we can compare the mean values of the decadic logarithms of the acute LC_{50} values, as in Table 6.4. Interestingly, a very similar picture is gained, if all effects data on crustaceans are pooled, regardless of the exposure time or if they are EC_{50}, LOEC or NOEC values, as can be seen in Table 6.5. The ranking of the more toxic biocides from most toxic to least toxic remains TBT > ZnPT2 > Sea-Nine. The acute to chronic ratio – as it can be seen from these data – is quite large for copper (also caused by the long exposure times and the use of NOEC values in the data set by Vega [201]), which causes the pooled average to be lower than the one for Irgarol.

If we look at the data on fish species, Tables 6.6 and 6.7 give the same ranking of the biocide activity for this taxonomic group. The picture changes a little bit as compared to the crustacean toxicities: TBT stays the most toxic substance, but Sea-Nine seems to be more toxic towards fish than ZnPT2, followed by Copper and the least fish-toxic Irgarol. Fish are the least sensitive of the four taxonomic groups investigated separately.

For Molluscs, only the pooled data give comparative information about the substances (Table 6.8). Clearly, they are the most sensitive taxonomic group concerning TBT, which is about one and a half orders of magnitude more toxic than the next toxic substance, copper, closely followed by Sea-Nine and Pyrithionate. For Irgarol, only one test with saltwater molluscs was available, which indicated a very low toxicity in comparison. The group of the molluscs is the most sensitive among the groups of crustacea, fish, molluscs and algae investigated here.

The very selective, but nevertheless high activity of Irgarol is revealed, when the pooled effects data for algae are analysed 6.9.[12] Irgarol is by far

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[12] Neither for Molluscs, nor for Algae acute LC_{50} values were sufficient for a compari-

Table 6.4: Average of logarithmic acute LC_{50} values in g/L for Crustacean species (mostly saltwater). `chent` means the evaluated compound, `count(*)` is the number of tests in the database

```
+----------+----------+----------------------+------+--------+
| chent    | count(*) | avg(log10(exposure)) | type | effect |
+----------+----------+----------------------+------+--------+
| Cu       |        2 |        -3.2          | EC50 | lethal |
| TBT      |       11 |        -6.0          | EC50 | lethal |
| Irgarol  |        1 |        -3.4          | EC50 | lethal |
| Sea-Nine |        4 |        -4.4          | EC50 | lethal |
| ZnPT2    |        2 |        -5.1          | EC50 | lethal |
+----------+----------+----------------------+------+--------+
```

Table 6.5: Average of decadic logarithms of pooled effect concentrations in g/L for Crustacean species (mostly saltwater)

```
+----------+----------+----------------------+
| chent    | count(*) | avg(log10(exposure)) |
+----------+----------+----------------------+
| Cu       |       15 |        -4.3          |
| TBT      |       17 |        -6.1          |
| Irgarol  |        4 |        -3.7          |
| Sea-Nine |       11 |        -5.1          |
| ZnPT2    |        7 |        -5.5          |
+----------+----------+----------------------+
```

Table 6.6: Average of decadic logarithms of acute LC_{50} values in g/L for Fish species (mostly saltwater)

```
+----------+----------+----------------------+------+--------+
| chent    | count(*) | avg(log10(exposure)) | type | effect |
+----------+----------+----------------------+------+--------+
| Cu       |        3 |        -3.8          | EC50 | lethal |
| TBT      |        6 |        -5.3          | EC50 | lethal |
| Irgarol  |        6 |        -2.9          | EC50 | lethal |
| Sea-Nine |       10 |        -4.7          | EC50 | lethal |
| ZnPT2    |       12 |        -4.1          | EC50 | lethal |
+----------+----------+----------------------+------+--------+
```

Table 6.7: Average of decadic logarithms of pooled effect concentrations in g/L for Fish species (mostly saltwater)

```
+----------+----------+----------------------+
| chent    | count(*) | avg(log10(exposure)) |
+----------+----------+----------------------+
| Cu       |        3 |        -3.8          |
| TBT      |       10 |        -5.6          |
| Irgarol  |        7 |        -3.1          |
| Sea-Nine |       13 |        -4.8          |
| ZnPT2    |       17 |        -4.5          |
+----------+----------+----------------------+
```

Table 6.8: Average of decadic logarithms of pooled effect concentrations in g/L for Mollusca (mostly saltwater)

```
+----------+----------+----------------------+
| chent    | count(*) | avg(log10(exposure)) |
+----------+----------+----------------------+
| Cu       |       20 |        -5.0          |
| TBT      |       16 |        -6.5          |
| Irgarol  |        1 |        -2.5          |
| Sea-Nine |        7 |        -4.7          |
| ZnPT2    |        2 |        -4.8          |
+----------+----------+----------------------+
```

Table 6.9: Average of decadic logarithms of pooled effect concentrations in g/L for Algae (mostly saltwater)

```
+----------+----------+----------------------+
| chent    | count(*) | avg(log10(exposure)) |
+----------+----------+----------------------+
| Cu       |        4 |         -4.7         |
| TBT      |        4 |         -5.4         |
| Irgarol  |        7 |         -6.5         |
| Sea-Nine |        8 |         -4.9         |
| ZnPT2    |        6 |         -4.0         |
+----------+----------+----------------------+
```

Table 6.10: Average of decadic logarithms of acute LC_{50} values in g/L for all species that are registered in the database `UFT_SAR`, except for Bacteria, Yeasts and Funghi

```
+----------+----------+----------------------+------+--------+
| chent    | count(*) | avg(log10(exposure)) | type | effect |
+----------+----------+----------------------+------+--------+
| Cu       |        8 |         -3.8         | EC50 | Lethal |
| TBT      |       29 |         -5.5         | EC50 | Lethal |
| Irgarol  |        7 |         -3.0         | EC50 | lethal |
| Sea-Nine |       15 |         -4.5         | EC50 | lethal |
| ZnPT2    |       15 |         -4.3         | EC50 | lethal |
+----------+----------+----------------------+------+--------+
```

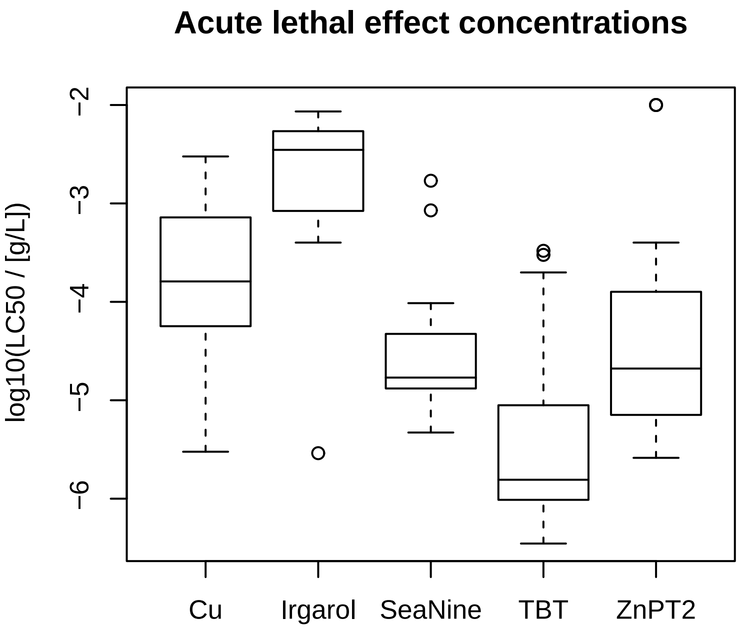


Figure 6.9: Box plots of acute LC$_{50}$ values for all species for which data were available. The boxes reach from the first to the third quartile and are split by a line at the median. The "whiskers" show the lowest, respectively the highest data points within a normal range, open circles show outliers.

Table 6.11: Average of decadic logarithms of pooled effect concentrations in g/L for all species that are registered in the database `UFT_SAR`, except for Bacteria, Yeasts and Funghi

```
+----------+----------+---------------------+
| chent    | count(*) | avg(log10(exposure)) |
+----------+----------+---------------------+
| Cu       |       50 |        -4.6          |
| TBT      |       57 |        -5.9          |
| Irgarol  |       19 |        -4.5          |
| Sea-Nine |       39 |        -4.9          |
| ZnPT2    |       49 |        -4.0          |
+----------+----------+---------------------+
```

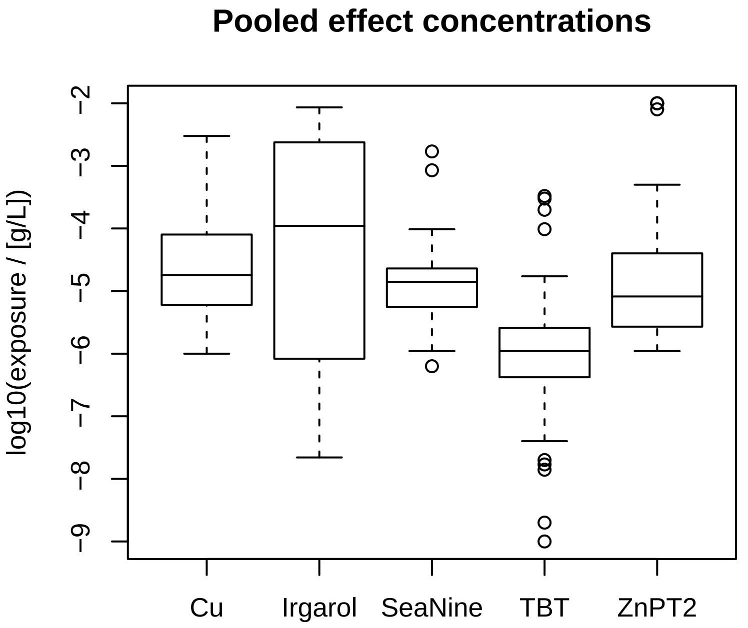


Figure 6.10: Box plots of pooled effect concentratons for all species for which data were available

the most toxic compound to algae in the set, which is not very surprising, since its only mode of specific action is believed to be inhibition of photosynthesis. Pyrithionates on the other hand do not seem to be specifically toxic to algae.

Pooling of all acute toxicity data and finally of all effect concentrations leads to the values in Tables 6.10 and 6.11. Box plots [202] for these data sets are shown in the pertaining Figures 6.9 and 6.10.[13]. Both the acute lethal and the pooled effect concentrations unequivocally reveal the exemptional biological activity of TBT. The activity of Sea-Nine and Pyrithione is quite similar judging from this dataset, except that the variability of Pyrithione effect concentrations was higher. While copper does not cause acute effects at concentrations as low as the acute effect concentrations of Sea-Nine and zinc pyrithione, its chronic toxicity, especially for molluscs, leads to pooled statistics which convey a very similar impression. It has to be stressed, though, that not nearly as many mollusc species have been tested against Sea-Nine and ZnPT2. Testing further mollusc species would likely change the picture of the overall statistics to the disadvantage of Sea-Nine and ZnPT2.

The differences between the biocides as seen in the pooled external effect concentrations result from differences in bioaccumulation *and* biological activity. Some of the differences in external effect concentrations that have been discussed above are at least partly paralleled by differences in bioaccumulation. For example, the very low effect concentrations of Irgarol towards Algae are analogous to a high bioaccumulation in this group of organisms. However, since differences in the indicator values for bioaccumulation were small and uncertain, they could hardly be accounted for. An example for subtraction of differences in bioaccumulation from the differences in effect concentrations is the small difference between the indicator values for the biological activity for TBT and Sea-Nine. While external effect concentrations would justify a larger difference, the contribution of bioaccumulation to the low external effect concentrations for TBT makes a smaller difference in internal effect concentration (i.e. biological activity) reasonable.

As shown in Figure 6.11, ratings from low to medium high would be justified for the biological activity of copper. For the biological activity of TBT, only high or very high seems appropriate (low uncertainty). For Irgarol, biological activity can be argued to be medium low, medium high,

---

son, except for TBT and Cu.

