Doctoral thesis

Modelling and evaluating the aquatic fate of detergents

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Abstract

Within this thesis an environmental assessment and evaluation method for analysing aquatic ecotoxicological impacts of household laundry is developed. The methodology allows comparative assessments of different product alternatives, washing habits, and wastewater treatment techniques in order to identify their relevance with respect to waterborne discharges. Elements from both analytical tools Life Cycle Assessment (LCA) and Environmental Risk Assessment of chemicals (ERA) are combined in this methodology. The core consists of the Geography-referenced Regional Exposure Assessment Tool for European Rivers (GREAT-ER), which calculates concentrations of 'down-the-drain' chemicals in surface waters due to point releases. In order to simulate the aquatic fate of detergents, a new GREAT-ER emission model is developed, called GREAT-ER product mode, which calculates calculates concentration increases of detergent ingredients in surface waters based on product formulations and assumptions concerning washing habits. Two evaluation methods, the Critical Length (CL) and the Product Risk Ratio (PRR_x), are defined for evaluating the results. CL is the sum of mean concentration increases, divided by substance-specific no effect concentrations (NECs), over all river stretches and all ingredients weighted by the lengths of the stretches. PRR_x is the (percentual) number of river stretches in a region, in which the x-percentiles of the predicted concentration increases of at least one ingredient exceed a substance-specific NEC. The emission model requires input data that can be derived from the functional unit of an LCA, which allows an assessment of other impact categories by using any existing LCA method.

The methodology is applied to a case study which is based on scenarios given in the comprehensive product assessment 'Washing and washing agents' (*'Produktlinienanalyse'*, PLA). In order to apply the GREAT-ER product mode, the Rur river basin in Western North-Rhine Westphalia is chosen as study area. The catchment integration includes the development of a simple hydrological model that combines a nonlinear regression analysis with a local refinement procedure. The quality of the integration of the Rur catchment data is analysed by a comparison of monitoring data and predicted concentrations of detergent and cleaning agent ingredients using actual consumption data of the two years 1993 and 2000. The product mode results show that use habits have a larger influence on the results than product formulations. However, the largest influence is caused by varying wastewater treatment techniques. Boron and the surfactants are the most relevant detergent ingredients. Furthermore, using different detergents for white and coloured laundry lowers the predicted emissions significantly.

Based on this methodology, sustainable development indicators (SDIs) for describing the aquatic aspects of household laundry are defined. CL is proposed as pressure indicator and PRR_x as state indicator for describing aquatic aspects of the sustainability of household laundry in a region. Different regions can be compared by normalising the CL by the region's population and expressing the PRR_x as a percentage of stretches in a region. Annually evaluating regional CLs and PRR_xs allows the assessment whether a region is moving towards a more sustainable state.

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Falstaff : *You shall hear (...) they conveyed me into a buck-basket.*

Ford : *A buck-basket?*

Falstaff : *Yea, a buck-basket: rammed me in with foul shirts and socks, foul stockings, and greasy napkins; that, master Brook, there was the rankest compound of villainous smell that ever offended nostril.*

William Shakespeare (1564 - 1616): *Merry wives of Windsor (Act III, Scene V)*

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Abbreviations

AE	Alcohol Ethoxylathe
AES	Alkyl Ether Sulphate or Alcohol Ethoxy Sulphate
AETP	Aquatic Ecotoxicity Potential
AETS	Aquatic Ecotoxicity Score
AISE	Association Internationale de la Savonnerie, de la Détergence et des Produits d'Entretien
APG	Alkyl Polyglucoside
AS	Alkohol Sulphate
AS+PS	Activated Sludge and Primary Settler
BKG	Bundesamt für Kartographie und Geodäsie
BRW	Bergisch-Rheinischer Wasserverband
BUA	GDCh-Beratergremium für Altstoffe
CERA	Cumulative Energy Requirements Analysis
CEFIC	European Chemical Industry Council
CESIO	Comité Européen des Agents de Surface et leurs Intermédiaires Organiques
CSD	United Nations Commission for Sustainable Development
CHAINET	European Network on Chain Analysis for Environmental Decision Support
CL	Critical Length
CMC	Carboxymethylcellulose
CML	Centre for Environmental Science
CST	Critical Surface Time
DAED	Diacetylethylenediamine
DAS-1	4,4'-bis-[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)Amino]Stilbene-2,2'-disulfonate
DID	Detergents Ingredients Database
DOC	Dissolved Organic Carbon
EC	Effect Concentration

ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECOSOL	European LCI Surfactant Study Group
EDIP	Environmental Design of Industrial Products
EDSI	Environmental Decision Support Instrument
EDTA	Ethylenediaminetetraacetate
EIA	Environmental Impact Assessment
ERA	Environmental Risk Assessment
ERASM	Environmental Risk Assessment Steering Committee
EUSES	European Union System for the Evaluation of Substances
FAS	Fatty Alkohol Sulphate
FFA	Free Fatty Alkohol
FWA	Flourescent Whitening Agent
GDCh	Gesellschaft Deutscher Chemiker
GIS	Geographical Information System
GREAT-ER	Geography-referenced Regional Exposure Assessment Tool for European Rivers
GUI	Graphical User Interface
HERA	Human and Environmental Risk Assessment
HHCB	(1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-Hexamethyl-Cyclopenta-[g]-2-Benzopyrane)
HPLC	High Performance Liquid Chromatography
IKW	Industrieverband Körperpflege- und Waschmittel e.V.
ISO	International Organisation for Standardisation
LAF	Local Adjustment Factor
LAS	Linear Alkylbenzene Sulphonate
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
LCIA	Life Cycle Impact Assessment
LUA	Landesumweltamt (State Environmental Agency)
LTE	Long Term Effect
MBAS	Methylene Blue Active Substances
MFA	Material Flow Accounting
MIA	Material Intensity Analysis
MTC	Maximum Tolerable Concentration
NEC	No Effect Concentration

NOEC	No-Observed Effect Concentration
NTA	Nitrilotriacetate
NVZ	Dutch Soap and Detergents Association
OECD	Organisation for Economic Co-Operation and Development
PEC	Predicted Environmental Concentration
PEG	Polyethylene Glycol
PLA	Produktlinienanalyse
PNEC	Predicted No-Effect Concentration
PRR_x	Product Risk Ratio
PS	Primary Settler
PVP	Polyvinylpyrrolidon
Q_5	95^{th} percentile low flow
Q_m	Mean flow
RCR	Risk Characterisation Ratio
RIVM	Dutch National Institute of Public Health and the Environment
SAS	Secondary Alkane Sulphonate
SDF	Stream Dilution Factor
SDI	Sustainable Development Indicator
SETAC	Society for Environmental Toxicology and Chemistry
SFA	Substance Flow Analysis
SMR	Soil Moisture Routing model
StUA	Staatliches Umweltamt (Regional Environmental Agency)
TAED	Tetraacetylethylenediamine
TEGEWA	Verband der Textilhilfsmittel-, Lederhilfsmittel-, Gerbstoff- und Waschrohstoff-Industrie e.V.
TF+PS	Trickling Filter and Primary Settler
TGD	Technical Guidance Document
ThOD	Theoretical Oxygen Demand
TOC	Total Organic Carbon
TPBS	Tetrapropylene Benzene Sulphonate
UBA	Umweltbundesamt (Federal Environmental Agency)
UNCED	United Nations Conference on Environment and Development
USES	Uniform System for the Evaluation of Substances
UVPG	Gesetz zur Umweltverträglichkeitsprüfung
VOC	Volatile Organic Compounds

VROM	Dutch Ministry of Housing, Spatial Planning and the Environment
WCED	World Commission on Environment and Development
WRMG	Gesetz zur Umweltverträglichkeit von Wasch- und Reinigungsmitteln
WVER	Wasserverband Eifel-Rur
WWTP	Wastewater Treatment Plant
ZEODET	Association for Detergent Zeolite Producers

1. Introduction

Throughout human history, but especially during the last century, negative impacts of human activities on the environment, including plants, animals, and the humankind itself have become apparent. More recently, it has become obvious that the uncontrolled depletion of resources and emissions into air, water, and soil can no longer be pursued. For this reason, the different human activities and needs should be analysed and optimised with respect to minimal environmental impacts. However, for many human activities, methodologies which are capable of analysing environmental implications are lacking.

1.1. The human activity and need household laundry

Due to the ubiquitous though spatially varying human desire to clean himself and his clothes, household laundry poses a large potential threat to the environment. In fact, several negative environmental effects have already occurred that could be ascribed to household laundry. These effects mainly occurred in surface waters below municipal discharges, which shows that the use phase is highly relevant for the environmental performance of this activity.

In the middle of the 20^{th} century, the formerly used anionic surfactant soap was replaced by non-degradable synthetic surfactants, above all the branched tetrapropylene benzene sulphonate (TPBS). This led to the formation of huge mountains of foam in many rivers. In Germany, this problem was solved by the passing of the detergents law in 1961, which defined minimum criteria for the primary degradability of the anionic surfactants used in laundry detergents (Stache, 1981, p. 540). Due to this law, TPBS was replaced by the non-branched and therefore degradable synthetic anionic surfactant linear alkylbenzene sulphonate (LAS). This led to a significant reduction of surfactant concentrations in surface waters (Stache, 1981, p. 541).

Due to a coaction of different political aspects (Stache, 1981, p. 542), in 1975 the detergents law was replaced by the German law on detergents and cleaning agents (*'Wasch- und Reinigungsmittelgesetz'*, WRMG, Deutscher Bundestag, 1987). This legislation defined degradability criteria not only for anionic, but also for nonionic surfactants. In conjunction with the area-wide operation of activated sludge type wastewater treatment plants in

Germany, a further significant reduction of environmental concentrations of surfactants was achieved. In addition, a further environmentally relevant aspect, which has become apparent as a consequence of the steadily growing use of laundry detergents, could be regulated by this law. Increasing emissions of phosphate, which was used in detergents as a builder, raised the problem of eutrophication. Due to the surplus supply of nutrients the algal bloom increased considerably. Decomposition of these larger quantities of biomass led to decreases of available oxygen. Finally, in some surface waters inversion occurred. Consequently, maximum limits of phosphate were defined by an ordinance pertaining the WRMG (*'Phosphathöchstmengenverordnung'*, Deutscher Bundestag, 1980). In parallel, phosphate-free detergents were put on the market due to the development of zeolite A, which in combination with polycarboxylates and sodium carbonate is able to replace phosphate[1] (Vollmer and Franz, 1994, p. 32). This substitution is a good example for the fact that in general detergent ingredients may be substituted by alternative compounds. Therefore, a method judging the environmental soundness of laundry detergents needs to be able to assess the influence of ingredient substitutions.

Unwanted detergent-related environmental impacts mostly occurred locally below discharge sites. The magnitude of the impact therefore depends on site-specific local conditions, e.g. the dilution ratio below the discharge sites, as well as on regional characteristics, e.g. the way in which wastewater is treated. In addition, laundry detergents contain considerable amounts of different salts, mainly sodium based, which are also discharged after use via the wastewater path. Hence, they contribute to the total salt content in freshwater systems, the significance of which again depends on the local dilution ratios below the discharge sites[2]. Assessment of the environmental soundness of detergents should be done spatially explicit for both analysing the fate of detergent ingredients and estimating the contributions of detergent-related salt emissions at measurable salt concentrations.

It may be stated that due to legislation and the invention of new and improved detergent ingredients, the most obvious negative aquatic impacts of doing the laundry in Germany have been eliminated. However, the development of modern detergents has increased the number of ingredients present in detergent formulations. For this reason, larger numbers of different chemicals with low concentrations are expected to occur in the environment. Interactions and toxic effects of mixtures may therefore pose greater concern than the unwanted effects of single substances. Thus, environmental assessment methods should address the potential combined aquatic impacts of detergents.

Besides waterborne emissions, energy-related emissions are also recognised as being environmentally relevant (CHAINNET, 1999, Grießhammer et al., 1997). Therefore, sev-

[1] Currently, further alternatives exist, which, however, have not yet reached economical relevance. A comparison of different available detergent builders was carried out by Bauer et al. (1999).

[2] The environmental relevance of these salt emissions is discussed controversially. According to Osnowski and Rubik (1987), problems may occur in slow-flowing rivers, while Schöberl and Huber (1988) conclude that the contribution of detergent-based salt to the total German salt load is negligible. However, the latter study is based on calculations of the total salt load rather than on an investigation of the situations in different rivers. This is a large simplification.

eral studies were carried out in order to assess energy usages of household laundry by assuming different types of washing machines and washing habits, and concerning the temperature used for washing (e.g. Group for Efficient Appliances, 1995). However, energy-related and waterborne emissions are related to each other. The decrease of the average washing temperature has become possible due to the development of new detergent ingredients such as the bleaching activator tetraacetylethylenediamine (TAED) and various enzymes (Vollmer and Franz, 1994). TAED enables bleaching with perborate even at temperatures below 60°C, while enzymes allow for an efficient removal of proteins, starch, and fat at these lower temperatures. This demonstrates that environmental product assessment methods should account for different environmental areas of concern.

Finally, it may be stated that most studies conclude that the use phase, in terms of environmental implications, is the most important phase of household laundry. This was pointed out, for example, by Grießhammer et al. (1997, p. 15) and in the CHAINNET (1999, p. 24) project. Both conclude that this is also true for energy-related emissions. Regarding waterborne emissions it is even more obvious. This has led to the establishment of respective criteria of an ecolabel for laundry detergents aimed at the reduction of water pollution from detergent ingredients occurring after the use phase (European Union, 1999a).

1.2. Instruments, tools, methods, and models

In order to assess and evaluate environmental implications of human activities and the products fulfilling or facilitating these needs, methodologies are required which support environmental decision-making processes. In this context, it is important to distinguish between models, methods, and decision support instruments or systems, which are sometimes also called analytical tools (Wrisberg and Udo de Haes, 2000). The relationship and interconnectivity of analytical tools with management and policy instruments is shown in Figure 1.1 (Wrisberg and Udo de Haes, 2000). In this figure, the core of the environmental aspects consists of so-called ‘analytical tools’ which are necessary for (sustainable) decision-making[3].

The denotation ‘analytical tool’ is debatable, since this word implicitly raises associations of a technical aid in order to solve a task. ‘Environmental Decision Support Instrument’ (EDSI) is a better term than ‘analytical tool’, while ISO (DIN, 1998) calls them ‘environmental management techniques’. In this thesis, the term ‘Environmental Decision Support Instrument’ (EDSI) is used.

EDSIs are processes aimed at evaluating environmental aspects of human activities. Their results are used in environmental decision-making. Examples of EDSIs are Life Cycle Assessment (LCA) and Environmental Risk Assessment (ERA).

[3]One may argue that the environmental aspects have too large a share compared to the technical, social, and economic aspects. This is most likely due to the fact that the study from which the figure is taken focuses on the environmental aspects.

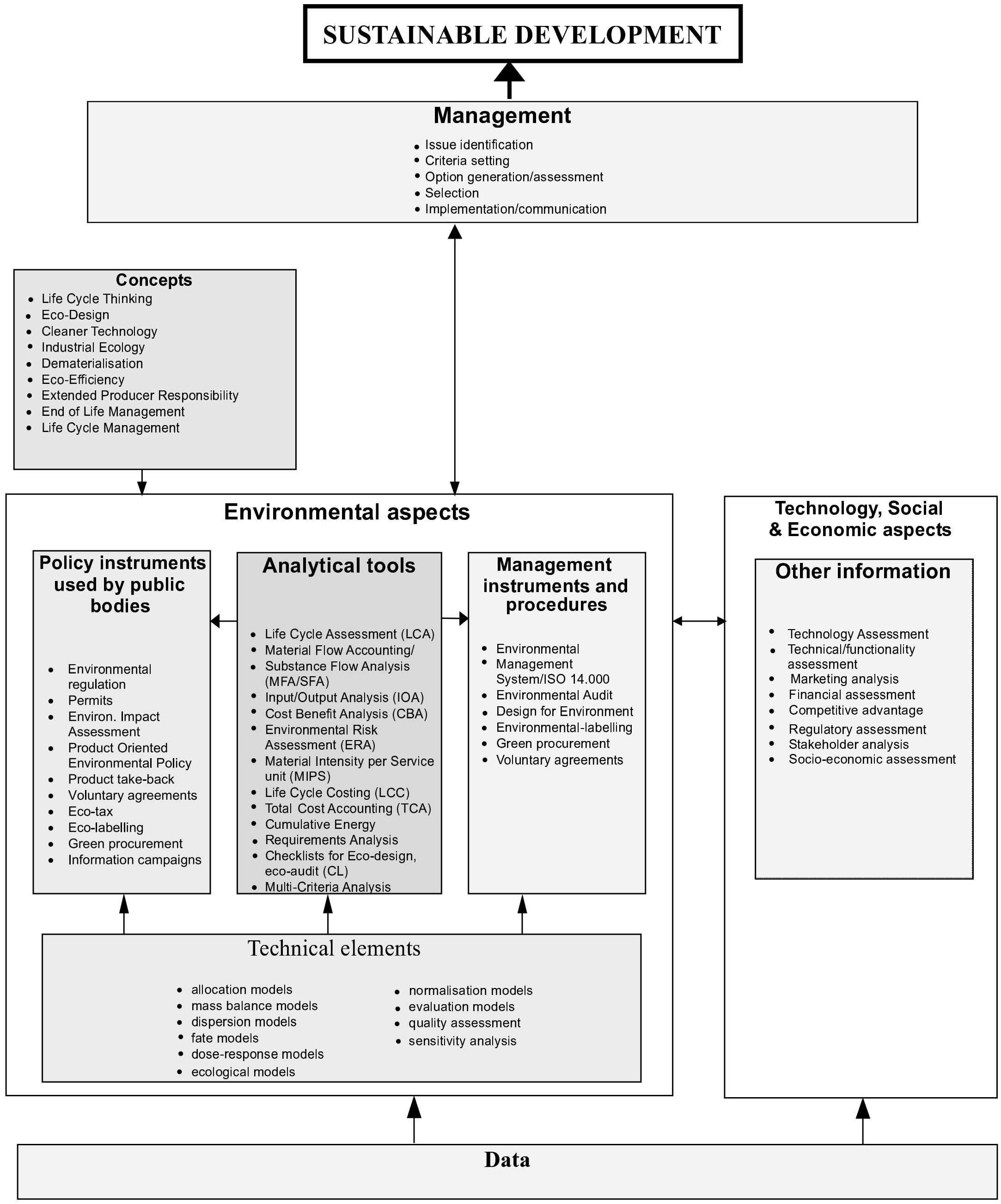

Figure 1.1.: **Relationship between elements necessary in decision-making processes** (from Wrisberg and Udo de Haes, 2000)

Methods are means to perform the evaluation within an EDSI, i.e. a method is in general a formal evaluation scheme. Methods are developed for their application in a specific EDSI. Examples of methods developed in the context of LCA are the *'Eco-Indicator 99'* methodology (Goedkoop et al., 1998, Goedkoop and Spriensma, 1999), the *'Environmental Design of Industrial Products'* methodology (EDIP, Hauschild et al., 1998), and the

'Critical Surface Time' method (CST, Jolliet and Crettaz, 1997). The central method applied in ERA is the calculation of deterministic risk characterisation ratios. Within this context, **models** are formal representations of environmental processes based on natural sciences[4]. They also have implicit assumptions inherent to them. Models may be applied to different methods and therefore within different EDSIs. Often models are adapted in order to apply them within different methods. In such an application, the consequences of such adaptions have to be analysed carefully, since small changes may cause significant impacts. An example of a model that is used in different methods is the multimedia fate model 'SIMPLEBOX' (Van de Meent, 1993), which was developed for and primarily is applied within ERA (Commission of the European Union, 1996a). More recently, it is used in the LCA method Eco-Indicator 99.

1.3. Aim of thesis and research questions

Section 1.1 pointed out environmental aspects of household laundry with a special emphasis on waterborne emissions. In order to assess the environmental soundness of detergents and household laundry these issues need to be considered. Thus, specific EDSIs, methods, and models are necessary, since some pecularities have to be considered. These comprise the importance of local and regional variabilities, the fact that different substances are emitted simultaneously, and the large quantities of emitted substances. The latter aspect was outlined by the European Commission, which stated that *"washing our laundry is not an innocuous activity. Laundry detergents have a significant contribution to water pollution. This is due not only to chemicals contained in the formulations but also to the sheer volume of the quantities used"* (European Union, 1999b). For this reason, an evaluation scheme focussing on water pollution from the use of detergents has to consider the ingredients of different products as well as the quantities required to fulfill the specific service of washing. In order to identify options for improvements of the state of the environment, information about the most relevant factors and actors have to be provided.

The aim of this thesis is to develop an environmental assessment and evaluation methodology for assessing aquatic ecotoxicological impacts of household laundry. It shall allow comparative assessments of different product alternatives, different washing habits and different wastewater treatment techniques. In addition, the aspects mentioned at the beginning of this section, i.e. dependency on regional and local conditions, potential toxicity of chemical mixtures, and quantities emitted versus washing performance, should be included. Since other environmental impacts of household laundry are known besides aquatic impacts, it ought to be possible to link results derived using this instrument to outcomes of other methodologies which analyse other environmental impacts of household laundry.

[4] In general, a model is defined as a simplified map of a relevant excerpt from reality. Its definition depends on the model's purpose (Bossel, 1992). The restriction to natural science is therefore only valid for the use of models within this context.

Based on this aim the following research questions are also addressed (in the order of appearance in the thesis):

1. Is there already an instrument available which fulfills the requirements given above? What are the limitations of current EDSIs, methods, and models?
2. How can such an instrument be designed?
3. What is the magnitude of aquatic impacts of household laundry and what are the relevant factors?

1.4. Outline of dissertation

In the following chapter, it is shown that LCA and ERA and methods developed for them are best suited for the assessment and evaluation of aquatic impacts of household laundry. Their underlying concepts are therefore briefly introduced. After this theoretical introduction, existing LCA methods as well as a fate model developed in the context of ERA, the *'Geography-referenced Regional Exposure Assessment Tool for European Rivers'* (GREAT-ER) model, are applied to detergent ingredients in order to evaluate their usefulness to assess aquatic impacts of household laundry. Subsequently, results from a literature review of existing studies addressing different environmental aspects of household laundry are summarised. From these findings conclusions are drawn, which show that the development of a new method based on the general framework of LCA is most appropriate. The method combines elements from both ERA and LCA.

Based on the findings described in chapter 2, the new method GREAT-ER *product mode* is defined in chapter 3. This method uses the GREAT-ER model as its core environmental fate model and allows the assessment and evaluation of the aquatic fate of detergents and washing habits. A case study in which the product mode is applied is then introduced (chapter 4).

Chapter 5 focuses on the main study area, the Rur river basin in Western North Rhine-Westphalia, Germany. Since the GREAT-ER model has considerable geographical data requirements, the setting up of the catchment database and the modelling steps necessary for this are presented. In chapter 6, the outcome of this integration is evaluated by a comparison of GREAT-ER simulation results obtained in the Rur catchment with measurements of different detergent ingredients. Scenarios based on data for two different years, i.e. 1993 and 2000, are used.

In chapter 7, results of the GREAT-ER product mode analysing the case study are reported. A discussion of the product mode and of the results obtained in chapter 7 is laid down in chapter 8.

As a further application of the new evaluation method, sustainable development indicators (SDIs) describing aquatic aspects of sustainable household laundry are proposed (chapter 9). Finally, in chapter 10, central conclusions are drawn.

2. Existing approaches

In this chapter, existing approaches are reviewed and analysed whether they are suitable for this thesis. Firstly, in section 2.1, the prime importance of the EDSIs LCA and ERA is shown, Their core elements and characteristics are discussed. Then, four existing LCA methods are analysed concerning the way in which they model aquatic ecotoxicological impacts. Afterwards, the GREAT-ER 1.0 model is applied to the Itter catchment in order to judge its capability in predicting riverine concentrations of detergent ingredients. Subsequently, an overview of existing studies dealing with environmental implications of household laundry is given. Since detergents and detergent ingredients have been subject to numerous studies investigating different environmental aspects, only the most relevant are discussed. Finally, conclusions are drawn from this review.

2.1. Environmental Decision Support Instruments

Different EDSIs used in environmental decision-making processes have been developed, see section 1.2. Since they have been developed with regard to certain objectives, they emphasise different aspects. In this section, the two most relevant ones for evaluating the environmental soundness of detergents are described. Prior to this description, the reason for choosing them is given.

2.1.1. Choice of EDSIs

In order to assess and evaluate the environmental soundness of household laundry, it is necessary to analyse their environmental impacts. Considering emission and resource consumption alone without an assessment of the likelihood of unwanted environmental effects is not sufficient. Therefore, EDSIs that do not have an impact assessment phase are excluded. From the list of available EDSIs, which are given in Figure 1.1 as analytical tools, the only ones that perform an evaluation of (either potential or actual) environmental impacts are LCA and ERA. Thus, aspects of LCA and ERA will be explored in further detail, since these instruments are indeed best suited for assessing and evaluating the environmental implications of household laundry. In fact, in almost all studies related to household laundry either LCAs or ERAs were carried out. For example, the appropriateness of both LCA and ERA in the context of household laundry was stated by Wrisberg and Gameson (1998) in the definition document of the CHAINET project, which is further described in section 2.4.3.