[13] They were generated with the software package R available at `http://www.r-project.org`. For a more detailed descripton, try `http://mathworld.wolfram.com/Box-and-WhiskerPlot.html`

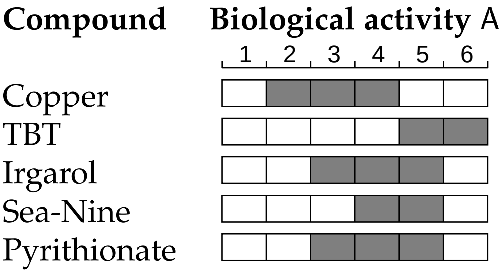


Figure 6.11: Indicator values resulting from the evaluation of the biological activity. The bar charts show the range of the indicator values, where 1 means the lowest and 6 means the highest activity.

or high (medium low uncertainty), depending mainly on the weighting of the specific effects against photoheterotrophic organisms. The biological activity of Sea-Nine appears medium high or high (low uncertainty), while the biological activity of Pyrithionate could be argued to be medium low, medium high or high (medium low uncertainty).

6.5 Uncertainty

The uncertainties of the four previous indicator evaluations are collected in Table 6.12, together with the resulting uncertainty of the whole evaluation for the five biocides, which is also shown in Figure 6.12. While the uncertainties for copper, TBT and Sea-Nine are comparatively low, and medium low for Irgarol, they are medium high for Pyritione compounds, which is an important result of the evaluation process.

Table 6.12: Collected uncertainties of the evaluation of release R, spatiotemporal range S, bioaccumulation B, biological activity A, and the resulting uncertainty indicator U

Biocide	R	S	B	A	U
Copper	–	1	2	3	2
TBT	3	2	2	2	2
Irgarol	3	2	3	3	3
Sea-Nine	2	2	3	2	2
Pyrithionate	3	3	6	3	4

Compound	**Uncertainty** U					
	1	2	3	4	5	6
Copper		▨				
TBT		▨				
Irgarol			▨			
Sea-Nine		▨				
Pyrithionate				▨		

Figure 6.12: Indicator values resulting from the evaluation of the uncertainty of the overall evaluation. The bar charts show the range of the indicator values, where 1 means the lowest and 6 means the highest uncertainty

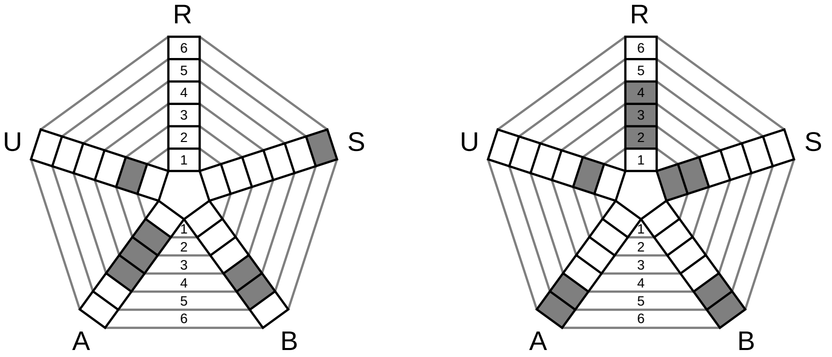
Chapter 7

Conclusions

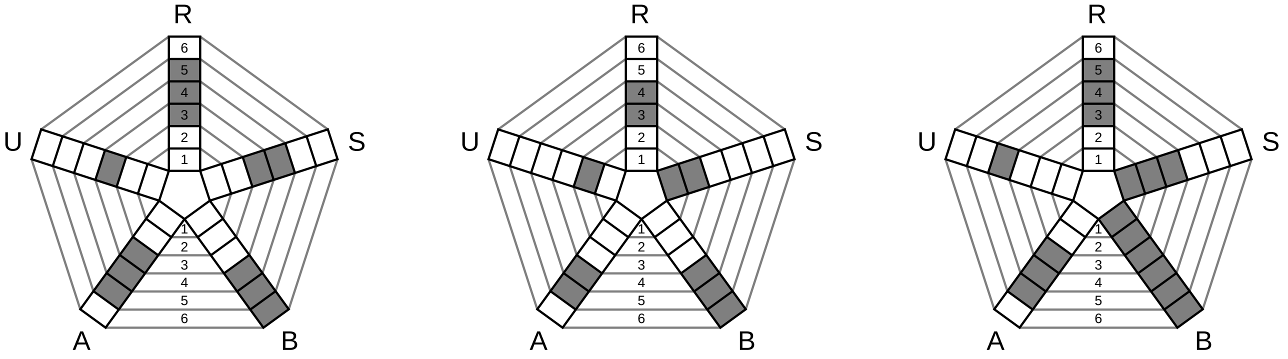
7.1 Comparative evaluation

A synopsis of the indicator values that have been derived in the previous section is shown in Figure 7.1. The comparative evaluation of the five antifouling biocides used in commercial shipping obviously does not give results of the form ”Using biocide A bears no risk of environmental damage, but using biocide B does”. Rather, possible candidates for a reduction of the risk of environmental damage can be identified. For the biocides other than copper, the ecotoxicological risk profile of TBT is the benchmark which has to be beaten, since the legal use of TBT will not be possible in the future. Copper, as mentioned in the beginning of the chapter, is a special case, since it is hardly dispensible in todays biocidal coatings, especially if they can not contain organotin compounds. The comparative risk analysis is only really useful, if no better alternatives are found, like the use of biocide-free coatings.

The difficult task in underbidding the ecotoxicological risk profile of TBT is its spatiotemporal range. Oftentimes it is stressed, that TBT and other organotin compounds are persistent in sediments. On the other hand, there is overwhelming evidence for the biological degradation of TBT in seawater. According to the results of the modelling study (Chapter 5), only a small percentage of the TBT released to the water from ship hulls in service will reach the sediments, which means that the overall persistence or mean residence time is much more like the persistence in water, than like the persistence in sediments (Table 6.2).



Copper TBT



Irgarol Sea-Nine Pyrithione

Figure 7.1: Five-dimensional representations of the indicator values for the five biocides of the case study. R indicates the release per functional unit (not evaluated for copper, see section 6.1), S the spatiotemporal range, B the bioaccumulation A the biological activity and U the uncertainty

Even this comparatively small spatiotemporal range of TBT causes significant environmental damage, which can be ascribed to the very high constant biocide input directly from ship hulls, amounting to an estimated 1900 metric tons per year (cp. Section 5.1), and to the additional inputs from drydock facilities, in whose vicinities extremely high concentrations of TBT in sediments up to values of more than 10 mg/kg dry weight are frequently measured. These TBT quantities could even have a larger spatiotemporal range, since they are partly enclosed in paint particles. The latter biocide inputs can be technically controlled, given the respective priorization, and do not have to be ascribed to TBT.

A second, even more elegant way to beat the ecotoxicological risk profile of TBT would be the use of a substance, which has to be used in such small amounts, that the amount to be released in order to get the functional unit is significantly smaller. The example of the highly effective plant protection products that are in use in modern agriculture point in this direction. Of course, the other indicators have to be kept in mind as well. The great variety of organisms that can settle on ship hulls [6, 203], however, excludes the application of very selective substances, at best a combination of selective biocides could be used.

As can be seen in the net diagrams in Figure 7.1, the release of TBT can possibly be matched by Irgarol, Sea-Nine and Pyrithionate, although it is likely that the same, complete antifouling effect obtained by the use of TBT, will require higher release rates. The spatiotemporal range of both Sea-Nine and Pyrithionate is possibly lower than for TBT, for Sea-Nine this even seems likely (see section 6.2), while the spatiotemporal range of Irgarol is higher than for TBT[1] and for copper, it is certainly extremely large. The bioaccumulation of Irgarol, Sea-Nine and Pyrithionate is likely to be lower than for TBT, although this is not even really obvious for Sea-Nine, because of rare data. The biological activity of TBT is without compare. Probably, the picture would be different, if it were based on internal effect concentrations, as would be necessary in order to gain an indicator independent of the bioaccumulation indicator. The uncertainty of the overall evaluation, still compared with TBT, is a little higher for Irgarol, and considerably higher for Pyrithionate.

Given the acceptability of the use of copper containing coatings, candidates for the substitution of TBT could be Sea-Nine and Pyrithionate. It can not be concluded for certain from this work, that their environmental impact will be lower. However, the risk of environmental damage, as shown by the ecotoxicological risk profiles, seems to decrease, if they are

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[1] This is contrary to the conclusion drawn two years ago during the preparation of [8]

used instead of TBT.

7.2 Long-term dynamics of copper

The relevance of the very long residence times of copper in the system for environmentally conscious selection of antifouling biocides is limited because only about 5 % of the estimated total copper input into the sea seem to stem from antifouling paints on commercial ships.

Independent from the comparison of biocides, the model results indicate that copper concentrations in pelagic sediments could increase by more than two orders of magnitude, if current input rates remain constant. This model result is quite robust, since it is dominated by only two quantities, namely the global input rate and the global removal by pelagic sediment burial[2]. The concentration in the pelagic sediment would be expected to rise, until it is high enough that the export by sediment burial matches the copper input which stems mostly from rivers. Since it is quite obvious that there are no other quantitatively important possibilities for copper to leave the system, the copper concentration in shelf and pelagic sediment is mainly dependent on the sedimentation rates, which translate in the rates of sediment burial, or their inverse, the residence times of sediment in these compartments, as given in Table 5.1.

Figure 7.2 shows the results of a numerical, time-dependent solution[3] of the differential equations of the fate model 5.1.3 for copper, starting approximately at the copper concentrations that are measured in the environment today. The figure illustrates that the time for the model system to reach steady state with todays input rates is of the order of thousands of years. This means that it is likely that the copper concentrations measured in pelagic water and pelagic sediment today result from pre-industrial input levels, and that they will not reach steady state with todays and tomorrows input levels in the near future.

So far, we have presumed that todays copper input from rivers into the oceans have risen in the course of industrialisation. Since even today, the estimation of this quantitiy is based on quite uncertain extrapolations [119], there is no reliable record of historical progression of copper input from rivers to oceans to the knowledge of the author.

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[2] This is in contrast to the model results for TBT, which highly depend on the degradation rates assumed for the different compartments

[3] Level IV calculations where carried out with the GNU octave software (`http://www.octave.org`), which is largely compatible with MATLAB®

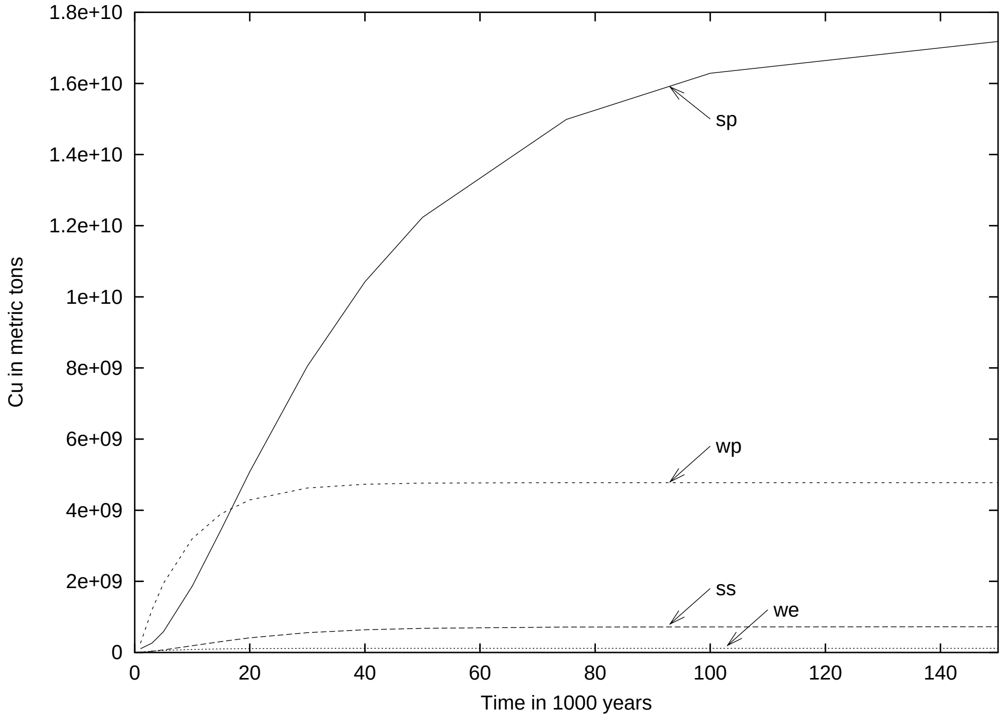

Figure 7.2: Progression of Cu mass in the quantitatively most important model compartments. sp = pelagic sediment, ss = shelf sediment, wp = pelagic water and we = epipelagic water

The possibility of a significant anthropogenic, or, more exactly, technogenic rise in copper inputs into the oceans is illustrated, comparing the total copper input estimated in section 5.2 with the global copper production. While todays total copper input from rivers to ocans was estimated by the author to amount to 580 thousand metric tons per year, the global copper production, as estimated for the 1970ies and 1980ies by Nriagu [158], was around 80 million metric tons per year. The global copper inputs into the oceans could therefore be accounted for by only about 0.7 % of the global copper production. Since this percentage does not seem to be unrealistic, it can be concluded that it is likely that the copper concentrations in pelagic water and pelagic sediment are currently rising.