Another EDSI that has been applied in the context of household laundry is material flow accounting (MFA), which is similar to substance flow analysis (SFA) (CHAINNET, 1998). SFA consists of three steps: definition of the system, quantification of stocks and flows, and interpretation of the results (Van der Voet et al., 1995a,b), but it does not perform an assessment of environmental impacts of the material flows. Baccini and Bader (1996) used the example of household laundry as a case study for an SFA, which helped to identify the quantity of substance flows. However, their environmental relevance has not been evaluated. In addition, Grießhammer et al. (1997) performed an SFA for the total quantity of German household laundry. By this, the contribution of household laundry to the total German emissions of selected parameters in 1993 was determined in order to prove the environmental relevance of household laundry. Nevertheless, the influence of consumer washing habits and variable product formulations was analysed by performing an LCA. The two reasons for refraining from the use of SFA/MFA approaches are the lack of the concept of working with functional units and the lack of an impact assessment phase.

2.1.2. Life Cycle Assessment

When focussing on an comparative environmental assessment of products, in most cases an LCA is carried out. A broad definition of LCA is given by Walter Klöpffer on the WWW presentation of the International Journal of LCA[1]: "*LCA is a process to evaluate the environmental burdens associated with a product, process, or activity by identifying and quantifying energy and materials used and wastes released to the environment, to assess the impact of those energy and material uses and releases to the environment, and to identify and evaluate opportunities to affect environmental improvements*".

The basic idea of an LCA is to perform a comparative assessment by working with functional units. These are defined according to the scope of the study. It allows the comparison of different product or service alternatives that fulfill the same functional unit with respect to all resource usages and emissions occurring throughout the entire life cycle. Thus, LCA is not an absolute assessment of environmental impacts of a specific product system. Due to this principle, a lack of accordance between an impact predicted by an LCA and the one actually being observable may occur (Potting, 2000, p. 7). This is caused by the lack of information regarding the time, duration, and location of an emission analysed in an LCA (White et al., 1995). Although many impacts only occur if thresholds are being exceeded, most LCA methods add all marginal emissions regardless of whether thresholds are being exceeded, which in turn may lead to unrealistic outcomes. This approach is known as the 'less-is-better' principle (Potting, 2000, p. 17). This approach is accepted, since "*LCA is primarily a tool for resource conservation and pollution*

[1] http://www.ecomed.de/journals/lca/welcome.htm

prevention" (Udo de Haes, 1996a, p. 12).

The basic framework of LCA was laid down by ISO (DIN, 1998). According to ISO, LCA is a *"compilation and evaluation of the inputs and the potential environmental implications of a product system throughout its life cycle"*. It consists of the four steps *Goal and Scope Definition, Life Cycle Inventory* (LCI), *Life Cycle Impact Assessment* (LCIA), and *Life Cycle Interpretation*. Their relationship is shown in Figure 2.1. As an LCA is a process, the findings from one step may lead to a reiteration of another step, which is denoted by the arrows.

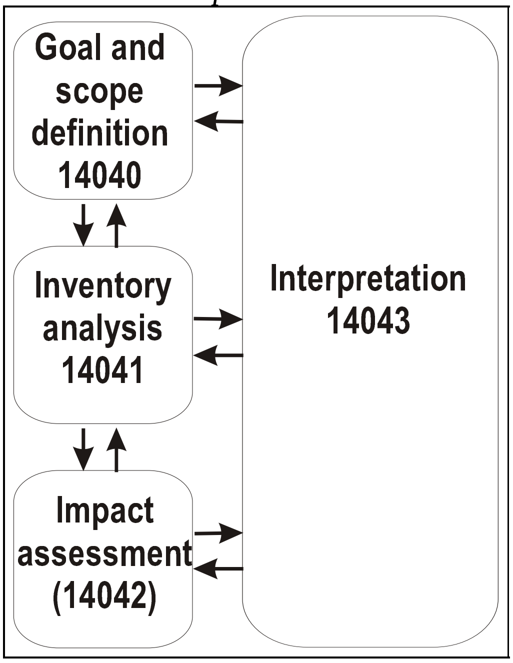

Figure 2.1.: The ISO LCA framework

In the first step, goal and scope of the study are defined. This includes the definition of the functional unit, the product system, the boundaries, the allocation procedures, assumptions, limitations, types of impact assessed, data requirements and their quality, and informations about the type of critical review (DIN, 1998).

The second phase is the LCI, which aims to compile and quantify inputs and outputs for a given product system throughout its life cycle (DIN, 1998). According to Klöpffer (1997), the LCI phase is *"the central, best developed and most scientific component of LCA"*. Its result is the inventory table, which is a list of all inputs and outputs per functional unit (Klöpffer, 1997).

The LCIA step follows the LCI. ISO defines LCIA as a *"phase of LCA aimed at understanding and evaluating the magnitude and significance of the potential environmental impacts of a product system"*. In this step, the items of the inventory table are translated into potential impacts of defined impact categories. Its aim is to understand and evaluate the magnitude and significance of the potential environmental impacts of the product system (DIN, 1998). LCIA consists of the steps *classification*, i.e. the assignment of the inventory table's items to the defined impact categories, and *characterisation*, i.e. the calculation of the magnitude of the potential environmental impacts, the latter giving the *category indicator results* (LCIA profile, DIN, 1999). Thus, all emissions considered to contribute to the same impact category that occur anywhere in the world are aggregated in a single value. Optional additional steps are the *normalisation* to a reference value, the *grouping*, i.e. a first aggregation of the category indicator results, *weighting*, i.e. the final aggregation into one single value and the *data quality analysis*, which is mandatory for comparative assertions that are intended to be published. The characterisation step is usually performed using an existing method, e.g. CST or the Eco-Indicator 99. However, such LCIA methods often have different equivalency principles, which determine the results. This has to be considered in the interpretation, which is the step following the LCIA. In this step, conclusions are drawn with respect to the goal and scope of the study based on the LCI and/or LCIA outcomes. Finally, a critical review should be conducted. In the case of a comparative assertion, a critical review is mandatory (DIN, 1998). Possibilities and limitations of LCA were often discussed (e.g. Barnthouse et al., 1998). Methodological developments are still processing, especially for the Life Cycle Impact Assessment (LCIA) phase, which is also stated by ISO (DIN, 1999). Overviews of the state-of-the-art of LCIA are supplied by Potting (2000) and, earlier, in the report of the first SETAC Europe working group on LCIA (Udo de Haes, 1996b). In these publications, several problems regarding LCIA are discussed, among them two of the major discussion points: the 'less-is-better' versus 'only-above-threshold' debate, and the question regarding the need for and the extent of spatial differentation. Both aspects are explained later. They are also related to the aforementioned possible lack of accordance of predicted and observable impact. A further reason for this is the aggregation of a huge number of emissions and resource uses in only a small number of values.

The first approaches to characterise ecotoxicological impacts within the LCIA phase only regarded the toxicological hazard. For example, in the case of the aquatic environment, the volume of freshwater being polluted during the life cycle of a functional unit to a maximum tolerable concentration (MTC) was calculated (Heijungs et al., 1992). More recently, different approaches of varying complexity also considered the environmental fate behaviour of substances in their characterisation steps, e.g. as done by Guinée et al. (1996), Hauschild et al. (1998), Jolliet and Crettaz (1997) or Huijbregts et al. (2000). Their differences and the implications on the outcome of a case study are analysed in section 2.2. However, all these methods, regardless of their inclusion of fate, have in common that they are based on the 'less-is-better' assumption. 'Less-is-better' favours that option causing the lowest score, regardless whether this alternative actually causes environmental impacts. Such methods may be used to compare product systems serving the same need on this basis, but they are insufficient in assisting the decision whether the use of, for example, a product is environmentally sound or not. This is a clear limitation for the use of LCA in many applications, which has often been pointed out (DIN, 1998, Barnthouse et al., 1998). Therefore, it has been proposed to combine LCAs with other approaches. For example, Udo de Haes (1996a) introduces two tracks which can be followed from a life cycle starting point. "*Track 1 deals with the assessment of potential impacts. (...) In contrast, track 2 deals with the prediction of actual impacts.*" (Udo de Haes, 1996a, p. 12). He continues, stating that a relationship between the two tracks can be established in order to further assess important processes of the actual case study. Also, Owens (1999) concludes that *"decisions should benefit from both the relative LCA approach and the actual approaches of other techniques such as environmental fate modelling, environmental modelling, environmental impact assessment and environmental risk assessment"*.

A question often debated concerns spatial differentiation. Udo de Haes et al. (1999) state that "*quite a number of applications may well need a spatially differentiated impact assessment*". However, in general temporal and spatial information on all emissions are not available. This implies that background concentrations of emitted substances cannot be obtained. However, again depending on the application, some spatial information is often available from the inventory: Some of the assumptions and choices of both system boundaries and functional unit made in the goal and scope analysis may imply spatial information that may be used in the LCIA step. For example, the assessment of transport processes in general requires geographical information. In addition, a product is often intended to be sold in only one country, which may already imply some spatial characteristics. Klöpffer (1995) states that *"in favourable cases site-specific data may be available (...) In this case, exposure analysis may be performed.*" However, from a general point of view especially the lack of temporal and spatial information for many emissions as well as for background concentrations inhibits the determination of actual impacts in an LCA (Saur, 1997). This is in general attempted in ERA.

Facing these problems, different opinions exist about the relevance and value of information gained from LCIA results. Some authors believe that LCIA results neither predict actual or potential effects nor estimate risks, but only analyse system in- and outputs (e.g. Owens, 1999). Other authors believe that *"LCIA should help us to decide whether and how much we should be concerned about certain emissions or resource uses connected with a product (...)"* (Hertwich and Pease, 1998). Heijungs et al. (1992) stated that *"LCA is not concerned with the degree to which a NOEC is actually exceeded, but with the degree to which it is potentially filled up"*. The latter two statements imply that LCA attempts to analyse potential effects. Klöpffer (1995) states that *"we do not have enough data to calculate actual concentrations needed for risk assessment. Hazard assessment is less demanding with regard to data and is therefore all we can expect to be manageable in impact assessment within LCA"*.

More generally, Hertwich and Pease (1998) see LCA as *"a tool that collects, organises, and evaluates scientific information useful for decision making"*. This broad understanding of an LCA allows for the application of different methods and models depending on the specific application. An example for such a method of procedure is given by Thiel et al. (1999), who take an LCA as a basis, but extend it using environmental fate models and complex expert systems in order to derive necessary information. They conclude that a *"regional decision system for the environmental assessment of anthropogenic emissions should therefore consist of the four elements LCA, fate modelling, assessing expert systems and GIS"*.

2.1.3. Environmental Risk Assessment

Unlike LCA, ERA addresses actual impacts or at least the likelihood of actual impacts. The main objective of ERA is to assess chemical substances or contaminated sites that pose a hazard to man and/or the environment. Other risks, e.g. by accidents, are not considered within ERA. Furthermore, in this thesis ERA means environmental risk assessment of single substances with respect to ecotoxic effects.

In general, ERA is not concerned with products or human activities as such. These applications are mainly assessed by the EDSIs LCA and SFA, depending on the purpose of the assessment. ERA investigates single substances with respect to human and ecotoxic effects. Of course, these substances are emitted due to the use of products and from human activities, but ERA deals with single substances, and not with products or activities. The main area of application of ERA is risk management and chemical legislation. For example, the methodology of environmental risk assessment of existing and new notified substances in the European Union is defined in the Technical Guidance Documents (TGD, European Economic Community, 1996).

The most common method to perform an ERA consists of the steps *hazard identification, effects assessment, exposure assessment,* and *risk characterisation,* which are followed by four further steps implementing the risk management phase (Van Leeuwen and Hermens, 1995). Hazard identification is the initial identification of adverse effects that *"a substance has an inherent capacity to cause"* (Van Leeuwen and Hermens, 1995, p. 3). The result is a list of potential effects a substance may cause without quantification of their probability. Effect assessment is the step in which predicted no-effect concentrations (PNECs) are derived from toxicological data. In the TGD, assessment factors are used, the magnitudes of which depend on the data availability. For example, in order to derive PNECs for aquatic and terrestrial compartments the toxicological data are divided by either 10, 50, 100, or 1000. The result is a set of PNECs for the different compartments. Exposure assessment aims at estimating predicted environmental concentrations (PECs) in the different compartments. The models applied in the exposure assessment assume emission scenarios depending on the characteristics of the substance and the produced or imported tonnage. For the risk assessment of existing substances, actual emission data need to be provided, while for new substances the intended production volume is used. Afterwards, a set of environmental fate models of varying complexity calculates concentrations in the different environmental compartments based on the emission scenarios. In the risk characterisation a comparison of PEC and PNEC is carried out for the different environmental compartments. According to the TGD this ratio is called the risk characterisation ratio (RCR).

Thus, the objective of an ERA is to estimate actual risks of a substance, which can be seen in the fact that the TGD also defines a procedure to use environmental monitoring data for the derivation of PECs (European Economic Community, 1996, Part II, section 2.2). Although the methods to perform an ERA are more advanced and more scientifically accepted than those of LCIA, some problems still need to be solved. For example, the emission scenarios are currently only rough estimates. An evaluation of the exposure part of the system currently used in the Europeean Union was performed by Berding et al. (2000). They concluded that some model parts meet their objectives, while others require improvements.

Single medium as well as multimedia models such as SIMPLEBOX (Van de Meent, 1993), CALTOX (McKone, 1993) or CHEMCAN (Mackay et al., 1996) are used. Their advantage is the fact that a large number of chemicals can be assessed using the same model, since they include all environmental compartments. However, this implies introducing a number of simplifications, e.g. regarding the degree of spatial variability. These simplifications may be avoided by using models that are designed for specific groups of chemicals with specific emission pathways. An example is the GREAT-ER model, which is specifically designed for ‘down-the-drain’ chemicals such as detergent ingredients. However, since this model also has disadvantages, such as the lack of a sediment compartment, it has to be decided which model should be used for the environmental risk assessment of a specific compound.

2.2. Review of LCIA methods regarding aquatic ecotoxicity

In order to analyse the capabilities and limitations of current LCIA methods for assessing aquatic ecotoxic impacts of household laundry, four published methods have been reviewed and applied to a case study of domestic clothes washing in former West Germany (Schulze et al., 2001a). In this section, a brief summary of the study is given, from which some conclusions relevant for this thesis are drawn.

The original purpose of the review was to answer the following set of questions: In which way and to what extent does the inclusion of fate models affect the LCIA results? Is it necessary to differentiate between sea- and freshwater compartments? Can the dominant degradation and inter-media transfer processes be identified? The analysis was carried out on the basis of the substance specific characterisation factors (aquatic ecotoxicity potentials, AETP), i.e. the product of F_i and E_i, and of the category indicator results.

In order to analyse the methods rather than a complete case study, emissions of only four ingredients have been considered. The emissions occur after the use phase. The functional unit is the overall amount of household laundry being washed in Germany in 1984. The substances are the anionic surfactant LAS, ethylenediaminetetraacetate (EDTA), the fluorescent whitening agent DAS-1, a diamino stilbene (4,4’-bis-[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2’-disulfonate), and finally the polycyclic musk oil HHCB (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-[g]-2-benzopyrane).

EDTA was used as a bleach stabiliser during the 1980s, but is no longer used in Germany due to its chelating properties and persistence. DAS-1 is one of the two most widespread detergent whitening agents, and HHCB is used as a representative of perfume oils. For further simplification, it was assumed that LAS is the only anionic surfactant, DAS-1 the only optical brightener and HHCB the only perfume substance used in detergents in 1984. Due to this, consumption data of detergent components published by Osnowski and Rubik (1987) could be used. Data describing the fate and effect behaviour of the substances have been derived from a literature review. Based on the consumption data and on assumptions concerning their fate in the washing machine and wastewater treatment, an LCI table has been derived providing quantified emissions of the four substances into surface water, agricultural soil (from sludges), and air (in the case of HHCB due to volatilisation during wastewater treatment) (Schulze et al., 2001a).

The four chosen LCIA methods considering ecotoxicity represent the development that has taken place within this impact category. The methods are (1) *CML*$_{\text{old}}$, i.e. the impact assessment procedure developed in 1992 by researchers at the Centre of Environmental Science in Leiden (CML, Heijungs et al., 1992), (2) EDIP (Environmental Development of Industrial Products), a method developed by the Institute for Product Development at the Technical University of Denmark (Hauschild et al., 1998), (3) the approach being developed at the Swiss Federal Institute of Technology Lausanne called Critical Surface-Time (CST, Jolliet and Crettaz, 1997), and (4) USES-LCA (Uniform System for the Evaluation of Substances, adapted to LCA, Huijbregts et al., 2000, Huijbregts, 1999), which was proposed for use in the new Dutch guide for LCA (Guinée, 2000). All four methods can be applied within the framework as developed by the first SETAC working group on LCIA (Jolliet, 1996). According to this framework, the category indicator result for the impact category aquatic ecotoxicity (aquatic ecotoxicity score, AETS) is the sum over all emitted substances i classified as contributing to aquatic ecotoxicity of the product of mass M_i emitted according to the inventory table, a substance specific fate factor F_i and a substance specific effect factor E_i:

$$AETS = \sum_{substances\ i} (F_i \cdot E_i \cdot M_i)$$

The correctness of the term effect factor is controversial, since an LCA in general is not capable of assessing whether an effect actually occurs from the use of the functional unit or not. However, in line with the SETAC nomenclature and the large majority of LCA literature, the term effect factor has been used. The main difference between the methods is the way the fate factor is derived. Apart from the fate factor, the estimation of the effect factor E_i partly differs. This turned out to be, however, only of minor relevance.

From the characterisation factors the following conclusions were drawn.

1. Fate matters. Its introduction causes a change in the results of over several orders of magnitude. Also the relative comparison is largely affected by it, which, for example, can be seen in the comparison of LAS and EDTA results.
2. It is necessary to distinguish between fresh- and seawater. AETP variability in the USES-LCA seawater compartment by emission to freshwater covers more than 5 orders of magnitude. This is due to the closed global model. However, detergents mainly cause negative impacts in freshwater. For this reason, a specific freshwater evaluation is necessary, as otherwise the freshwater assessment would be dominated by the seawater assessment.
3. On the contrary, the different ways of extrapolating toxicological data performed in the CML$_{\text{old}}$ and EDIP methods have only limited influence on the characterisation factors.

In this section, it is investigated whether the four methods are able to contribute to the aim of this thesis. This discussion is based on the category indicator results (impact scores, AETS) for aquatic ecotoxicity which have been estimated from the AETPs and the LCI table. They are given in Table 2.1. The purpose of the table is to demonstrate the relative contribution the different methods assign to the substances.

Table 2.1.: **Category indicator results for aquatic ecotoxicity (AETS)**. The substances' percentual contributions to the total scores are shown.

Impact Score	LAS	EDTA	DAS-1	HHCB	Total
CML_{old}	26.6	40.9	0.6	31.9	100
EDIP acute	44.0	31.2	0.1	24.7	100
EDIP chronic	11.6	87.0	1.4	0.0	100
CST	1.8	95.9	0.8	1.5	100
USES-LCA fresh	1.3	89.7	1.8	7.2	100
USES-LCA sea	0.0	99.0	0.3	0.7	100

The category indicator results show the relative importance of the four ingredients in the assessment of the investigated example, as calculated by the four methods. The results differ largely. The introduction of fate parameters decreases the contribution of LAS significantly. USES-LCA apportions greater significance to HHCB than to LAS, which seems debatable. In addition, the dominance of EDTA, which only accounts for 0.3% of the detergent compared to 8% for LAS, surprises and seems also debatable.

However, no information regarding the environmental soundness of the ingredients can be derived from the figures, since the category indicator results do not contain information of the environmental relevance of the emissions. The advantage of an LCA approach remains therefore in the concept of relative assessments based on a functional unit. This approach only allows the evaluation of different product alternatives or washing habits.

Further conclusions may be and have been drawn with respect to the application of the four methods in LCIAs. These are presented in the article (Schulze et al., 2001a). However, they do not give further insight relevant for the aim of this thesis. For this reason, they are not further elaborated here.

2.3. Applying GREAT-ER to the Itter catchment

Having reviewed and tested existing LCIA methods regarding the way they assess aquatic ecotoxicological impacts, an aquatic fate model developed in the context of ERA is analysed in this section with respect to its usefulness in this thesis.

2.3.1. The GREAT-ER model

The *Geography-referenced Regional Exposure Assessment Tool for European Rivers* (GREAT-ER) is specifically developed to assess the fate of ‘down-the-drain’ chemicals, to which detergent ingredients belong. This makes GREAT-ER highly suitable for use in the fate assessment of detergents. In this section, GREAT-ER’s core principles are explained and its ability to predict observable concentrations of detergent ingredients in surface water is investigated.

Model concepts

GREAT-ER is a simulation model to calculate distributions of predicted environmental concentrations of ‘down-the drain’ chemicals in different river stretches. It simulates the environmental fate of chemicals in riverine water, which is polluted by point source emissions via the sewerage system and a wastewater treatment plant. The steady-state model calculates concentrations that are likely to be found in rivers due to a regular use of these chemicals; it is thus not a model system addressing accidential releases. A more detailed description of the model approach and the background leading to its development was given by Feijtel et al. (1997), and Matthies et al. (1997, 2000).

GREAT-ER combines the Geographical Information System (GIS) ARCVIEW^{TM} and its possibilities to store, analyse and visualise georeferenced data with a set of models simulating the emission of chemicals, treatment in wastewater treatment plants (WWTP) and fate in the receiving riverine water by considering various elimination processes.

The heart of the model system is a digital representation of a river network which is represented by the coordinates of river segments, in GREAT-ER called stretches, together with topological information, e.g. flow directions, confluences, or bifurcations, and the river attribute data for each stretch such as the length of a stretch and its flow statistics, given as lognormal distributions. The main part of the simulation model is an application of the CEMOS/WATER MODEL (Trapp and Matthies, 1998) which calculates a longitudinal one-dimensional spatial concentration profile in a single river stretch downstream from a point source. A possible upstream concentration is included by performing a mass-balance to estimate an initial concentration in the stretch. The concentration profile in a river stretch is obtained by considering removal processes. Different modes of complexity exist which calculate the elimination processes in a varying detail.

This model is applied to the complex river network by simulating the concentration profile separately for each stretch. The emission data in GREAT-ER are based on a per-capita consumption of the substance. As the population connected to a discharge site is part of the input data, the load entering the sewerage system can be determined for each site. Based on this information GREAT-ER simulates the environmental fate in the sewerage system, the WWTP and finally the receiving surface waters. GREAT-ER offers the possibility to model additional input into the surface waters, given as additional load at the defined discharge sites. Furthermore, a (possibly geogenic) background concentration can be entered.

GREAT-ER combines deterministic and stochastic parts in order to deal with the uncertainties and temporal variations of the input parameters by means of Monte Carlo simulations: A simulation consists of carrying out a chosen number of runs, e.g. 10,000. In each run a value is estimated for each distributed input parameter depending on a random number. All parameters except for the consumption rate may be distributed. At least the hydrological parameters, i.e. flow and flow velocities, are lognormally distributed, since they belong to the core catchment data. When a simulation run, called Monte Carlo shot, is defined, the deterministic simulation for this run is carried out. This is repeated the chosen number of times, resulting in a two-dimensional distribution of predicted environmental concentrations for each stretch of the river network. A graphical user interface (GUI) developed on top of the ArcView GUI permits that the use of the model is easy. A typical GREAT-ER screen can be seen in Figure 2.2.

GREAT-ER results

The GREAT-ER model calculates various results. In general, GREAT-ER calculates a two-dimensional spatial and temporal distribution of predicted environmental concentrations for each river stretch. The spatial aspect is described by concentration profiles for each stretch, which are described by three different concentrations, i.e. the starting ($C_{\mathrm{sim,start}}$), the end ($C_{\mathrm{sim,end}}$), and the mean concentration ($C_{\mathrm{sim,internal}}$). The data uncertainty- and variability-based distribution is due to the Monte Carlo analysis and is expressed by the mean and standard deviation for each of the calculated concentrations mentioned above. From this information, different percentiles of calculated concentrations can be derived. This second distribution implicitly includes some temporal variations, because the hydrological data reflect annual flow distributions. Results are stored in dBase tables for further processing. The user interface displays the results and allows to examine them.

An attempt to aggregate the numerous results calculated in a scenario into only a few figures is the calculation of two concentrations for the whole catchment, i.e. $PEC_{\mathrm{catchment}}$ and PEC_{initial}. $PEC_{\mathrm{catchment}}$ can be compared to PEC_{regional}, as defined in the TGD, and represents a mean concentration in the catchment, whereas PEC_{initial} can be interpreted analogously to PEC_{local} of the TGD, and represents a mean concentration directly below discharges. Different options concerning the weighting of the $PEC_{\mathrm{catchment}}$ are implemented. Both values have a certain power to describe the environmental concentrations on a catchment scale. The advantages and problems of these new PEC definitions are discussed by Boeije et al. (2000). One aspect is also addressed in the discussion given in section 8.1.5.