Figure 7.2 is only the result of a very simple model, and probably the most misleading assumption is that the copper reservoirs of the earth are so big that the steady input can be kept up for a timespan as big as 100 000 years. For comparison, a recent case study about the long term mass balances of Cu and Cd in waste deposits assumes that from the year 3500, Cu fluxes will reduce by 1 % per ten years, i.e. by 75 % per 1000 years (assuming exponential decline) because the copper ore grade will be very low which will reduce production and use of copper. This is of course only an advantageous estimation. The important point for the assessment of copper, as tentatively illustrated in Figures 6.2 and 7.2 is that steady state of deep sea sediment concentrations will never occur at the current input rates of copper. Since the model is linear, this does not mean that the residence times are wrong. It does mean, that the prognostic power of Figure 7.2 is very small. This brings out once more, that the antifouling fate model presented here should not be used for the estimation of environmental concentrations.

The above considerations lead also to a very simple answer to the question, if the present use of copper in antifouling biocides is sustainable or not: Since the sustainability perspective per se does not imply a cut-off time in the future, which does not have to be considered any more, we can safely say, that from today's perspective, the present use of copper in antifouling paints is not sustainable, simply from the economic point of view: it will run out.

Part III

Outlook

Chapter 8

Sustainable development of chemicals

The conception of ecotoxicological risk profiles was introduced in order to address the risk of causing environmental damage by the incorporation of biologically active chemicals into products, and by the demand of such products. It is intended as a means for the manufacturer to compare alternative substances – and for the customer to compare alternative products – which might fulfill the same purpose.

A sustainable development of products will be promoted if both producers and buyers are conscious of such damages. Such a consciousness highly depends on risk communication. It has to be kept in mind, though, that the risk of causing environmental damage is only one aspect that has to be considered in a sustainable product development.

A sustainable development is generally defined as a development of our society as a whole, which takes the needs and claims of future generations into account, and which balances ecological, social and economic requirements.

The global scope of the definition of a sustainable development makes it difficult to exactly define, if a specific development in a specific region or a specific industry branch is sustainable.[1] However, the main criteria are set in the definition of a sustainable development and they can be applied also to types of products. The idea of a sustainable development of chemicals is that these criteria are already applied in the early design phases of product development.

Figure 8.1 shows the elements of a sustainable development of prod-

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[1] It is easier to see developments that are unsustainable, like the emission of flourinated and chlorinated hydrocarbons to the atmosphere was.

ucts especially focussed for product types where single substances are important. The development is shown as a circular process, similar to Figure 3.1 and similar to the circular conceptions of integrated development processes presented by Hungerbühler et al. [204]. The theoretical analysis of the chemical structures of the substances (cp. Jastorff [83]) plays an important role, since it provides the possibility to predict/estimate properties of the substance without any testing. The result of the theoretical analysis of the structures is a defined set of candidate substances for the product.

This set of substances is then obtained by synthesis or purchase. The testing should equally consider the technical applicability, possible impacts on human health, and possible environmental impacts. The results of the testing phase are then evaluated, aiming at equal weights for economical, social and ecological criteria. These evaluations lead to a selection of substances from the set which will be used in production. At the same time, the results of testing and evaluation trigger a new cycle, starting with the analysis of the currently used structures, and by enlarging this set with replacement candidates, which seem promising regarding a further improvement of the sustainability of the product palette.

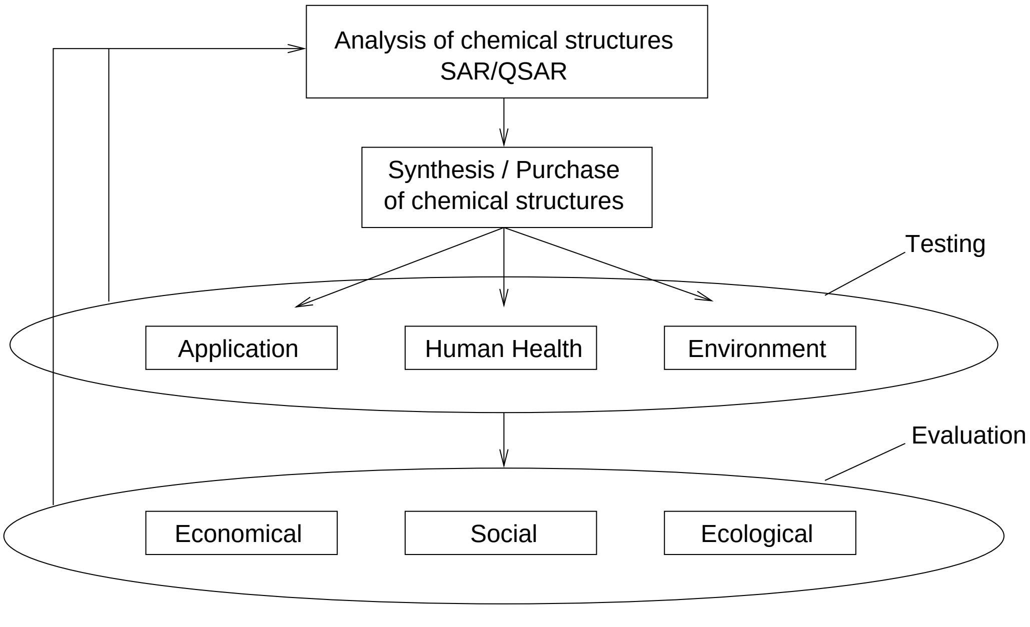

Figure 8.1: Elements of a sustainable design of chemical products

The concept of ecotoxicological risk profiles presented in this dissertation is a method for the evaluation of substances according to ecological criteria. It draws on results from the structure analysis at the very top of the graph, and from the results of the testing. Information from all three areas of testing might enter into the ecotoxicological risk profile generation, even though most information will be drawn from ecotoxicological tests.

It has to be pointed out, that the ecological evaluation will not be sufficient if only ecotoxicological risk profiles of biologically active substances are considered. For an evaluation from the viewpoint of ecology, the whole product, not only its biologically active ingredients, has to be looked at, and the whole life cycle, including the history of the incorporated substances, the environmental impacts during the use phase, and the fate of the product after use, has to be taken into account. In other words, Life-Cycle Analysis methods (LCA) should be applied complementing the use of ecotoxicological risk profiles[2].

The evaluation of the social aspect of the sustainability of products is a task which is even less clearly defined. Different approaches including such an evaluation for the area of chemical products have been published [205, 206]. Generally, the social aspects of sustainability assessment deal with the opinion of others, be they individuals (e.g. a concerned citizen calling in for information), or social groups (e.g. the ministry for human health, a fishery organzation, consumers in remote countries).

The economical aspect is concerned with the financial sustainability of a certain product design. The degree of coupling between social and ecological aspects and economical return of invest has been subject to many debates and will depend on the type of product, the type of consumers or purchasing industries and the general mentalitiy of the time. This degree of coupling can be enhanced by true risk communication. The concept of ecototoxicological risk profiles is intended to serve this purpose.

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[2] A combination of indicators for substances and LCA has been exemplified in [58]

Appendix A

Database UFT_SAR

The database UFT_SAR is a publicly accessible repository of data collected about antifouling biocides during the doctoral studies of the author, and about vulcanization agents during the diploma studies of F. Stock. It was started by the author in January 2000, as it became apparent that the data necessary for a comparative risk assessment where to manifold for comfortable working with conventional tables in word processing programs or spreadsheet tables.

The Entity Relationship Model → G (ERM) of the database is quite simple: There is a master table, defining short names for the chemicals in the database and providing all information necessary for the identification of the substances, called `chents`. The short names that are used for cross-reference with the main data-containing tables are called `chent`, which is derived from `ch`emical `ent`ity. These entities are partly defined by Chemical Abstracts Service (CAS)-Numbers, but some `chents` represent a combination of different forms of a substance, which have been combined for the purposes of the comparative evaluation. One example for such a combined group is the `chent` "TBT", which represents, if appropriate, bis-tributyltin-oxide, tributyltin chloride and the other tributyltin compounds, which are supposed to release the aqueous tributyltin species (Chapter 6).

The main body of data is made up by tables ("relationships", in the terminology of the ERM), which contain the `chent` as a key to the substance identification table `chents`, and some representation of the results of a laboratory experiment and/or field observation A.1. The table `sources` contains the bibliography of the database. A special feature of the database is the differentiation between the "effective source"and the "primary source". The effective source (`eff_source`) given in the main data-containing tables refers to the source where the information factually came from during the

Table A.1: Most important tables in the database UFT_SAR

`t_name`	**Content**
`chents`	Chemical entities
`p0`	Vapor pressure
`water_sol`	Water solubility
`pKa`	Acidity constant
`KH`	Air-water partitioning
`logKow`	Octanol-water partitioning
`Koc`	Organic carbon-water partitioning
`Kpw`	Particle-water partitioning
`kd`	Degradation
`bioacc`	Bioaccumulation
`bioactivity`	Biological Activity
`water_conc`	Water concentrations
`soil_conc`	Soil concentrations
`sed_conc`	Sediment concentrations
`sources`	Sources

setup of the database. The primary source (`prim_source`) gives additional information, if the effective source is not the experimental report itself, but only some kind of review or summary. The referencing from data table to the table `sources` uses a unique key in form of a number (integer), which is generated when the reference is entered into the common literature database of the SAR-group of Prof. Jastorff, which is a Reference Manager®database.

In order to guarantee accessibility over the internet for the data in the main database, it was implemented with the database software MySQL®, [1], which is based on the common data retrievel language ″Structured Query Language (SQL)″. MySQL is purely command-line oriented software. The MySQL-client software can be installed on all common operating systems, and the connection to the database can be established with the command `mysql -u uftguest -h eckehaat.uft.uni-bremen.de -p`. The password for the guest account (read-only) is currently **2sw10sd6**. In order to use the database, the command `use uft_sar;` has to be issued. From this point,

---

[1] `http://www.mysql.org`

SQL queries on the tables listed above can be entered.[2]

A more graphically oriented interface to the database was derived from the database administration software phpMyAdmin[3]. It can be accessed with the same username (uftguest) and password (2sw10sd6) at its website `http://eckehaat.uft.uni-bremen.de/UFT_SAR`. However, working with the database without usage of SQL-queries is quite tedious.

A.1 SQL queries used for Tables in subsection 6.4

Table 6.4:
```
select chents.chent,count(*),avg(log10(exposure)),type,effect
from chents,bioactivity where bioactivity.chent=chents.chent and
chents.pri>0 and organism like "crust%" and effect like "lethal"
and type like "EC50" and time_obs<345601 and time_obs > 0
group by chents.pri;
```

Table 6.5:
```
select chents.chent,count(*),avg(log10(exposure))
from chents,bioactivity where bioactivity.chent=chents.chent and
chents.pri>0 and organism like "crust%"
group by chents.pri;
```

Table 6.6:
```
select chents.chent,count(*),avg(log10(exposure)),type,effect
from chents,bioactivity where bioactivity.chent=chents.chent and
chents.pri>0 and organism like "Fish%" and effect like "lethal"
and type like "EC50" and time_obs>0 and time_obs< 345601
group by chents.pri;
```

Table 6.7:
```
select chents.chent,count(*),avg(log10(exposure))
from chents,bioactivity where bioactivity.chent=chents.chent and
chents.pri>0 and organism like "fish%"
group by chents.pri;
```

Table 6.8:
```
select chents.chent,count(*),avg(log10(exposure))
from chents,bioactivity where bioactivity.chent=chents.chent and
chents.pri>0 and organism like "Mollusc%"
group by chents.pri;
```

Table 6.9:
```
select chents.chent,count(*),avg(log10(exposure))
from chents,bioactivity where bioactivity.chent=chents.chent and
```

---

[2] The documentation of the MySQL syntax can be accessed online or downloaded from `http://www.mysql.org`, as well as the client software, which is free for home and academic use.