2.3.2. Case study Itter catchment

In order to assess whether and how GREAT-ER is capable of predicting observable concentrations of detergent ingredients in Germany, the Itter catchment is used as a test catchment, as it is the only German catchment provided on the GREAT-ER CD (ECETOC, 2000). These simulations are also used to generally judge the accuracy of GREAT-ER in predicting LAS and boron concentrations[2]. In this context, accuracy is defined as an agreement between estimated and observed concentrations.

The Itter is a smaller tributary of the river Rhine. It dewaters a catchment area of 45 km^2 and is strongly impaired by treated waste water. Water management in the catchment is carried out by the local water authorities '*Bergisch-Rheinischer Wasserverband*' (BRW), which collects and maintains all necessary input data related to hydrology, discharges, and environmental monitoring of water quality. The catchment area and relevant geographical information are shown in Figure 2.2.

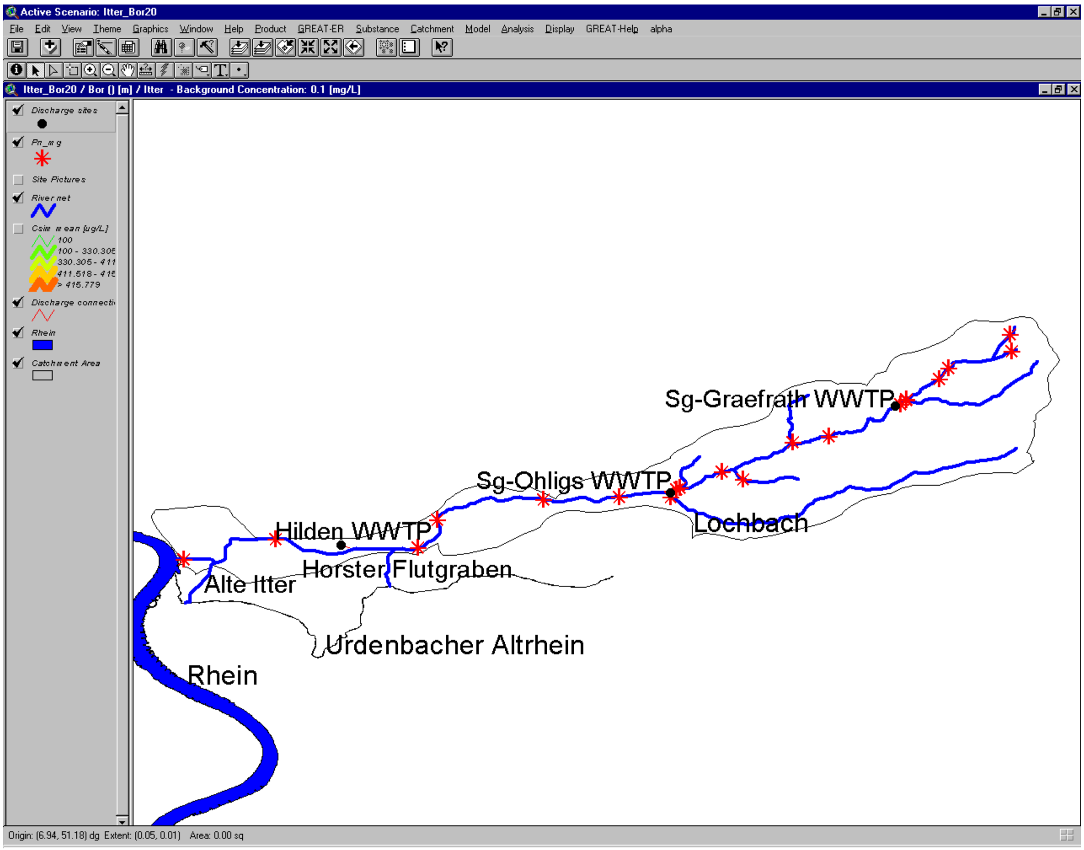

Figure 2.2.: **The Itter catchment:** WWTPs (dots), monitoring sites (asterisks), the river network and the catchment area

Discharge site data

Three WWTPs (i.e. Solingen (Sg)-Gräfrath, Sg-Ohligs, and Hilden) discharge treated wastewater into the Itter. These are all activated sludge plants. 70% of the mean dry

[2] An article addressing this containing results given here as well as further results, was published (Schröder et al., 2001).

weather flow at the confluence with the Rhine consists of treated waste water, which shows the significance of anthropogenic influences. The discharge site data are given in Table 2.2.

Table 2.2.: **Discharge site data in the Itter catchment**

	Sg-Gräfrath	Sg-Ohligs	Hilden	$\sum$
Population	11,672	88,180	64,383	164,235
Effluent flow (m^3/s)	0.08	0.314	0.173	0.495

Hydrological data

In the headwaters of the Itter, which are only moderately impaired by human activities, several smaller tributaries flow into the Itter. Also, Sg-Gräfrath, a smaller activated sludge type wastewater treatment plant, discharges into this section of the catchment. In the middle part of the Itter, the largest WWTP, Sg-Ohligs, and the largest tributary, the Lochbach, discharge into the Itter: At Sg-Ohligs, a mean effluent flow rate of 0.314 m^3/s is discharged into the Itter which upstream from this point only has a mean dry weather flow of 0.22 m^3/s. Immediately after the Sg-Ohligs discharge the Lochbach flows into the Itter, which increases the Itter mean flow by 0.07 m^3/s. Thus, below this point the Itter's mean flow is more than doubled.

Further downstream, upstream from the Hilden WWTP, which has a mean discharge of 0.173 m^3/s, the Itter bifurcates: Assuming mean flow conditions, 0.72 m^3/s flow into the Itter and 0.1 m^3/s leave the catchment via the Horster Flutgraben. A second bifurcation is located upstream from the Itter's confluence with the River Rhine. The added mean flow of these two river courses that both discharge into the Rhine is 0.89 m^3/s. Hydrological scenarios derived from the BRW data were published by Schulze et al. (1999). Apart from the discharges, other human activities such as the straightening of the lower course also have a large impact on the river's ecosystem.

Monitoring data

The objective of the Itter monitoring programme, set up in 1996, was to determine concentrations of LAS and boron as well as water quality parameters (Schröder et al., 2000). Altogether, thirteen sites, including the effluents of the three WWTPs, were sampled using automatic samplers. Additional grab samples were taken in all tributaries of the Itter and at additional sites of interest. All measured concentrations referred to in this section are mean values based on 12 to 72 single measurements.

All measured data are given as means and as standard deviations. However, no statistical analysis was conducted with respect to the distribution type of the monitoring data. It has not been analysed in the monitoring programme, whether a symmetric distribution is realistic.

Model input parameters

The main input parameters required by the GREAT-ER model are the release rate (i.e. amount of chemical discharged per time unit into the river), the flow rate of the river, and the in-stream removal rate. In the case of detergent ingredients, the release into the river can be calculated if consumption figures and information on the removal in the sewerage system and WWTP are known.

The test substances of the GREAT-ER development phase, i.e. LAS and boron, are chosen as example substances. For these substances, IKW[3] and TEGEWA[4], the German associations of detergent and surfactant manufacturers, collect production figures for Germany. In 1996, the year of the monitoring programme, LAS and boron consumption from the use in detergents and cleaning agents were estimated to be 39,000 t LAS (TEGEWA, 1994), i.e. 0.4875 kg per capita and year, and 66,000 t sodiumperborate tetrahydrate (IKW, 1994) respectively, which is equivalent to 0.0579 kg boron per capita and year.

Physico-chemical parameters, which are required for simulations applying the mode 1 models, are supplied with the GREAT-ER model. For the sewerage system, mode 2 was applied, i.e. a constant elimination factor for modelling the losses that occur during transport in the sewers was chosen. 10,000 Monte Carlo shots were performed in each simulation.

2.3.3. Results

Boron was chosen as an inert tracer that does not undergo elimination processes. Thus, the accuracy of the hydrological scenarios may be judged by comparing the goodness of simulation results for boron. Therefore, first the boron simulation results are given. Afterwards, the results concerning LAS are presented.

Boron

During the washing process, the bleaching agent sodium perborate tetrahydrate breaks down into dissolved borate, which remains stable during transport in the sewerage system and during wastewater treatment. In addition, no elimination processes from the water column occur in the surface waters, so that the only factors determining riverine boron concentrations are emission, dilution in the different stretches, and the geogenic background concentration. As boron can be analysed rather simply in water samples, it is a suitable compound for checking the quality of the hydrological part of the GREAT-ER system.

Anthropogenic boron emissions are mainly due to its use in detergents and other cleaning products. Additionally, it is used in the photochemical, glass, and galvanic industries as well as to some extent as a fertilizer in agriculture (Metzner et al., 1999). Further information on the use of boron compounds as well as results of monitoring programmes is

[3] Industrieverband Körperpflege- und Waschmittel e.V.
[4] Verband der Textilhilfsmittel-, Lederhilfsmittel-, Gerbstoff- und Waschrohstoff-Industrie e.V.

given by Dietz (1975), Raymond and Butterwick (1992), Haberer (1996), and Metzner et al. (1999).

An annual per-capita consumption of 0.0579 kg boron and a background concentration of 55 μg/l were used. The background concentration was determined by analytical measurements in the headwaters of the Itter. In addition, an additional discharge of 5470 kg boron per year was assumed to occur at Sg-Ohligs WWTP. This is based on measurements taken from the effluents of the WWTP, which were higher than expected due to the use of perborate in detergents. These additional discharges are most probably due to industrial activities. In Solingen about 70 companies are active in the field of electroplating (BRW, 2000), in which boron is used for cleaning metallic surfaces or for neutralisation processes (Dietz, 1975). GREAT-ER results compared to monitoring data are given in Figure 2.3.

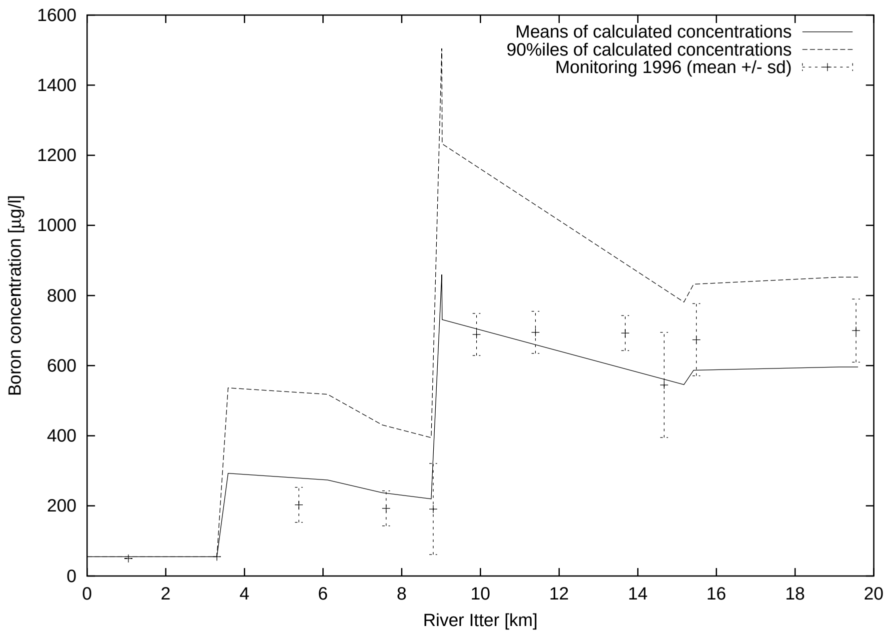

Figure 2.3.: **GREAT-ER results for boron in the Itter vs. measurements** At Sg-Ohligs WWTP (near 9 km), an additional boron input of 5 470 kg/a was applied, based on measurements from the WWTP effluent.

Despite some minor deviations between measured and predicted mean concentrations, GREAT-ER gives an accurate picture of the actual boron concentrations in the Itter. Therefore, it may be concluded that generic consumption figures are apt to describe concentrations in the water column. The only necessary site-specific expert knowledge is the additional input at Sg-Ohligs WWTP, the value of which was determined comparing monitoring and simulation data, and which may well be explained by industrial effluents.

LAS default scenario - ECETOC data set

LAS is one of the major surfactants used in detergents. Unlike boron, LAS can be eliminated from wastewater and surface waters by adsorption and by biodegradation. In the easiest GREAT-ER complexity mode removal in the WWTP is calculated on the basis of a percentage removal while removal in the river is based on pseudo-first-order kinetics. Both values are lumped figures which combine both biodegradation and adsorption.

A first simulation was carried out based on generic German consumption data and substance data provided by ECETOC (2000, i.e. 25% sewer removal and 98% removal in the WWTP respectively as well as a pseudo-first-order in-stream removal rate of 0.06 h^{-1}). In the remainder this data set is referred to as the ECETOC data set. In addition, a background concentration of 5 μg/l is applied, which seems surprising, but which was repeatedly measured in the headwaters of the catchment. Run-off from agricultural soils that are fertilised with sewage sludge containing LAS may be a reason for this.

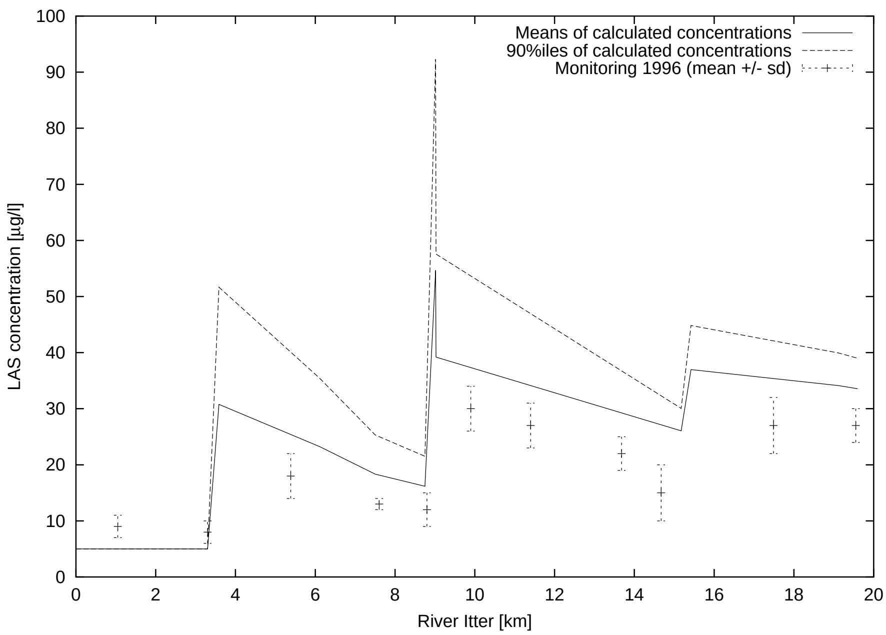

Figure 2.4.: **GREAT-ER results for LAS in the Itter vs. measurements (ECETOC data set)**

It can be seen in Figure 2.4 that GREAT-ER overestimates mean riverine LAS concentrations by less than a factor of 2, which is a good result for a first simulation. However, calibration is carried out to increase the model's accuracy. As the results of the boron simulation revealed that the basic assumptions about the hydrology are correct and that generic consumption figures can be applied, the effect of the WWTP and in-stream removal figures was investigated in subsequent steps, while the sewer removal rate remained.

Improved LAS scenario - Itter data set

Different combinations of in-stream removal rates and WWTP efficiencies were tested, from which a combination of 25% sewer removal efficiency, 98% WWTP efficiency (for activated sludge plants) and an in-stream removal rate, which is uniformly distributed between 0.03 and 0.35 h^{-1}, gives best results. The upper value was determined in the Rur (Schröder, 1995a) and the Anger (Schröder and Reichensperger, 1998, Schröder et al., 1999) rivers, while the lower value corresponds to a half-life of 23 hours, which was determined in the Itter stretches below Hilden WWTP. Figure 2.5 shows simulation results for the Itter river by using this data set, which in the remainder is referred to as the Itter data set. Again, the above-mentioned background concentration of 5 μg/l was assumed.

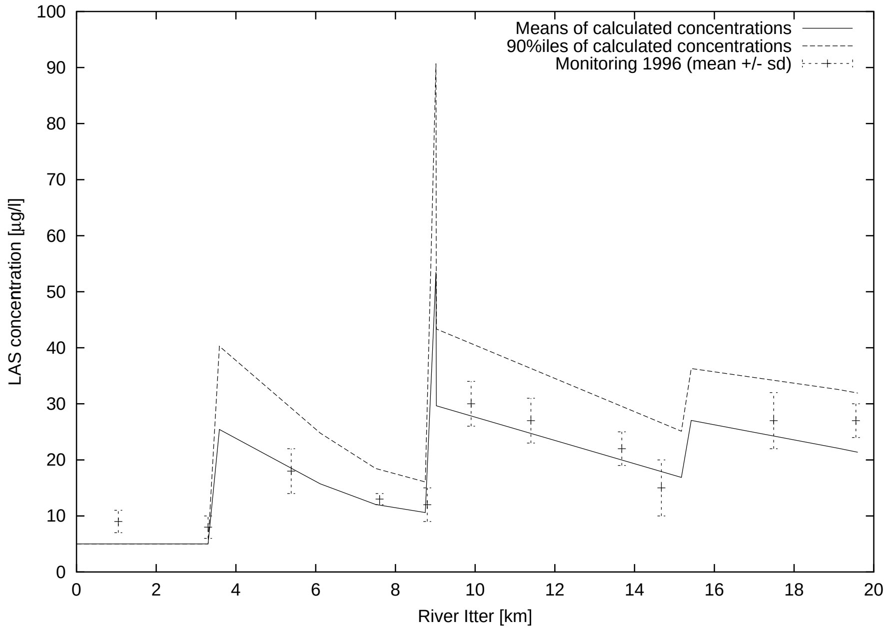

Figure 2.5.: **GREAT-ER results for LAS in the Itter vs. measurements (Itter data set)**

Only close to the catchment's outlet a small discrepancy between measured and simulated mean values can be seen, which is due to the fact that there the observed in-stream removal rate is very small, i.e. equal to the lower bound of the in-stream removal rate distribution used in the simulation.

2.3.4. Discussion

The aim of this section was to assess whether GREAT-ER is able to predict concentrations of detergent ingredients that are in the range of the measured values. As a first result it can be stated that by using default values next to generic German consumption data the aim of GREAT-ER, i.e. an accuracy of up to a factor of 3, is achieved with respect to the calculations of boron and LAS in the Itter catchment. The results can be further improved by applying more site-specific values. In addition, the work reveals that release rates play a crucial role in the prediction of environmental concentrations.

An analysis of the boron results reveals that for the mean concentrations the margin of error was a maximum of 30% and that the calculated concentration profile gives a true picture of the boron concentrations in the Itter. This leads to the conclusion that generic consumption data can be used for the simulation of typical detergent ingredients.

While boron is not removed from wastewater, LAS is eliminated by adsorption as well as biodegradation. These processes can take place in sewers as well as in WWTPs and surface waters. GREAT-ER is able to take these various processes into account. The amount of data GREAT-ER needs depends on the chosen complexity mode of the calculation. In its simplest mode, elimination in the WWTP is based on simple percentual removal figures. ECETOC (2000) suggested a generic data set for removal in sewerage systems, WWTPs, and rivers which was mainly based on data generated in the UK. Application of these data leads to deviations between monitoring and simulation results. By adjusting the in-stream removal rates the accuracy is significantly improved. As this derived in-stream removal rate is not a fixed value but is rather described as a distribution, it is more likely that this parameter can be transferred to a different catchment.

An observation currently not reflected by the model is spatial variability of the in-stream removal rates. In principle, the GREAT-ER software could be extended to account for this if model equations for different substances and catchments were available. A statistical approach to derive LAS in-stream removal rates based on the water quality parameters TOC and ammonia was formulated and calibrated for the Itter catchment (Schulze et al., 1999), but no similar studies are known for other substances and/or catchments. It is, however, questionable, whether this increased accuracy is needed in the context of an environmental risk assessment of chemicals, for which GREAT-ER was developed. With respect to a comparison of detergents as intended in this thesis, it is even more questionable, as such accurate modelling would then have to be conducted for all considered detergent ingredients.

Concluding, it can be stated that GREAT-ER is able to predict realistic LAS and boron concentrations in the water column of the Itter. It is therefore a potentially useful tool in assessing aquatic ecotoxicological impacts caused by household laundry. However, a current weakness of the model is the fact that no concentrations in the river sediments are calculated.

2.4. Environmental assessment studies related to household laundry

Within the first three sections of this chapter, a theoretical discussion of ERA and LCA and a practical application of methods and models developed for these instruments have been performed. Within this section, existing studies are introduced. This analysis aims to identify existing approaches and studies useful in the context of this thesis. Studies using both LCA and ERA are reviewed. Furthermore, this overview demonstrates the relevance of the waterborne emissions occurring after the use phase of household laundry, since almost all listed studies, except for the LCI given in section 2.4.4, analysed these emissions to some extent.

2.4.1. Comprehensive product assessment 'Washing and washing agents'

The goal of the comprehensive product assessment 'Washing and Washing Agents' (*Produktlinienanalyse 'Waschen & Waschmittel'*, PLA) was *"to optimise the use of washing agents, to determine the washing agent concepts that are particularly suited for such optimisation, and to establish the specific contributions of the various actors to product system optimisation"* (Grießhammer et al., 1997, p. 9). The optimisation goals follow from the model of sustainable development. The core of the study consists of an LCA for which a methodology has been developed on the basis of the method provided by CML/SETAC (Consoli et al., 1993). In addition, the ecoscarcity method (Müller-Wenck, 1994) has been applied and normalisation has been performed with respect to national and international environmental policy targets (Grießhammer et al., 1997, p. 10). Finally, a scoring model to assess potential aquatic ecotoxicological impacts resulting from the use of laundry detergents has been applied. This scoring system is part of the evaluation system used by the European Union in the Ecolabel Award Scheme (European Union, 1995, 1999a). The LCA was carried out in a collaborative effort by industry and the Öko-Institut e.V., which has been the leading organisation in this project. In addition, different stakeholders, among others industrial and governmental organisations as well as consumer associations, accompanied the process. The PLA is peer-reviewed. Next to the LCA, an MFA with respect to overall household laundry in Germany has been performed, which calculated the contribution to selected national pollutant emissions.

Within the PLA, model detergents and use habits were defined. The model detegents are based on information provided by industry, while the use habits are based on statistical data. Both model detergents and use habits are given in chapter 4. The study identified aquatic ecotoxicity, global warming, acidification, and photochemical smog as the most relevant impact categories, the first due to waterborne releases of detergent ingredients after use, the latter three mostly due to energy-related emissions (Grießhammer et al., 1997, p. 12).

The scoring system for evaluating aquatic ecotoxicological impacts occurring after the use phase analyses detergent ingredients with respect to the eight criteria total chemicals, critical dilution volume, phosphates, insoluble inorganics, soluble inorganics, non-biodegradable organics (aerobic and anaerobic), and biological oxygen demand. The scoring system is accompanied by the Detergent Ingredients Database (DID), in which 85 detergent ingredients are listed with values for the eight criteria are given. From this database and a product formulation, a product specific score is estimated (European Union, 1999a) using a defined procedure. However, this scoring system, and especially the thresholds and exclusion hurdles contained, are difficult to interpret, since they do not allow for the verification of their appropriateness by environmental monitoring. The environmental relevance of this system can therefore only be evaluated with great difficulty.

Besides an ecological evaluation, economic and social aspects have also been addressed. It was concluded that the ecologically preferable option was also the economically optimal alternative. An interesting social aspect concerns the time requirements of household laundry, which have remained constant in recent decades despite the introduction of washing machines. One reason for this is the steadily increasing amount of laundry which is observable for the same time span (Grießhammer et al., 1997, p. 16).

The study closes with recommendations for further improvements, namely the substitution of conventional heavy duty detergents, the optimisation of products with respect to energy consumption and emissions as well as a reduction of the ecotoxicological potential by improvements or substitutions of single substances (Grießhammer et al., 1997, p. 154).

2.4.2. Environmental risk assessment of detergent chemicals

During the nineties a joint project was carried out by the Dutch Ministry of Housing, Spatial Planning and the Environment (VROM) and the Dutch Soap and Detergents Association (NVZ) aiming at an environmental risk assessment of detergent chemicals. Based on this, the European Industrial Associations related to detergents, *Association Internationale de la Savonnerie, de la Détergence et des Produits d'Entretien* (AISE) and *Comité Européen des Agents de Surface et leurs Intermédiaires Organiques* (CESIO), organised a series of workshops in which the experiences gained in the project have been reviewed. Proceedings have been published (AISE/CESIO, 1996). The main results have also been published in a report released by the Dutch National Institute of Public Health and the Environment (RIVM Feijtel and Van de Plassche, 1995) and in a series of articles (Matthijs et al., 2000, Feijtel et al., 2000, Van de Plassche et al., 2000).