[3] `http://phpwizard.net/projects/phpmyadmin`

```
chents.pri>0 and organism like "Alga%"
group by chents.pri;
```

Table 6.10:

```
select chents.chent,count(*),avg(log10(exposure)),type,effect
from chents,bioactivity where bioactivity.chent=chents.chent and
chents.pri>0 and effect like "lethal" and type like "EC50"
and time_obs<345601 and time_obs > 0 group by chents.pri;
```

Table 6.11:

```
select chents.chent,count(*),avg(log10(exposure))
from chents,bioactivity where bioactivity.chent=chents.chent and
chents.pri>0
group by chents.pri;
```

A.2 Data tables not shown in the main text

Table A.2: TBT concentrations in water compartments from various sources

Location	Comp.	Concentration(s)	Unit	Source
Bremerhaven harbor	wh	204	ng/L	[91]
Bremerhaven harbor	wh	340	ng/L	[91]
Bremerhaven harbor	wh	212	ng/L	[91]
Copenhagen harbor	wh	73	ng/L	[91]
Rotterdam harbor	wh	38	ng/L	[91]
Rotterdam harbor	wh	47	ng/L	[91]
Milford Haven, UK	wh	9	ng/L	[91]
Milford Haven, UK	wh	6	ng/L	[91]
Genova harbor	wh	88	ng/L	[91]
Genova harbor	wh	115	ng/L	[91]
Genova harbor	wh	142	ng/L	[91]
Weser estuary	wt	25	ng/L	[91]
Weser estuary	wt	35	ng/L	[91]
Weser estuary	wt	21	ng/L	[91]
Rotterdam estuary	wt	29	ng/L	[91]
Rotterdam estuary	wt	21	ng/L	[91]
Tyne estuary	wt	68	ng/L	[91]
Tyne estuary	wt	17	ng/L	[91]
Test estuary	wt	100	ng/L	[207]
United States	wt	1.3	ng/L	[208]
United States	wt	7	ng/L	[208]
United States	wt	1	ng/L	[208]
Bremerhaven coast	ws	9	ng/L	[91]
Bremerhaven coast	ws	6	ng/L	[91]
Rotterdam coast	ws	8	ng/L	[91]
Rotterdam coast	ws	4	ng/L	[91]
Central North Sea	ws	0.01	ng/L	[81]
British Channel	ws	0.5	ng/L	[81]

Table A.3: TBT concentrations in sediment from various sources

Location	Comp.	Concentration(s)	Unit	Source
Spanish Mediterranean harbor	sh	9	μg/kg	[209]
Honolulu harbor	sh	154	μg/kg	[210]
Hamburg harbor	sh	404	μg/kg	[211]
Trondheim harbor	sh	15	μg/kg	[212]
Trondheim harbor	sh	60	μg/kg	[212]
Tromsø harbor	sh	190	μg/kg	[212]
Tromsø harbor	sh	51	μg/kg	[212]
Haugesund harbor	sh	1.27	mg/kg	[212]
Stavanger harbor	sh	55	μg/kg	[212]
Stavanger harbor	sh	83	μg/kg	[212]
Osaka bay	st	10	μg/kg	[213]
Tromsøysund	st	10	μg/kg	[212]
Tromsøysund	st	21	μg/kg	[212]
Elbe estuary	st	141	μg/kg	[211]
Lisbon coast	ss	21	μg/kg	[214]
Sines coast	ss	7	μg/kg	[214]
Sagres coast	ss	134	μg/kg	[214]
Huelvo coast	ss	8	μg/kg	[214]
Huelvo coast	ss	16	μg/kg	[214]
Trafalgar coast	ss	7	μg/kg	[214]

Table A.4: Cu concentrations in water compartments from various sources

Location	Comp.	Concentration(s)	Unit	Source
Chesapeake Bay, harbor	wh	7.0	μg/L	[93]
La-Trinit-sur-Mer Harbor	wh	2.45	μg/L	[56]
Cork harbor, Ireland	wh	4.1	μg/L	[56]
Cochin estuary, India	wt	7.0	μg/L	[93]
Humber estuary, England	wt	4.85	μg/L	[56]
Mississippi	wt	1.5	μg/L	[93]
Guadalquivir	wt	40	μg/L	[93]
Irish coastal sea	ws	2.6	μg/L	[56]
North Sea	ws	0.7	μg/L	[56]
North Sea, Sweden	ws	0.45	μg/L	[56]
North Atlantic	we	0.09	μg/L	[93]
California Current (N Pacific)	we	0.1	μg/L	[93]
Central Pacific	we	0.035	μg/L	[93]
Deep North Atlantic	wp	0.2	μg/L	[93]
Deep Pacific Ocean	wp	0.24	μg/L	[93]

Table A.5: Cu concentrations in sediment compartments from various sources

Location	Comp.	Concentration(s)	Unit	Source
Victoria Harbor, Hong Kong	sh	34800	mg/kg	[215]
East Johore Strait, Singapore	sh	61.7	mg/kg	[216]
East Johore Strait, Singapore	sh	244	mg/kg	[216]
UK estuaries	st	141	mg/kg	[93]
East Johore Strait, Singapore	st	11.2	mg/kg	[216]
Off Besos river, Spain	ss	350	mg/kg	[93]
80 km from smelter, N Sweden	ss	37	mg/kg	[93]
North Sea	ss	42	mg/kg	[217]
Malaysian Peninsula	ss	2.9	mg/kg	[218]
Southeastern USA	ss	2	mg/kg	[219]
Terranova Bay, Antarctica	ss	34	mg/kg	[220]
”Pristine marine sediment”	sp	1.4	mg/kg	[98]

Glossary of terms

Bioaccumulation The enrichment of a substance in an organism as compared to its environment resulting from uptake from the surrounding medium and from food organisms

Bioconcentration The enrichment of a substance in an organism as compared to its surrounding medium resulting from uptake from this medium. Generally used for laboratory tests with aquatic organisms

Biomagnification The enrichment of a substance in a consumer organism as compared to its food organisms

Compartment The environment is divided into several compartments for fate modelling, which differ in their physical and chemical properties to a degree which is relevant for the model. Generally, water, air and soil are considered as compartments, often sediments are seen as a separate compartment. Compartments can be divided into *Segments*. Additional compartments like suspended particulate matter which is located within the water compartments have been defined [69], in another example the soil medium has been divided into several compartments [221]

EC_{50} Concentration of a substance in water, resulting in the observation of a specified effect in 50 % of the tested organisms

Epipelagic Sea The upper 200 m of the oceans, without the coastal seas above the continental shelves

Entity-Relationship Model A way of describing the world using the definition of entities and their relationships. Entity-Relationship Models are commonly used as a first step in the construction of a database and is well compatible with SQL-based databases

Estuary The mouth of the river, up to the point where there the tidal influence is insignificant

Marina A small harbor used mainly for pleasure boats

Marine biosphere The biotope of the marine organisms

Metabolites Products of biotic transformations of a mother substance by living organisms

NOEC The highest concentration of a substance – usually in water – which did not result in an observeable effect on the tested species

Pelagic sea The deap sea, as opposed to the coastal seas above the contintental shelves

SAR This term which is originally an abbreviation for Structure- Activity-Relationship generally refers to the different kinds of estimation methods which are based on the structural properties of a chemically defined substance. Quantitative Structure-Activity Relationships (QSAR)s, Structure-Degradability-Relationships as well as quantitative and qualitative Property-Property-Relationships are included in this term

Shelf The seafloor around the continents, up to the edge where the slope of the seafloor suddenly becomes a lot steeper. As a rule of thumb, the shelf sea has a depth of up to 200 m

Segment Any spatially confined part of the environment. In fate modelling, segments are often treated as homogeneous, well-mixed boxes. A segment usually belongs to a *Compartment*, althouth some authors use the term compartment just like segment is defined here and in [222]

Spatiotemporal range The tendency of a substance and its ecotoxicologically relevant transformation products to cause exposure of organisms, once it is released to the environment in a defined way

Steady-State An idealized state of a system, where the observables describing the state of the system have constant values, while mass or energy can be moving within the system and across the system boundaries

Substance Chemical elements and their compounds as they occur in the natural state or as produced by industry [223]

Transformation products A general term for the substances to which a mother substance is being transformed in the environment, regardless if the transformation is abiotic or biotic

Bibliography

[1] J. Ranke. Persistence of antifouling biocides in the marine biosphere. *Environmental Science and Technology*, accepted, 2002.

[2] P. Slovic. Perception of risk. *Science*, 236(4799):280–285, 1987.

[3] N. Luhmann. *Soziologie des Risikos*. Walter de Gruyter, Berlin, 1991.

[4] N. Luhmann. *Risk: A sociological theory*. Aldine de Gruyter, New York, 1993.

[5] N. Stehr and G. Bechmann. The communication of risks and the risks of communicating scientific knowledge. In *Abstracts of the 9th annual meeting of SETAC-Europe 25-29 May 1999, Leipzig, Germany*. Society of Environmental Toxicology and Chemistry, 1999.

[6] J. Ranke and B. Jastorff. Stand und Perspektiven des chemischen Bewuchsschutzes. In Warrelmann J, editor, *Vorstudie zum Bewuchsschutz für Seeschiffe*. UFT Zentrum für Umweltforschung und Umwelttechnologie, Bremen, 1999.

[7] K. Mathes and J. Ranke. Erfassung des Gefahrenpotentials von Chemikalien - ein alternativer Ansatz aus ökologischer Sicht. *Zeitschrift für angewandte Umweltforschung (ZAU)*, Sonderheft 10:97–104, 1999.

[8] J. Ranke and B. Jastorff. Multidimensional risk analysis of antifouling biocides. *Environmental Science and Pollution Research*, 7(2):105–114, 2000.

[9] M. Goedkoop, P. Hofstetter, R. Müller-Wenk, and R. Spriesmsma. The Eco-Indicator 98 explained. *International Journal of Life Cycle Assessment*, 3(6):352–360, 1998.

[10] World Commission on Environment and Development. *Our common future*. Oxford University Press, Oxford, 1987.

[11] United Nations. *Agenda 21: Programme of Action for Sustainable Development*. United Nations, Departement of Public Information, New York, 1993.

[12] L. Pinter. Performance measurements for sustainable development: Compendium of experts, initiatives and publications. Technical report, International Institute for Sustainable Development IISD, Winnipeg, 1995.

[13] P. Hardi and L. Pinter. *Models and methods of measuring sustainable development performance*. International Institute for Sustainable Development IISD, Winnipeg, 1994.

[14] A. MacGillivray and S. Zadek. Accounting for change - the role of sustainability indicators. *Briefings from the GEC Programme*, 1995(4):1–4, 1995.

[15] C. J Van Leeuwen and J. L. M. Hermens. *Risk Assessment of Chemicals*. Kluwer Academic Publishers, Dordrecht, 1995.

[16] *Technical Guidance Document in Support of Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances*. Office for Official Publications of the European Communities, Luxembourg, 1996.

[17] J. Ahlers, R. Diderich, U. Klaschka, A. Marschner, and B. Schwarz-Schulz. Environmental risk assessment of existing chemicals. *Environmental Science and Pollution Research*, 1(2):117–123, 1994.

[18] Peter M. Chapman, Anne Fairbrother, and Derek Brown. A critical evaluation of safety (uncertainty) factors for ecological risk assessment. *Environmental Toxicology and Chemistry*, 17(1):99–108, 1998.