The ERA was carried out for four major surfactants used in detergents, which are the 3 anionic surfactants linear alkylbenzene sulphonate (LAS), alkyl ether sulphate (AES), and soap, and the nonionic surfactant alcohol ethoxylathe (AE). It was concluded that the four surfactants neither posed significant risks to Dutch river ecosystems nor to the marine environment, provided secondary treatment is performed in the WWTPs. Regarding the terrestrial environment, a lack of effect data was emphasised, which made an overall conclusion difficult. However, no immediate concern was indicated by the assessment. (AISE/CESIO, 1996, p. 53).

As part of the ERA a monitoring programme aimed at the determination of WWTP efficiencies for the considered surfactants as well as for boron and BOD was carried out in 7 WWTPs (Matthijs et al., 2000). Efficiencies were distinguished between primary, i.e. after having passed the primary settler, and total removal. Model calculations using the WWTP models SIMPLETREAT (Struijs et al., 1991) and WWTREAT (Cowan et al., 1993) were then compared to the measurements. In addition, average removal efficiencies in the sewerage systems were estimated by comparing measured influent concentrations to calculated emissions based on generic Dutch consumption data. Finally, predicted instream mean concentrations at 1000 metres below a discharge considering an average dilution ratio (determined by De Greef and De Nijs, 1990) and assuming different instream removal rates were calculated (Feijtel et al., 2000, AISE/CESIO, 1996, p. 20).

Besides exposure assessment, both an effect assessment and a risk characterisation were carried out. Toxicological data were taken from literature. Normalisation, which intends to achieve comparability of the different homologues of a substance, was carried out within the ERA. For the marine environment, PNECs were derived from freshwater PNECs (AISE/CESIO, 1996, p. 52), which is seen as reasonable with respect to existing experimental data published by Feijtel and Van de Plassche (1995). However, some open questions and research needs were addressed in this topic, such as sedimentation of surfactants into anaerobic environments and differing speciation and bioaccumulaton rates in saline waters (AISE/CESIO, 1996, p. 52).

Further investigated aspects are the toxicity of mixtures, uncertainties in both exposure and effect modelling, and the risk characterisation of sediments. Finally, remaining questions and uncertainties in the assessment were discussed. Among these are the temperature-dependency of microbial degradation and the extrapolation in space and time. Concerning the mixture toxicity of surfactants, additive toxicity is seen as the appropriate conservative approach (AISE/CESIO, 1996, p.46). Geographical extrapolations need to take into account spatial variabilities of many parameters, e.g. hydrological variabilities or the percentage of population being connected to a WWTP. The aforementioned GREAT-ER model is seen as a possible way to consider these variabilities (AISE/CESIO, 1996, p. 55-56).

Within this thesis, the measured elimination efficiencies of the 4 compounds are used. In addition, the conclusions drawn in the study concerning mixture toxicity are referred to later in this thesis.

2.4.3. CHAINET case study 'Domestic washing of clothes'

CHAINET is a concerted action of the EU environment and climate programme. It was initiated in December 1997 and ended in October 1999 (Wrisberg and Gameson, 1998).

The aim of CHAINET was to develop a guidebook advising practitioners on how to select the most relevant and helpful environmental assessment tools for a specific decision. The guidebook, which is not yet complete, includes results from 3 case studies, one of which is domestic washing of clothes. Preliminary results of this case study are sampled in the 2nd draft report (CHAINNET, 1999).

Within this draft report, no results of actually performed environmental assessments are given, but aspects of household laundry relevant for an environmental assessment are laid out. In addition, stakeholders controlling these aspects are identified. At the end, past and ongoing research activities related to household laundry are listed.

The project explicitly mentions the decision-oriented approach. Different instruments should be used, either exclusive or combined, depending on the specific questions. Concerning household laundry, LCA is mentioned in order to identify the dominant impacts and ERA is proposed for the environmental assessment of the detergent constituents, which shall consider local conditions (Wrisberg and Gameson, 1998, p. 26). Further mentioned tools are MFA for solid waste disposal and both Material Intensity Analysis (MIA) and Cumulative Energy Requirements Analysis (CERA) for assessing possibilities to improve the eco-efficiency of the product chain. In line with the findings of the CHAINET case study, elements from both LCA and ERA are combined in this thesis.

2.4.4. European LCI for detergent surfactants production

In 1995, the outcome of a Life Cycle Inventory (LCI) for the major surfactants LAS, alkohol sulphate (AS), AES, soap, secondary alkane sulphonate (SAS), AE, and alkyl polyglucoside (APG) was published. The LCI was conducted by the European LCI surfactant study group (CEFIC/ECOSOL). A large database should be developed containing data for all processes involved in the production of these compounds (Tenside, Surfactants, & Detergents, 1995). Energy and material requirements as well as environmental emissions and solid waste associated with all phases of the surfactant production were collected (Stalmans et al., 1995). Conclusions of the peer-review were published (Klöpffer et al., 1995).

Besides production of the detergent ingredients, an LCI for the confection of typical household detergents was performed (Franke et al., 1995). Since only these steps of the life-cycle are considered and no link is drawn to detergent usages, the studies are only of limited relevance to this thesis. In addition, no impact assessment has been performed in this LCI. Thus, it does not permit to draw conclusions about the environmental relevance of the various production processes. However, due to the large effort involved in developing this database and since it provides a basis for the aforementioned PLA, it is touched upon here. Furthermore, some substance data given in the LCI are used within this thesis.

2.4.5. Further related studies

In this section, some further studies are listed. Many of these were carried out by a small group, in contrast to the larger projects discussed above. Almost all studies either perform an LCA or an ERA.

A large number of studies investigate environmental risks due to the use of single substances in detergents. These studies combine laboratory tests, field studies and modelling. Since all existing studies in this field are too numerous, they are not listed in this thesis, unless their results are later referred to. *'The German standing technical committee on synthetic detergents'* performed a literature review of ecologically relevant data for detergent ingredients, both surfactants and other ingredients. They investigated aspects such as toxicity, degradability, bioaccumulation, metabolites, interaction with metals and contribution to eutrophication and salt content. The results were published in two articles, one discussing the surfactants (Schöberl et al., 1988), the second dealing with the other ingredients (Schöberl and Huber, 1988).

A couple of studies attempt to assess the mixture toxicity of detergents and their ingredients. Laboratory tests on detergents as well as on their ingredients are conducted (Warne and Schifko, 1999, Warne, 1995). Most authors conclude that additive toxicity is an appropriate model for describing mixture toxicity of detergents (Guhl, 1997, 1999, Grimme et al., 1996, AISE/CESIO, 1996).

A current activity in the field of ERA, which has not yet been published, is the *'Human and Environmental Risk Assessment'* (HERA) project carried out by the European Detergent Industry. HERA aims to improve risk assessment for detergent ingredients. One of the first results is the development of an improved emission scenario for detergents, which was developed for boron (Wind, 2000).

Existing LCA studies mainly deal with the production step, i.e. they perform a 'cradle-to-gate' instead of a 'cradle-to-grave' approach, for example the LCI discussed above. However, some studies also focus on the use phase. For example, the Group for Efficient Appliances (1995) analysed the influence of consumer washing habits in Denmark, but only concerning energy consumption from the use of washing machines and driers. Gutzschebauch and Klüppel (1998) analysed differences in CO_2 emissions, theoretical oxygen demand (ThOD) of waterborne emissions, energy consumption, and solid waste due to variabilities in formulation and washing habits, i.e. dosage and filling the washing machine, energy scenario, and further variables. However, only an LCI, but no impact assessment was carried out.

2.5. Conclusions

An instrument as envisaged in the research aim is not yet available. Furthermore, current EDSIs do not directly permit the development of a new method within the framework of a single EDSI that meets all requirements. Limitations of directly using LCA concern the lack of ability to calculate environmentally relevant quantities and to include local variabilities. Limitations of ERA are the lack of the concept of a functional unit which is useful for comparing different product alternatives. Some of the limitations of LCA are solved by the GREAT-ER model, since it is able to calculate observable concentrations of detergent ingredients when using actual consumption data. For this reason, a combination of the basic LCA concept and the GREAT-ER model from ERA is suitable within this context.

An approach combining LCA and ERA was also envisaged for suitable case studies (Udo de Haes, 1996a, p. 13). In addition, Klöpffer (1995) explicitly mentions surfactants emitted to surface waters as an example for which concentration may be estimated within an LCA framework.

A further advantage of the GREAT-ER model is its focus on freshwater systems. Since detergents mainly consist of degradable organic substances and inorganic salts (see, for example, Table 4.1), the marine compartment is not of prime concern. For example, AISE/CESIO (1996, p. 53) conclude that the risk ratio of surfactants in marine ecosystems is smaller than the risk ratio in freshwater. The degradable organic substances are eliminated by the time the water has reached the ocean, and inorganic salts do not pose an environmental hazard in seawater. Consequently, Udo de Haes (1996a) proposed to differentiate between fresh- and seawater compartments in some LCAs in order to more appropriately assess salt emissions.

3. The GREAT-ER product mode

Based on the conclusions derived in the previous chapter, the GREAT-ER *product mode* is defined in this chapter. It allows to perform comparisons of products, use habits, wastewater treatment techniques, and of further spatially varying characteristics. A product comparison is important, since consumers have the possibility to choose between different alternatives and producers have the option of varying formulations or promoting one or the other alternative by means of marketing. Use habits are important, since they may vary from country to country but also even between neighbouring households. Wastewater treatment is highly relevant, since the organic ingredients may be eliminated from the water column if wastewater treatment is conducted. Finally, a spatial explicit assessment is important, since locally and regionally varying factors such as dilution ratios below discharges or the population density in a region may have large influences on the probability of environmental impacts.

In the following, the methodology is described. This description is subdivided into the principles of the model and possibilities to interpret the results. The implementation principles and the main user dialogs are presented in appendix D. Finally, a first approach to assess potential toxic effects of mixtures is described that is based on the GREAT-ER product mode.

3.1. Model Principles

The concept of the model is based on the functional unit 'annual household laundry in a region'. This functional unit may be fulfilled using different product alternatives a varying number of times a year at varying dosages. The main steps of the method are i) calculation of per-capita consumptions of detergent ingredients, ii) GREAT-ER simulations of these ingredients, and iii) evaluation of the GREAT-ER results.

Per-capita consumption data can be calculated for all detergent ingredients as a function of use habit and detergent formulation based on some assumptions, which are described in section 3.1.1. The subsequent GREAT-ER simulations predict concentration increases for all ingredients as a function of the predicted per-capita consumption. Since in these GREAT-ER simulations only those emissions are assessed that are related to an investigated product whereas other anthropogenic sources or natural background concentrations are not considered, only concentration increases, or increments, are predicted rather than concentrations. The denotation concentration increase is used throughout this thesis, since this term is commonly used in literature related to LCA.

Finally, evaluation is carried out using two new quantities called *Critical Length* (CL) and *Product Risk Ratio* (PRR_x). The PRR_x evaluation is following the 'only-above-threshold' approach, while the CL evaluation is based on the 'less-is-better' paradigm. Based on the functional unit chosen above, conventional LCA methods are used to derive category indicator results of other impact categories. The principle of this method is shown in Figure 3.1.

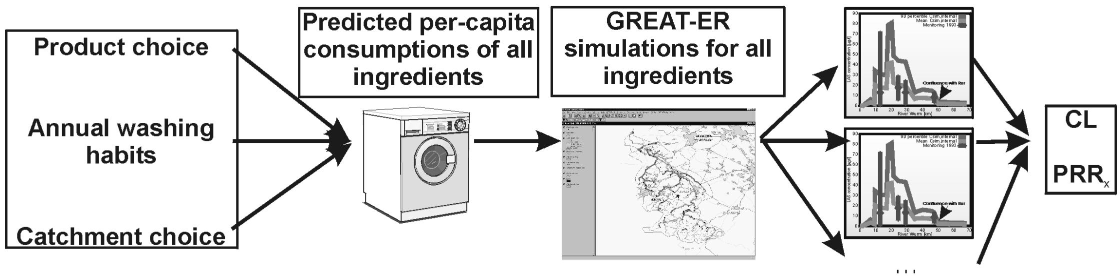

Figure 3.1.: **GREAT-ER product mode flowchart**

The GREAT-ER product mode is located in the framework of LCA, since the life cycle concept inherent to LCA provides the best basis for a comparison of products. It allows to compare different product alternatives and washing habits on a regional level by a combination of both LCA methods and the GREAT-ER product mode. Simultaneously, LCA results and predicted concentration increases in surface waters are evaluated. Although this thesis mainly addresses the latter part, within the case study both LCA results and results of the GREAT-ER product mode are analysed.