[19] F. O. Beese, K. Fraedrich, P. Klemmer, J. Kokott, L. Kruse-Graumann, C. Neumann, O. Renn, H.-J. Schellnhuber, E.-D. Schulze, M. Tilzer, P. Velsinger, and H. Zimmermann. *Welt im Wandel: Strategien zur Bewältigung globaler Umweltrisiken*, volume 1998. Springer, Berlin, 1999.

[20] F. Schmidt-Bleek and W. Haberland. Zur Bewertung von Umweltchemikalien. *Zeitschrift für Umweltpolitik*, 79(2):127–144, 1979.

[21] F. Schmidt-Bleek, W. Haberland, A.W. Klein, and S. Caroli. Steps toward environmental hazard assessment of new chemicals (including a hazard ranking scheme, based upon directive 79/831/EEC). *Chemosphere*, 11(4):383–415, 1982.

[22] D. Freitag, H. Geyer, A. Kraus, R. Viswanathan, D. Kotzias, A. Attar, W. Klein, and F. Korte. Ecotoxicological profile analysis vii. screening chemicals for their environmental behaviour by comparative evaluation. *Ecotoxicology and Environmental Safety*, 6:60–81, 1982.

[23] R. Frische, G. Esser, W. Schönborn, and W. Klöpffer. Criteria for assessing the environmental behavior of chemicals: Selection and preliminary quantification. *Ecotoxicology and Environmental Safety*, 6:283–293, 1982.

[24] E. Halfon and M. Reggiani. On ranking chemicals for environmental hazard. *Environmental Science and Technology*, 20(11):1173–1179, 1986.

[25] M. Weiß, W. Kördel, D. Kuhnen-Clausen, A.W. Lange, and W. Klein. Priority setting of existing chemicals. *Chemosphere*, 17(8):1419–1433, 1988.

[26] W. Klein, W. Kördel, A.W. Klein, D. Kuhnen-Clausen, and M. Weiß. Systematic approach for environmental hazard ranking of new chemicals. *Chemosphere*, 17(8):1445–1462, 1988.

[27] B. G. Hansen, A. van Haelst, K. van Leeuwen, and P. van der Zandt. Priority setting for existing chemicals: European union risk ranking method. *Environmental Toxicology and Chemistry*, 18(4):772–779, 1999.

[28] E. M. Snyder, S. A. Snyder, J. P. Giesy, S. A. Blonde, G. K. Hurlburt, C. L. Summer, R. R. Mitchell, and D. M. Bush. Scram: A scoring and ranking system for persistent, bioaccumulative, and toxic substances for the North American Great Lakes Part I. Structure of the scoring and ranking system. *Environmental Science and Pollution Research*, 7(1):52–61, 2000.

[29] E. M. Snyder, S. A. Snyder, J. P. Giesy, S. A. Blonde, G. K. Hurlburt, C. L. Summer, R. R. Mitchell, and D. M. Bush. Scram: A scoring and ranking system for persistent, bioaccumulative, and toxic substances for the North American Great Lakes Part II. Bioaccumulation potential and persistence. *Environmental Science and Pollution Research*, 7(2):116–121, 2000.

[30] E. M. Snyder, S. A. Snyder, J. P. Giesy, S. A. Blonde, G. K. Hurlburt, C. L. Summer, R. R. Mitchell, and D. M. Bush. Scram: A scoring and ranking system for persistent, bioaccumulative, and toxic substances for the North American Great Lakes Part III. Acute and subchronic or chronic toxicity. *Environmental Science and Pollution Research*, 7(3):176–184, 2000.

[31] E. M. Snyder, S. A. Snyder, J. P. Giesy, S. A. Blonde, G. K. Hurlburt, C. L. Summer, R. R. Mitchell, and D. M. Bush. Scram: A scoring and ranking system for persistent, bioaccumulative, and toxic substances for the North American Great Lakes Part IV. Results from representative chemicals, sensitivity analysis, and discriminatory power. *Environmental Science and Pollution Research*, 7(4):220–224, 2000.

[32] J. Reus, P. Leendertse, C. Bockstaller, I. Fomsgaard, V. Gutsche, K. Lewis, C. Nilsson, L. Pussemier, M. Trefisan, H. van der Werf, F. Alfarroba, S. Blümel, J. Isart, D. McGrath, and T. Seppälä. Comparing environmental risk indicators for pesticides. results of the european CAPER project. Technical report, Centre for Agriculture and Environment (CLM), Utrecht, 1999.

[33] M. S. Stephenson. An approach to the identification of organic compounds hazardous to the environment and human health. *Ecotoxicology and Environmental Safety*, 1:39–48, 1977.

[34] W. Klöpffer. Environmental hazard - assessment of chemicals and products, Part II: Persistence and degradability of organic chemicals. *Environmental Science and Pollution Research*, 1(2):107–116, 1994.

[35] U. Müller-Herold. A simple general limiting law for the overall decay of organic compounds with global pollution potential. *Environmental Science and Technology*, 30(2):586–591, 1996.

[36] E. Webster, D. Mackay, and F. Wania. Evaluating environmental persistence. *Environmental Toxicology and Chemistry*, 17(11):2148–2158, 1998.

[37] M. Scheringer. Persistence and spatial range as endpoints of an exposure-based assessment of organic chemicals. *Environmental Science and Technology*, 30(5):1652–1659, 1996.

[38] U. Müller-Herold and G. Nickel. A closed analytical formula for the characteristic spatial range of persistent organic pollutants. *Ecological Modelling*, 126(2-3):191–200, 2000.

[39] D. H. Bennett, T. McKone, M. Matthies, and W. E. Kastenberg. General formulation of characteristic travel distance for semi-volatile organic chemicals in a multimedia environment. *Environmental Science and Technology*, 32(4023):4030, 1998.

[40] A. Beyer, D. Mackay, M. Matthies, F. Wania, and E. Webster. Assessing long-range transport potential of persistent organic pollutants. *Environmental Science and Technology*, 34(4):699–703, 2000.

[41] D. Mackay. *Multimedia Environmental Models, the Fugacity Approach*. Lewis, Chelsea, MI, USA, 1991.

[42] M. Scheringer. Characterization of the environmental distribution behavior of organic chemicals by means of persistence and spatial range. *Environmental Science and Technology*, 31(10):2891–2897, 1997.

[43] M. Scheringer, F. Wegmann, K. Fenner, and K. Hungerbühler. Investigation of the cold condensation of persistent organic pollutants with a global mulitmedia fate model. *Environmental Science and Technology*, 34:1842–1850, 2000.

[44] A.W. Klein. OECD fate and mobility test methods. In *Handbook of Environmental Chemistry*, volume C2, pages 1–28. Springer, Berlin, 1 edition, 1985.

[45] K. Fenner, M. Scheringer, and K. Hungerbühler. Persistence of parent compunds and transformation products in a level IV multimedia model. *Environmental Science and Technology*, 2000.

[46] R. Quartier and U. Müller-Herold. On secondary spatial ranges of transformation products in the environment. *Ecological Modelling*, 2000.

[47] W Klöpffer, G. Rippen, and R. Frische. Physicochemical properties as useful tools for predicting the environmental fate of organic chemicals. *Ecotoxicology and Environmental Safety*, 6:294–301, 1982.

[48] C. Heidorn. IUCLID: Database on chemical substances information as a tool for the EU-risk-assessment program. *Journal of Chemistry, Information and Computer Science*, 36:949–954, 1996.

[49] A.M. Finkel. Confronting uncertainty in risk management. Resources for the future, Center for Risk Management, Washington DC, 1990.

[50] M. G. Morgan and M. Henrion. *Uncertainty*. Cambridge University Press, Cambridge, 1990.

[51] W. Klein, H. Geyer, D. Freitag, and H. Rohleder. Sensitivity of schemes for ecotoxicological hazard ranking of chemicals. *Chemosphere*, 13(1):203–211, 1984.

[52] R. Brüggemann and H.-G. Bartel. A theoretical concept to rank environmentally significant chemicals. *Journal of Chemistry, Information and Computer Science*, 39:211–217, 1999.

[53] M. Scheringer. *Persistenz und Reichweite von Umweltchemikalien*. Wiley-VCH, 1999.

[54] O. Mosbach-Schulz. Methodische Aspekte probabilistischer Modellierung. *Umweltwissenschaften und Schadstoff-Forschung*, 11(5):292–298, 1999.

[55] S. Schwartz, V. Berding, and M Matthies. Aquatic fate assessment of the polycyclic musk fragrance HHCB: Scenario and variability analysis in accordance with the EU risk assessment guidelines. *Chemosphere*, 41(5):671–679, 2000.

[56] L. W. Hall and R. D. Anderson. A deterministic ecological risk assessment for copper in European saltwater environments. *Marine Pollution Bulletin*, 38(3):207–218, 1999.

[57] M. Scheringer, B. Escher, D. Steinbach, and Hungerbühler K. Probabilistic assessment in the effect assessment of toxic chemicals: What are the benefits and limitations? *Environmental Science and Pollution Research*, submitted, 2001.

[58] A. Beck, M. Scheringer, and K. Hungerbühler. Fate modelling within LCA: The case of textile chemicals. *The International Journal of Life Cycle Assessment*, 5(6):335–344, 2000.

[59] F. Stock. Beurteilung der ökotoxikologischen Risiken verschiedener Vulkanisationsbeschleuniger. Diplomarbeit, Universität Bremen, 2001.

[60] R. Brandsch, K.-E. Nowak, B. Binder, and B. Jastorff. Untersuchungen zur Nachhaltigkeit der Sanierung von mit Tributylzinn kontaminierten Hafensedimenten durch Landablagerung. *Umweltwissenschaften und Schadstoff-Forschung*, accepted.

[61] K. Mathes. Ökotoxikologische Wirkunsabschätzung – Das Problem der Extrapolation auf ökosysteme. *Umweltwissenschaften und Schadstoff-Forschung*, 9:17–23, 1997.

[62] M. Berg and M. Scheringer. Problems in environmental risk assessment and the need for proxy measures. *Fresenius Environmental Bulletin*, 3:487–492, 1994.

[63] M. Scheringer. *Räumliche und zeitliche Reichweite als Indikatoren zur Bewertung von Umweltchemikalien*. PhD thesis ETH Nr. 11746, Swiss Federal Institute of Technology, 1996.

[64] D. Mackay, E. Webster, M. MacLeod, and I. Cousins. Role of models for evaluating persistence and long-range transport. In *Abstracts of the Tenth Annual Meeting of SETAC Europe*, page 19, Brighton, 2000. Society of Environmental Toxicology and Chemistry.

[65] G. W. Suter II. *Ecological Risk Assessment*. Lewis Publishers, Boca Raton, 1993.

[66] Uniform System for the Evaluation of Substances (USES), version 3.0. Technical report, National Institute of Public Health and the Environment (RIVM), Ministry of Housing, Spatial Planning and the Environment (VROM), Ministry of Health, Welfare and Sports (VWS), The Netherlands, 1999.

[67] F. Wania, D. Mackay, Y.-F. Li, T. F. Bidleman, and A. Strand. Global chemical fate of α-hexachlorocyclohexane. 1. Evaluation of a global distribution model. *Environmental Toxicology and Chemistry*, 18(7):1390–1399, 1999.

[68] F. Wania and D. Mackay. Global chemical fate of α-hexachlorocyclohexane 2. use of global distribution model for mass balancing, source apportionment, and trend prediction. *Environmental Toxicology and Chemistry*, 18(7):1400–1407, 1999.

[69] D. Mackay, S. Paterson, and W. Y. Shiu. Generic models for evaluating the regional fate of chemicals. *Chemosphere*, 24(6):695–717, 1992.

[70] C. M. Lalli and T. R. Parsons. *Biological Oceanography: An Introduction*. Pergamon Press, Oxford, 1 edition, 1993.

[71] The role of bioaccumulation in environmental risk assessment: The aquatic environment and related food web. Technical Report 67, European Chemical Industry Ecology & Toxicology Centre (ECETOC), 1995.

[72] B. Beek. The assessment of bioaccumulation. In *Handbook of Environmental Chemistry*, volume 2J. Springer, Berlin, 2000.

[73] L. Marsili, C. Gaggi, A. Bortolotto, L. Stanzani, A. Franchi, A. Renzoni, and E. Bacci. *Chemosphere*, 31(8):3919, 1995.

[74] P.T. Egeler, J. Römbke, Th. Knacker, M. Meller, C. Franke, G. Studinger, and R. Nagel. Bioaccumulation of lindane and hexachlorobenzene by tubificide sludgeworms (oligochaeta) under standardised laboratory conditions. *Chemosphere*, 35:835–854, 1997.

[75] P.T. Egeler, J. Römbke, M. Meller, Th. Knacker, C. Franke, G. Studinger, and R. Nagel. Bioakkumulation: Vorstellung eines Sedimenttests mit benthischen Oligochaeten. In *Chemikalienbewertung – Konzepte für Sedimente und marine Ökosysteme. 8. BUA-Kolloquium*, number 17 in Monographie, 2000.

[76] D.T.H.M. Sijm and J.L.M. Hermens. Internal effect concentration: Link between bioaccumulation and ecotoxicity for organic chemicals. In *Handbook of Environmental Chemistry*, volume 2J. Springer, Berlin, 2000.

[77] I. Lunn. *Antifouling: A Brief Introduction to the Origins and Development of the Marine Antifouling Industry*. BCA Publications, Thame, 1974.

[78] The Council of the European Communities. Council Directive 89/677/EEC of 21 December 1989 amending for the eighth time Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the member states relating to restrictions on the marketing and use of certain dangerous substances and preparations. *Official Journal of the European Communities*, L 398:19–23, 1989.

[79] K. Bosselmann. Environmental law and tributyltin in the environment. In S.J. De Mora, editor, *Tributyltin: case study of an envronmental contaminant*, number 8 in Cambridge environmental chemistry series, pages 237–263. Cambridge University Press, Cambridge, 1996.

[80] Pesticides 1998: Your guide to approved pesticides. Technical report, Pesticide Safety Directorate (PSD) and Health and Safety Executive (HSE), London, 1998.

[81] Utilisation of more 'environmentally friendly' antifouling products. Report, CEPE (European Council of Paint, Printing Ink and Artists' Colours Industry), 1999.

[82] V. F. Vetere, M. C. Perez, R. Romagnoli, M. E. Stupak, and B. Del-Amo. Solubility and toxic effect of the cuprous thiocyanate antifouling pigment on barnacle larvae. *Journal of Coatings Technology*, 69(866):39–45, 1997.

[83] B. Jastorff. *Struktur-Wirkungsdenken in der Chemie - eine Chance für mehr Nachhaltigkeit*. 2001.

[84] S. Dobson and R. Cabridenc. Tributyltin compounds. IPCS Environmental Health Criteria 116 116, World Health Organization, Geneva, 1990.

[85] M. A. Champ and P. F. Seligman, editors. *Organotin: Environmental Fate and Effects*. Chapman and Hall, London, 1996.

[86] S.J. De Mora, editor. *Tributyltin: case study of an envronmental contaminant*. Cambridge environmental chemistry series. Cambridge University Press, Cambridge, 1996.

[87] K. Fent. Ecotoxicology of organotin compounds. *Critical Reviews in Ecotoxicology*, 26(1):1–117, 1996.

[88] R. J. Maguire. Review of the persistence, bioaccumulation and toxicity of tributyltin in aquatic environments in relation to canada's toxic substances management policy. *Water Quality Research Journal of Canada*, 35(4):633–679, 2000.

[89] J. P. Meador and C. A. Rice. Impaired growth in the polychaete armandia brevis exposed to tributyltin in sediment. *Marine Environmental Research*, 51(2):113–129, 2001.

[90] L. W. Hall, M. C. Scott, W. D. Killen, and M. A. Unger. A probabilistic ecological risk assessment of tributyltin in surface waters of the chesapeake bay watershed. *Human and Ecological Risk Assessment*, 6(1):141–179, 2000.

[91] S. Karlsson. Literature survey on ecotoxicology and environmental exposure of organotin compounds with emphasis on use in antifouling paints. Technical report, KEMI (National Chemicals Inspectorate Sweden), Solna, 1997.

[92] Tributyltin oxide. Technical report, GDCh-Advisory Committee on Existing Chemicals of Environmental Relevance (BUA), Stuttgart, 1994.

[93] C. Dameron. Copper. IPCS Environmental Health Criteria 200, World Health Organization, Geneva, 1998.

[94] W. Slooff, R.F. Cleven, F.A. Janus, and J.P. Ros. Integrated criteria document copper. Technical report, RIVM (National Institute of Public Health and Environmental Protection), The Netherlands, Bilthoven, 1989.

[95] J. A. Janus, C. A. Canton, J. H. van Gestel, and E. Heijna-Merkus. Appendix to integrated criteria document copper: Effects. Technical report, RIVM (National Institute of Public Health and Environmental Protection), Bilthoven, 1989.

[96] A. Elzvik and K. Hanze. Ecotoxicological evaluation of copper in antifouling paints: Copper, cuprous oxide, cuprous thiocyanate. Technical report, KEMI, Solna, 1992.

[97] J. Bard. Supplement 1 to the ecotoxicological evaluation of copper in antifouling paints: Copper, cuprous oxide, cuprous thiocyanate. Technical report, KEMI, Solna, 1997.

[98] M. Sadiq. *Toxic Metal Chemistry in Marine Environments*. Marcel Dekker, New York, 1992.

[99] T. Madsen, L. Samsøe-Petersen, K. Gustavson, and D. Rasmussen. Ecotoxicological assessment of antifouling biocides and nonbiocidal antifouling paints. Environmental Project no. 531, Miljstyrelsen, Danish EPA, DHI Water and Environment, Kopenhagen, 2000.

[100] P. Dollenmeier. *Irgarol-9807: Information on active components*. Ciba Specialty Chemicals, Basel, 1998.

[101] J. Bard and A. Pedersen. Ecotoxicological evaluation of the antifouling compound 2-(tert-butylamino)-4-(cyclopropylamino)-6-(methylthio)-1,3,5,-triazine Irgarol. Technical report, KEMI (National Chemicals Inspectorate Sweden), Solna, 1992.

[102] J. Bard. Supplement 1 to the ecotoxicological evaluation of the antifouling compound 2-(tert-butylamino)-4-(cyclopropylamino)-6-(methylthio)-1,3,5,-triazine Irgarol. Technical report, KEMI (National Chemicals Inspectorate Sweden), Solna, Sweden, 1992.

[103] E. Tiberg. Supplement 2 to the ecotoxicological evaluation of the antifouling compound 2-(tert-butylamino)-4-(cyclopropylamino)-6-(methylthio)-1,3,5,-triazine irgarol: aquatic algae and higher plants tests. Technical report, KEMI, Solna, 1994.

[104] J. Bard. Supplement 3 to the ecotoxicological evaluation of the antifouling compound 2-(tert-butylamino)-4-(cyclopropylamino)-6-(methylthio)-1,3,5,-triazine irgarol. Technical report, KEMI, Solna, 1997.

[105] L. W. Hall, J. M. Giddings, K. R. Solomon, and R. Balcomb. An ecological risk assessment for the use of irgarol 1051 as an algaecide for antifoulant paints. *Critical Reviews In Toxicology*, 29(4):367–437, 1999.

[106] M. Björk and S. Karlsson. Ecotoxicological evaluation of 4,5-dichloro-2-n-octyl-4-isothiazolone-3-one (RH-287, RH-5287). Technical report, KEMI (National Chemicals Inspectorate Sweden), Solna, Sweden, 1992.

[107] E. Dryselius. Ecotoxicological evaluation of the biocide 4,5-dichloro-2-n-octyl-4-isothiazolone-3-one (RH-287, RH-5287): Supplementary documentation. Technical report, KEMI (National Chemicals Inspectorate Sweden), Solna, Sweden, 1998.

[108] W. D. Shade, S. S. Hurt, A. H. Jacobson, and K. H. Reinert. Ecological risk assessment of a novel marine antifoulant. Standard technical publication, American Society for Testing and Materials, Philadelphia, 1993.

[109] H. Sönnichsen. Abschlussbericht zur Studie: Risikoabschätzung von Bioziden in Antifoullingfarben. Technical report, Umweltbundesamt, 1995.

[110] P. A. Turley, R. J. Fenn, and J. C. Ritter. Pyrithiones as antifoulants: Environmental chemistry and preliminary risk assessment. *Biofouling*, 1:1–8, 2000.

[111] D. Mackay, A. di Guardo, S. Paterson, and C. E. Cowan. Assessing the fate of new and existing chemicals: A five-stage process. *Environmental Toxicology and Chemistry*, 15(9):1618–1626, 1996.

[112] W. S. Broecker. A kinetic model for the chemical composition of sea water. *Quaternary Research*, 1:188–207, 1971.

[113] H. U. Sverdrup, M. W. Johnson, and R. H. Fleming. *The Oceans: Their Physics, Chemistry, and General Biology*. Prentice-Hall, Englewood Cliffs, 1942.

[114] S. Neshyba. *Oceanography: Perspectives on Fluid Earth*. John Wiley and Sons, New York, 1987.

[115] K. Kranck. Sedimentation processes in the sea. In Otto Hutzinger, editor, *Handbook of Environmental Chemistry*, volume 2A, pages 61–75. Springer, Berlin, 1980.

[116] P. Schatzberg. Measurement and significance of the release rate for tributyltin. In M. A. Champ and P. F. Seligman, editors, *Organotin: Environmental Fate and Effects*, book chapter 19, pages 383–403. Chapman and Hall, London, 1996.

[117] *Shipping Statistics Yearbook*. Institute of Shipping Economics and Logistics, 1998.

[118] J. Isensee, B. Watermann, and H.-D. Berger. Emissions of antifouling-biocides into the North Sea - an estimation. *Deutsche Hydrographische Zeitschrift*, 46(4):355–365, 1994.

[119] S. W. Poulton and R. Raiswell. Solid phase associations, oceanic fluxes and the anthropogenic perturbation of transition metals in world river particulates. *Marine Chemistry*, 72:17–31, 2000.

[120] W. S. Broecker and T.-H. Peng. *Tracers in the Sea*. Lamont-Doherty Geological Observatory, Palisades, 1982.

[121] R. Collier and J. Edmond. The trace element geochemistry of marine biogenic particulate matter. *Progress in Oceanography*, 13:113–199, 1984.

[122] F. T. Mackenzie, R. J. Lantzy, and V. Paterson. Global trace metal cycles and predictions. *Journal of the International Association of Mathematical Geology*, 11(2):99–142, 1979.

[123] J. O. Nriagu and J. M. Pacyna. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature*, 333(6169):134–139, 1988.

[124] K. R. Dyer. Estuaries and estuarine sedimentation. In K. R. Dyer, editor, *Estuarine Hydrography and Sedimentation*, pages 1–18. Cambridge University Press, 1979.

[125] J. M. Huthnance. Circulation, exchange and water masses at the ocean margin: The role of physical processes at the shelf edge. *Progress in Oceanography*, 35:353–431, 1995.

[126] R. A. Davis Jr. *Depositional Systems: An Introduction to Sedimentology and Stratigraphy*. Prentice Hall, Englewood Cliffs, 2nd edition, 1992.

[127] W. Ricken. *Sedimentation as a Three-Component System: Organic Carbon, Carbonate, Noncarbonate*. Springer, Berlin, 1993.

[128] E. A. Romankevich. *Geochemistry of Organic Matter in the Ocean*. Springer, Berlin, 1984.

[129] R. J. Maguire and R. J. Tkacz. Degradation of the tri-n-butyltin species in waters an sediment from Toronto harbor. *Journal of Agricultural and Food Chemistry*, 33:947–953, 1985.

[130] J. R. W. Harris and J. J. Cleary. Particle-water partitioning and organotin dispersal in an estuary. In *Proceedings of the Oceans*, volume 4, pages 1370–1374, New York, 1987. Institute of Electrical and Electronics Engineers.

[131] A. O. Valkirs, P. F. Seligman, and R. F. Lee. Butyltin partitioning in marine waters and sediments. In *Proceedings of the Oceans*, volume 4, pages 1165–1170, Washington DC, 1986. Institute of Electrical and Electronics Engineers and the Marine Technology Society.

[132] A. O. Valkirs, M. O. Stallard, and P. F. Seligman. Butyltin partitioning in marine waters. In *Proceedings of the Oceans '87 Organotin Symposium*, volume 4, pages 1375–1380, New York, 1987. Institute of Electrical an Electronics Engineers.

[133] D. Adelman, K. R. Hinga, and M. E. Q. Pilson. Biogeochemistry of butyltins in an enclosed marine ecosystem. *Environmental Science and Technology*, 24:1027–1032, 1990.

[134] H. Harino, M. Fukushima, Y. Kurokawa, and S. Kawai. Susceptibility of bacterial populations to organotin compounds and microbial degradation of organotin compounds in environmental water. *Environmental Pollution*, 98(2):157–162, 1998.

[135] H. Harino, M. Fukushima, Y. Kurokawa, and S. Kawai. Degradation of the tributyltin compounds by the microorganisms in water and sediment collected from the harbor area of Osaka City, Japan. *Environmental Pollution*, 98(2):163–167, 1997.

[136] P. F. Seligman, A. O. Valkirs, and R. F. Lee. Degradation of tributyltin in San Diego Bay, California, waters. *Environmental Science and Technology*, 20:1229, 1986.

[137] P. F. Seligman, C. M. Adema, J. Grovhoug, R. L. Fransham, A. O. Valkirs, and P. M. Stang. Persistence and fate of tributyltin in aquatic ecosystems. In M. A. Champ and P. F. Seligman, editors, *Organotin: Environmental Fate and Effects*, book chapter 21, pages 429–458. Chapman and Hall, London, 1996.

[138] S. J. de Mora, N. G. King, and M. C. Miller. Tributyltin and total tin in marine sediments: Profiles and the apparent rate of TBT degradation. *Environmental Technology Letters*, 10:901–908, 1989.

[139] S. J. de Mora, C. Stewart, and D. Phillips. Sources and rate of degradation of tri(n-butyl)tin in marine sediments near Auckland, New Zealand. *Marine Pollution Bulletin*, 30:50–57, 1995.

[140] P. H. Dowson, J. N. Lester, and J. M. Bubb. Persistence and degradation pathways of tributyltin in freshwater and estuarine sediments. *Estuarine, Coastal and Shelf Science*, 42(5):551–562, 1996.

[141] C. Stewart and S. J. de Mora. A review of the degradation of tri(n-butyl)tin in the marine environment. *Environ. Technol.*, 11:565–570, 1990.

[142] M. T. Grassi, B. Shi, and H. Allen. Sorption of copper by suspended particulate matter. *Colloids Surfaces A*, 120:199–203, 1997.

[143] C. Pohl and U. Hennings. The effect of redox processes on the partitioning of Cd, Pb, Cu, and Mn between dissolved and particulate phases in the Baltic Sea. *Marine Chemistry*, 65:41–53, 1999.

[144] E. Helmers. Trace metals in suspended particulate matter of Atlantic Ocean surface water. *Marine Chemistry*, 53:51–67, 1996.

[145] P. W. Balls. The partition of trace metals between dissolved and particulate phases in European coastal waters: A compilation of field data and comparison with laboratory studies. *Netherlands Journal of Sea Research*, 23(1):7–14, 1989.

[146] I. Tolosa, J. W. Readman, A. Blaevoet, S. Ghilini, J. Bartocci, and M. Horvat. Contamination of Mediterranean (Cote d'Azur) coastal waters by organotins and Irgarol 1051 used in antifouling paints. *Marine Pollution Bulletin*, 32(4):335–341, 1996.

[147] R. C. Doyle. Photodegradation of 14C-Irgarol 1051 in sterile seawater. Technical report, IIT Research Institute, 1991.

[148] J. M. Schmidt and L. L. Head. Aerobic aquatic metabolism of 14C-Irgarol 1051. ABC final Report No. 38889, Analytical Bio-Chemistry Laboratories, Inc., Columbia, Missouri, USA, 1991.

[149] Warren. Determination of adsorption/desorption constants of C-9211/14C-RH-5287. ABC Report No 32116, Rohm & Haas Technical Report No. 310-86-31, Analytical Bio-Chemistry Laboratories, Inc., Columbia, Missouri, USA, 1986.

[150] M. S. Gene, L. Olson and L. J. Lawrence. Soil adsorption/desorption of [14C]RH-5287 by the batch equilibrium method. PTRL Report No. 1246, Rohm & Haas Technical Report No. 34-90-28, Pharmacology and Toxicology Research Laboratory, Richmond, Kentucky, USA, 1991.

[151] A. Jacobson and V. Kramer. Additional information on water-sediment partitioning and half-life of DCOI in a harbor. Note prepared for VKI, 1999.

[152] L. J. Lawrence and et al. Aerobic aquatic metabolism of [13/14C]RH-5287. PTRL Report No. 1291, Rohm & Haas Technical Report No. 34-91-01, Pharmacology and Toxicology Research Laboratory, Richmond, Kentucky, USA, 1991.

[153] G. L. Willingham and A. H. Jacobson. Designing an environmentally safe marine antifoulant. *ACS Symposium Series*, 640(Designing Safer Chemicals):224–233, 1996.

[154] A. Kesterson and R. Atkins. Supplemental study on the anaerobic aquatic metabolism of [13/14C]RH-5287. PTRL Report No. 1313, Rohm & Haas Technical Report No. 34-92-46, Pharmacology and Toxicology Research Laboratory, Richmond, Kentucky, USA, 1992.

[155] C. G. Arnold, A. Weidenhaupt, M. M. David, S. R. Müller, S. B. Haderlein, and R. P. Schwarzenbach. Aqueous speciation and 1-octanol-water partitioning of tributyl- and triphenyltin: Effect of pH and ion composition. *Environmental Science and Technology*, 31(9):2596–2602, 1997.

[156] D. Amouroux, E. Tessier, and O. F. X. Donard. Volatilization of organotin compounds from estuarine and coastal environments. *Environmental Science and Technology*, 34:988–995, 2000.

[157] J. Ranke, F. Stock, and C. Grimmer. Database UFT_SAR. http://eckehaat.uft.uni-bremen.de/UFT_SAR.

[158] J. O. Nriagu. A history of global metal pollution. *Science*, 272(5259):223–224, 1996.

[159] P. J. Collier, A. J. Ramsey, R. D. Waigh, K. T. Douglas, P. Austin, and P. Gilbert. Chemical reactivity of some isothiazolone biocides. *Journal of Applied Bacteriology*, 69:578–584, 1990.

[160] W. D. Crow and Nelson J. Leonard. 3-isothiazolone-cis-3-thiocyanoacrylamide equilibria. *Journal of Organic Chemistry*, 30:2660–2665, 1965.

[161] M. E. Callow and J. A. Finlay. A simple method to evaluate the potential for degradation of antifouling biocides. *Biofouling*, 9(2):153–165, 1995.

[162] M. E. Callow and G. L. Willingham. Degradation of antifouling biocides. *Biofouling*, 10(1-3):239–249, 1996.

[163] K. V. Thomas. Determination of the antifouling agent zinc pyrithione in water samples by copper chelate formation and high-performance liquid chromatography atmospheric pressure chemical ionisation mass spectrometry. *Journal of Chromatography A*, 833(1):105–109, 12-2-1999.

[164] P. Lindgren, B. Olsson, and C. Unger. Antifoulingprodukter för yrkesmässigt bruk - fartyg längre än 12 meter. Pm-beslut, KEMI (National Chemicals Inspectorate Sweden), 1998.

[165] K.V. Thomas, K. Raymond, J. Chadwick, and M.J. Waldock. The effects of changes in environmental parameters on the releas of organic booster biocides from antifouling coatings. In *Additional Papers from the 10th International Congress on Marine Corrosion and Fouling. University of Melbourne, February 1999*, page in press, 2001.

[166] R.F. Lee. Metabolism of tributyltin by aquatic organisms. In M. A. Champ and P. F. Seligman, editors, *Organotin: Environmental Fate and Effects*, chapter 16, pages 369–382. Chapman and Hall, 1996.

[167] R. B. Laughlin Jr, H. E. Guard, and W. M. Coleman. Tributyltin in seawater: Speciation and octanol-water partition coefficient. *Environmental Science and Technology*, 20:201–204, 1986.

[168] Copper omadine(r) bactericide fungicide powder, industrial grade. Technical product information, Olin Biocides (now part of Arch Chemicals, Inc.), 1998.

[169] R. J. Maguire, R. J. Tkacz, Y. K. Chau, G. A. Bengert, and P. T. S. Wong. Occurrence of organotin compounds in water and sediment in Canada. *Chemosphere*, 15(3):253–274, 1986.

[170] I. Tolosa, J. W. Readman, A. Blaevoet, S. Ghilini, J. Bartocci, and M. Horvat. Contamination of Mediterranean (Cote d'Azur) coastal waters by organotins and Irgarol 1051 used in antifouling paints. *Marine Pollution Bulletin*, 32(4):335–341, 1996.

[171] K.V. Thomas, S.J. Blake, and M.J. Waldock. Antifouling paint booster biocide contamination in UK marine sediments. *Marine Pollution Bulletin*, 40(9):739–745, 2000.

[172] Y. Yonezawa, M. Fukui, T. Yoshida, A. Ochi, T. Tanaka, Y. Noguti, T. Kowata, Y. Sato, S. Masanuga, and Y. Urushigawa. Degradation of tri-n-butyltin in Ise Bay sediment. *Chemosphere*, 29(6):1349–1356, 1994.

[173] P. F. Seligman, J. G. Grovhoug, A. O. Valkirs, P. M. Stang, R. Fransham, M. O. Stallard, B. Davidson, and R. F. Lee. Distribution and fate of tributyltin in the United States marine environment. *Applied Organometallic Chemistry*, 3:31, 1989.

[174] L. Randall and J. H. Wedig. Adsorptive behavior of butltin compounds under simulated estuarine conditions. *The Science of the Total Environment*, 57:191, 1986.

[175] G.W. Kilby and G.E. Batley. Chemical indicators of sediment chronolgy. *Australian Journal of Marine and Freshwater Research*, 44:635–647, 1993.

[176] G. Batley. Distribution and fate of tributyltin in the marine environment. In S.J. De Mora, editor, *Tributyltin: case study of an envronmental contaminant*, number 8 in Cambridge environmental chemistry series, pages 139–166. Cambridge University Press, Cambridge, 1996.

[177] P. M. Stang, R. F. Lee, and P. F. Seligman. Evidence for rapid non-biological degradation of tributyltin in fine-grained sediments. *Environmental Science and Technology*, 26:1382–1387, 1992.

[178] K. Martinez, I Ferrer, and D. Barcelo. Part-per-trillion level determination of antifouling pesticides and their byproducts in seawater samples by off-line solid- phase extraction followed by high-performance liquid chromatography-atmospheric pressure chemical ionization mass spectrometry. *Journal of Chromatography A*, 879(1):27–37, 2000.

[179] D. Liu, R. J. Maguire, Y. L. Lau, G. J. Pacepavicius, H. Okamura, and I Aoyama. Transformation of the new antifouling compound Irgarol 1051 by Phanerochaete chrysosporium. *Water Research*, 31(9):2363–2369, 1997.

[180] J. Giddings, J. Hoberg, R. Diever, and R. Balcomb. The fate and toxicity of a triazine antifoulant in marine microcosms. preliminary report submitted to ciba specialty chemicals, tarrytown, ny. Technical report, Springborn Laboratories Inc., Wareham, MA.

[181] B. König, R. Balcomb, and S. Lord. Environmental risk assessment of irgarol 1051. In *10th Internatinal Congress on Marine Corrosion and Fouling*. Melbourne, Australia, 1999.

[182] J. M. Schmidt. Aerobic soil metabolism of 14C-Irgarol 1051. ABC final Report No. 38885, Analytical Bio-Chemistry Laboratories, Inc., Columbia, Missouri, USA, 1992.

[183] Cranor and Daly. Anaerobic aquatic metabolism of 14C-RH-5287. ABC final Report No. 32115, Analytical Bio-Chemistry Laboratories, Inc., Columbia, Missouri, USA, 1986.

[184] P.-J. Sun, Q. Fernando, and H. Freiser. Formation constants of transition metal complexes of 2-hydroxypyridine-1-oxide and 2-mercaptopyridine-1-oxide. *Analytical Chemistry*, 36(13):2485–2488, 1964.

[185] R. A. Neihof, C. A. Bailey, C. Patouillet, and P. J. Hannan. Photodegradation of mercaptopyridine-N-oxide biocides. *Archives of Environmental Contamination and Toxicology*, 8:355–368, 1979.

[186] J.C. Ritter. Summary of the aerobic and anaerobic aquatic metabolism of [pyridine-2,6-14C] copper omadine and [pyridine-2,6-14C] zinc omadine in marine water and sediment. Technical report, Olin Research Centre, Cheshire, CT. Arch Chemicals, 1999.

[187] J.C. Ritter. Aerobic aquatic metabolism of [pyridine-2,6-14C] copper omadine in marine water and sediment. Technical report, Olin Research Centre, Cheshire, CT. Arch Chemicals, 1999.

[188] J.C. Ritter. Aerobic aquatic metabolism of [pyridine-2,6-14C] zinc omadine in marine water and sediment. Technical report, Olin Research Centre, Cheshire, CT. Arch Chemicals, 1999.

[189] J.C. Ritter. Anaerobic aquatic metabolism of [pyridine-2,6-14C] copper omadine in marine water and sediment. Technical report, Olin Research Centre, Cheshire, CT. Arch Chemicals, 1999.

[190] J.C. Ritter. Anaerobic aquatic metabolism of [pyridine-2,6-14C] zinc omadine in marine water and sediment. Technical report, Olin Research Centre, Cheshire, CT. Arch Chemicals, 1999.

[191] J. C. Amiard, C. Amiard-Triquet, B. Berthel, and C. Metayer. Comparative study of the patterns of bioaccumulation of essential (Cu, Zn) and non-essential (Cd,Pb) trace metals in various estuarine and coastal organisms. *Journal of Experimental Biology and Ecology*, 106:73–89, 1987.

[192] R. B. Laughlin Jr. Bioaccumulation of tbt by aquatic organisms. In M. A. Champ and P. F. Seligman, editors, *Organotin: Environmental Fate and Effects*, chapter 16, pages 331–355. Chapman and Hall, 1996.

[193] S. Toth, K. Becker Van Slooten, L. Spack, L.-F. De-Alencastro, and J. Tarradellas. Irgarol 1051, an antifouling compound in freshwater, sediment, and biota of Lake Geneva. *Bulletin of Environmental Contamination and Toxicology*, 57:426–433, 1996.

[194] W. M. Meylan and P. H. Howard. Atom/fragment contribution method for estimating octanol-water partition coefficients. *Journal of Pharmaceutical Sciences*, 84(1):83–92, 1995.

[195] E J. Baum. *Chemical Property Estimation - Theory and Application*. CRC Press, Boca Raton, 1998.

[196] T. M. Florence, H. K. J. Powell, J. L. Stauber, and R. M. Town. Toxicity of lipid-soluble copper(II) complexes to the marine diatom Nitzschia closterium: Amelioration by humic substances. *Water Research*, 26(9):1187–1193, 1992.

[197] J. T. Phinney and K. W. Bruland. Uptake of lipophilic organic Cu, Cd, and Pb complexes in the coastal diatom thalassiosira weissflogii. *Environmental Science and Technology*, 28(11):1782–1790, 1994.

[198] G. W. Bryan, P. E. Gibbs, R. J. Hugett, L. A. Curtis, D. S. Bailey, and D. M. Dauer. Effects of tributyltin pollution on the mud snail, Ilyanassa obsoleta, from the York River and Sarah Creek, Chesapeake Bay. *Marine Pollution Bulletin*, 20:458, 1989.

[199] R. De Nys, T. Leya, R. Maximilien, A. Afsar, P. S. Nair, and P. D. Steinberg. The need for standardised broad scale bioassay testing: A case study using the red alga laurencia rigida. *Biofouling*, 10(1-3):213–224, 1996.

[200] N. P. Skoulis, S. J. Barbee, Kram D. Jacobson, D. L. Putman, and R.-H. C. San. Evaluation of the genotoxic potential of zinc pyrithione in the Salmonella mutagenicity (Ames) assay, CHO/HGPRT gene mutation assay and mouse micronucleus assay. *Journal Of Applied Toxicology*, 13(4):283–289, 1993.

[201] M. M. Vega, A. Urzelai, and E. Angulo. Regression study of environmental quality objectives for soil, fresh water, and marine water, derived independently. *Ecotoxicology and Environmental Safety*, 38:210–238, 1997.

[202] J. W. Tukey. *Explanatory Data Analysis*. Addison-Wesley, Reading, MA, 1977.

[203] H. A. Rathsack. *Schiffsanstriche: Korrosions- und Bewuchsschutz am Schiffsboden*. Akademischer Verlag, Berlin, 1967.

[204] K. Hungerbühler, J. Ranke, and T. Mettier. *Chemische Produkte und Prozesse: Grundkonzepte zum umweltorientierten Design*. Springer, Berlin, 1998.

[205] C. Ewen, F. Ebinger, C.-O. Gensch, R. Grießhammer, C. Hochfeld, and V. Wollny. *Hoechst Nachhaltig*. Öko-Institut Verlag, Freiburg, 1997.

[206] Steuerungsgruppe zum "Dialogprojekt PVC und Nachhaltigkeit"und Arbeitsgemeinschaft PVC und Umwelt e.V., editor. *PVC und Nachhaltigkeit: Systemstabilität als Maßstab. Ausgewählte Produktsysteme im Vergleich.* Deutscher Instituts-Verlag, Köln, 1999.

[207] W. J. Langston. Tributyl tin in the marine environment: A review of past and present risks. *Pesticides Outlook*, 6(6):18–24, 1995.

[208] D. Russell, M. S. Brancato, and H. J. Bennett. Comparison of trends in tributyltin concentrations among three monitoring programs in the United States. *Journal of Marine Science and Technology*, 1:230–238, 1996.

[209] I. Tolosa, L. Merlini, N. de Bertrand, J. M. Bayona, and J. Albaiges. Occurence and fate of tributyl- and triphenyltin compounds in western mediterranean coastal enclosures. *Environmental Toxicology and Chemistry*, 11:145–155, 1992.

[210] J. G. Grovhoug, P. F. Seligman, G. Vafa, and R. L. Fransham. Baseline measurements of butyltin in u.s. harbors and estuaries. In *Proceeding of the Ocean '86 Organotin Symposium*, volume 4, pages 1283–1288, New York, 1986. Institute of Elektrical and Electronics Engineers, New York.

[211] J. Krinitz and B. Stachel. Herkunft und Verteilung von Organozinnverbindungen in der Elbe und ihren Nebenflüssen. Technical report, Wassergütestelle Elbe, Hamburg, 1999.

[212] J. A. Berge, L. Berglind, E. M. Brevik, N. Følsvik, N. Green, J. Knutzen, R. M. Konieczny, and M. Walday. Levels and environmental effects of TBT in marine organisms and sediments from the Norwegian coast. A summary report. Overvkingsrapport, Norwegian Institute for Water Research (NIVA), Oslo, 1997.

[213] H. Harino, M. Fukushima, S. Kawai, and K. Megumi. Measurement of butyltin contamination of water and sediment in Osaka Bay, Japan. *Appl. Organomet. Chem.*, 12:819–825, 1998.

[214] J.L.G. Ariza and M.A. Santos. Information on TBT levels and the occurrence of imposex in certain marine species in the North Sea, the Mediterranean and the coastal waters of Portugal. Annex 2: Impact of organotins in open sea along the Iberian Coast, contribution by Spain and Portugal. MEPC 46/INF.2, Spain and Portugal, 2001.

[215] J. W. C. Wong and CL. Yang. The effect of pH and redox potential on the release of nutrints and heavy metals from a contaminated marine sediment. *Toxicology and Environmental Chemistry*, 62(1-4):1–10, 1997.

[216] B. P. L. Goh and L. M. Chou. Heavy metal levels in marine sediments of Singapore. *Environmental Monitoring and Assessment*, 44(1-3):67–80, 1997.

[217] J. M. Everaarts and C. V. Fischer. The distribution of heavy metals (Cu, Zn, Cd, Pb) in the fine fraction of surface sediments of the North Sea. *Netherlands Journal of Sea Research*, 29(4):323–331, 1992.

[218] A. Ismail, M. A. Badri, and M. N. Ramlan. The background levels of heavy metal concentration in sediments of the west coast of Peninsular Malaysia. *The Science of the Total Environment, Supplement*, pages 315–323, 1993.

[219] H. L. Windom, S. J. Schropp, F. D. Calder, J. D. Ryan, R. G. Smith Jr., L. C. Burney, F. G. Lewis, and C. H. Rawlinson. Natural trace metal concentrations in estuarine and coastal marine sediments of the Southeastern United States. *Environmental Science and Technology*, 23:314–320, 1989.

[220] E. Magi. Determination of trace metals complexed with humic acids in Antarctic marine sediments. *Chemical Speciation and Bioavailability*, 9(2):67–70, 1997.

[221] M. Matthies and R. Brüggemann, Trenkle. Multimedia modelling approach for comparing the environmental fate of chemicals. In *Environmental Modelling for Priority Setting among Existing Chemicals*, pages 211–252, Landsberg/Lech, 1986. gsf Gesellschaft für Strahlen- und Umweltforschung GmbH, ecomed.

[222] L. A. Burns. Exposure analysis modeling system (EXAMS): User manual and system documentation. EPA/600/R-00/081, U.S. Environmental Protection Agency, Ecosystems Research Division U.S. Environmental Protection Agency 960 College Station Road Athens, Georgia 30605-2700, 2000.

[223] The Council of the European Communities. Council Directive 76/769/EEC of 27 July 1976 on the approximation of the laws, regulations and administrative provisions of the member states regarding to restrictions on the marketing and use of certain dangerous substances and preparations. *Official Journal of the European Communities*, L 262:201–203, 1976.

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Liste der wissenschaftlichen Publikationen

Ranke J (1997) Was bedeutet Nachhaltigkeit in einem Industrieareal? In: Zentrum Zürich Nord: Stadt im Aufbruch. Scholz RW, Bösch S, Mieg HA, Stünzi J (Hrsg.) vdf Hochschulverlag, Zürich

Hungerbühler K, Ranke J, Mettier T (1998) Chemische Produkte und Prozesse: Grundkonzepte zum umweltorientierten Design. Springer, Berlin

Mathes K, Ranke J (1999) Erfassung des Gefahrenpotentials von Chemikalien: Ein alternativer Ansatz aus ökologischer Sicht. Zeitschrift für angewandte Umweltforschung, Sonderheft 10/99 Umweltrisikopolitik, 97-104

Ranke J, Jastorff B (2000) Multidimensional risk analysis of antifouling biocides. Environmental Science and Pollution Research 7(2), 105-114

Klausen J, Ranke J, Schwarzenbach R (2001) Influence of solution composition and column aging on the reduction of nitroaromatic compounds by zero-valent iron. Chemosphere 44(4), 511-517

Ranke J (2002) Persistence of antifouling biocides in the marine biosphere. Environmental Science and Technology, accepted

Konferenzbeiträge

Ranke J, Jastorff B (1999) A simple fate model for the evaluation of antifouling biocides. In: Abstracts of the 9th Annual Meeting of SETAC-Europe 25-29 May 1999 in Leipzig, Germany

Ranke J, Jastorff B (1999) Chemicals for tomorrow. In: Proceedings of the OECD workshop on sustainable chemistry, 15-17 October 1998 in Venice, Italy. OECD Environmental Health and Safety Publications Series on Risk Management No. 10

Ranke J (2000) Wie persistent sind Antifouling-Biozide. In: Kurzreferate und Teilnehmerverzeichnis der Jahrestagung der GDCh vom 7. bis 10. Oktober 2000 in Bayreuth

Ranke J, Stock F, Jastorff B (2001) Multidimensional Risk Analysis of Chemicals. In: Abstracts of the 11th Annual Meeting of SETAC-Europe 6-10 May 2001 in Madrid, Spain

Ranke J (2001) The global fate of antifouling biocides: Implications from a box-model approach. In: Abstracts of the 11th Annual Meeting of SETAC-Europe 6-10 May 2001 in Madrid, Spain