3.1.1. Emission estimates and aquatic fate modelling

GREAT-ER 1.0 calculates concentration profiles in surface waters due to actual emission data. The calculation of concentration increases due to the use of a specific product has not yet been considered. The GREAT-ER 1.0 model derives emission data at a discharge site by multiplying per-capita consumption data of the selected substance by the connected population of the discharge site. For this reason, an emission model preceding the GREAT-ER calculations has to provide per-capita consumptions for single substances. These are derived from the formulation of a product and assumptions about its usage.

The central assumption of the GREAT-ER product mode claims that during the whole year the entire population in a region uses the same product. Having also defined the average number of times the product is used by a certain dosage per usage, per-capita consumptions of the product are calculated, from which per-capita consumptions of the different ingredients are derived. The washing habits may be derived from statistical surveys or have to be based on assumptions. By also choosing a region, hypothetical concentration increases can be predicted for each ingredient using the GREAT-ER 1.0 model. These concentration increases are expected in the surface waters of the selected catchment, if the assumptions made in the definition of the product scenario would be valid.

Consumer washing habits, hereafter called use habits, may be defined in different ways. In the PLA (Grießhammer et al., 1997), a use habit is described by the choice of a detergent, total mass per year of laundry, laundry per washing cycle and finally dosage per washing cycle, given either per capita or per household. The products are defined by their formulations, which is a list of substances including their percentages. However, in this model a detergent formulation has to reflect the detergent as it enters the sewerage system, not as it is poured into the washing machine, since substance-specific processes occur during the laundry.

Summarising, within the GREAT-ER product mode a so-called product scenario is characterised by the choice of a product, a use habit, and a catchment. Concentration increases in the selected catchment are then calculated for all product ingredients based on their percentage within the product formulation, their fate properties in wastewater treatment and surface waters, as well as on the use habit. The predicted concentration increases are analysed using either an 'only-above-threshold' or a 'less-is-better' approach.

3.1.2. 'Only-above-threshold' evaluation - PRR$_x$

The 'only-above-threshold' evaluation is carried out on the basis of potential product risk ratios (PRR$_x$). These are defined for each ingredient and in each stretch as the ratio of the predicted concentration increase calculated in a product scenario[1] and a no effect concentration (NEC). *x* depicts the percentile of the GREAT-ER product mode results which is to be used. This gives a results table of product risk ratios with one column for each ingredient and a row for each stretch. These PRR$_x$ do not represent actual risk characterisation ratios known from ERA, since not all emissions of the substances are taken into account, but only those resulting from the use of the product in a manner defined by the use habit. The absolute or percentual number of stretches of a catchment in which a defined threshold is exceeded by at least one substance is then used for evaluation. The most obvious value for the product risk ratio threshold is a value of 1. However, since only specific emissions given by the selected product scenario are taken into acount, the user may specify another preferred value and perform the evaluation on the basis of this value.

A reasonable worst-case value for the percentile *x* is 90, since this is a percentage often used in ERA. For example, according to the TGD concerning the use of monitoring data within ERA of notified substances (Commission of the European Union, 1996b, Part II, Section 2.2) this percentile has to be used.

[1] In this analysis, the $C_{\mathrm{sim,internal}}$s are used, see section 2.3.1.

If the environmental soundness of the results of a product scenario shall be judged, a further decision has to be made. Typically, the river network in a catchment consists of a large number of stretches. Often, thresholds are exceeded in only a few of these stretches. Therefore, in such an application it has to be decided, which percentage of stretches in which thresholds may be exceeded is considered acceptable.

3.1.3. 'Less-is-better' evaluation - CL

If, on the contrary, a 'less-is-better' evaluation is intended, the critical length (CL) can be estimated. The CL of a product scenario, i.e. the exclusive use of a specified product in a catchment according to a chosen use habit, is defined as

$$CL = \sum_{ingredients\ i} \sum_{stretches\ s} \frac{L_s \cdot C_{i,s}}{NEC_i}$$

where $C_{i,s}$ represents the predicted mean concentration increase of ingredient *i* in stretch *s*, L_s is the length of that stretch, and NEC_i is a no-effect concentration for ingredient i. CL is a hypothetical value, which describes the total length of river stretches polluted by the different ingredients of the detergent to the ingredient-specific NECs. CL allows to aggregate the predicted concentration increases of the different substances in the different river stretches into a single figure. If a comparison of different catchments is performed in an actual case study, the CLs may be normalised by the population living in the catchment.

Next to the CL, the CLs of the single substances are stored, which allows to analyse the contributions of the ingredients. The CL is similar to the critical volume used in earlier LCIA methods (for example Heijungs et al., 1992). However, more aspects are influencing the CL assessment. Firstly, it is based on a fate assessment considering instream removal and wastewater treatment behaviour. Secondly, it considers detailed spatial conditions, which are important to appropriately reflect local impacts. Thirdly, it is based on an open model, whereas in many LCIA methods closed models are applied, e.g. in the Eco-Indicator 99 methodology. The difference of an open model compared to a closed model lies in the fact that in a closed model persistent substances are receiving much more weigt. This is unwanted in an environmental assessment of detergents, in which degradable and persistent substances are being aggregated (Schulze et al., 2001a).

3.2. Interpretation of the results

Within this section, possible ways to interpret PRR_xs and CLs are laid down.

3.2.1. Product Risk Ratios

The PRR_x does not provide the information necessary for an environmental risk assessment of substances. However, the results are valuable for a comparison of different product alternatives, use habits, and regional conditions. This is shown by discussing different possible outcomes.

If the PRR_x of a substance, based on a chosen precentile x, in a product scenario is very low, i.e. far below 1, then its aquatic ecotoxicological potential can be omitted or at least considered less relevant. This is due to the following reason. If an ERA of this single substance, based on actual emission data for this substance, concluded that no risk exists, the right decision would have been taken. If, on the other hand, such an ERA indicates a risk, then the risk reduction measures should first aim to tackle those applications contributing most significantly to this risk, and only in later stages focus on those applications with only a small share. Thus, the use of such a substance in the product assessed in the GREAT-ER product mode assessment would not be of immediate concern.

On the contrary, if the calculated PRR_x were near to or above 1 in a considerable number of stretches, then the use of this substance in the analysed product should be reviewed. In this case, if an actual ERA for this substance also concludes that a risk is indeed present, the product calculation would rightly have identified an environmental concern. If, on the other hand, an ERA based on actual emission data gives no reason for concern, the falsely prognosticated potential risk is most probably caused by the two hypothetical assumptions concerning choice of product and use habit. In such a case these assumptions should be reviewed. If the results remain similar when assuming different use habits, this product should not be classified as environmentally sound or sustainable, as the exclusive use of this product according to the underlying use habits would indeed pose a risk. No regulatory decision should be based on this result, since the exclusive use of this product is an unrealistic assumption. However, the environmental soundness of product alternatives can be judged. Concluding, without having performed an ERA based on actual consumption and emission data, decisions concerning product formulations can be made on the basis of an evaluation of a threshold exceedance.

Next to the product formulation, PRR_xs depend on use habits and regional conditions. Wastewater treatment is important in the case of laundry detergents, which is a conclusion stated in most ERA studies (e.g. AISE/CESIO, 1996, p. 49). For this reason, different use habits and regional conditions should be analysed in a set of scenarios prior to any decisions in order to derive which factors are most relevant.

Sometimes a product is only intended for sale in a specific country. For example, detergent formulations vary with countries. Thus, assessment of the influence of regional conditions can be limited to realistic variabilities in the region the investigated product is used. Still, a scenario considering best available techniques concerning wastewater treatment should always be performed. This allows for the assessment of the potential for improvements concerning wastewater treatment.

3.2.2. Critical Lengths

Most LCA methods are based on a ‘less-is-better’ approach. This is justified by the fact that information on the background concentration and the site and time of emissions of all processes related to a functional unit are generally unknown. The CL is developed for a ‘less-is-better’ evaluation. As already mentioned, the CL is defined in a way such that not only the total value of a scenario, but also the CLs of the different ingredients are calculated. It is therefore possible to examine contributions of different substances to the total CL.

This information can be used when determining options for potential improvements of product formulations. For example, detergents consist of different components, which have different functions in the washing process. In most cases, these functions can be fulfilled by different substances in different substance-specific loadings per alternative. An example for this is the choice between different anionic surfactants, the washing performances of which vary. In order to compare different anionic surfactants, their mass per washing process, environmental fate behaviour, and toxicological information need to be brought together. The CL is a way of achieving this. This information cannot be obtained from the PRR_xs.

Of course, both types of information, PRR_xs and CLs, are related to each other, since they both depend on the same simulation results. However, they emphasise different aspects, which will be further explored in the discussion of the results of the case study.

3.3. Mixture toxicity

When analysing and evaluating the aquatic fate and effect of products, the combined toxicity of the ingredients should also be adressed. However, risk assessment of chemicals primarily focuses on the assessment of risks caused by the use of a single substance, since in most cases toxicological tests analyse the response of a single species to a single substance under laboratory conditions.

Although the toxicity of mixtures has been subject to research for a long time (Grimme et al., 1996), application of this knowledge in the evaluation of products or substances is limited. This is presumably due to the fact, that the actual mixtures occurring in the environment are unknown. Different concepts to describe combined toxic effects of substances have been developed that can be subdivided into those assuming interaction between the different substances and those assuming no interaction (Guhl, 1997). If the first is expected, no general statements concerning the mixture toxicity can be made, as all forms of interaction between all different substances would need to be understood and quantified (Guhl, 1997). The latter group can be subdivided into the two groups assuming either additive or independent toxicity. The former can be quantified following the model from Loewe (1953), while the latter implies an absence of mixture toxicity (Grimme et al., 1996).

Some studies have addressed the mixture toxicity of detergent ingredients. Warne and Schifko (1999) tested the toxicity of detergents used in Australia. A comparison of acute toxicity of detergents assuming different builders was also carried out (Warne, 1995). AISE/CESIO (1996, p. 46) propose to assume additive toxicity for surfactants. This approach has been tested and judged as appropriate by Guhl (1997, 1999). Furthermore, Grimme et al. (1996) investigated the combined effects of selected detergent ingredients and also concluded that additive toxicity is best suited for assessing mixture toxicity of this group of compounds.

Following the model for additive toxicity given by Loewe (1953), the ecotoxicity of a product can be calculated in the following way (Guhl, 1997)

$$EC_{prod} = 1/(\sum_{ingredients\ i} \frac{c_i}{EC_i})$$

where EC_{prod} is the corresponding effect concentration of the product, derived from the effect concentrations EC_i of the different ingredients *i* being in the product at percentages c_i. Obviously, the EC values have to be comparable.

Typically, this equation is applied to detergent formulations as they are filled into a washing machine, but not as they enter the surface waters(e.g. Grimme et al., 1996, Guhl, 1997). However, the expected detergent's composition in surface waters is more relevant, as organisms are exposed to the detergent ingredients in the surface waters rather than in the washing machine. For this reason, the results of the product mode calculations are used to calculate a mixture product risk ratio.

In appendix B it is proven that by assuming additive toxicity, i.e. based on the equation given above, the sum of the calculated product risk ratios of the different ingredients in a stretch describes the hypothetical product risk of the product in that stretch, i.e.

$$\sum_{ingredients\ i} PRR_{x,i} = \frac{\sum_{ingredients\ i} C_{x,i}}{EC_{prod}} = \frac{C_{x,prod}}{EC_{prod}}$$

In this equation, $PRR_{x,i}$ is the product risk ratio of substance *i* in a stretch based on the predicted *x*-percentile concentration $C_{x,i}$. $C_{x,prod}$ is the predicted concentration of the entire product and EC_{prod} is the effect concentration of the product. Based on this proof, the mixture product risk ratio of a product scenario can be calculated for each stretch by adding the product risk ratios of the single substances. However, it is debatable, whether all ingredients should be considered in such an analysis. One may argue that a combined toxicity assessment of surfactants on the one hand and inorganic salts on the other is not meaningful. In fact, most of the studies above analysed only the surfactants and omitted the inorganic compounds. However, most LCA methods typically aggregate all emissions. Due to these contradicting approaches, different options have been analysed in the case study.

However, the significance of these mixture product risk ratios is limited, since the actual composition of substances present in the environment is not considered, but only the concentration increases due to the use of a product in a manner defined in the product scenario. For this reason, it is only a first step towards an assessment of combined toxic effects of detergents occurring in the environment. In an actual risk assessment, the background concentrations of other substances present in the environment would also have to be considered.

4. Case study household laundry

The detergents and use habits are derived on the basis of the PLA (Grießhammer et al., 1997). In addition, use habits based on European detergent consumption statistics are used in the catchment comparison. Consequently, scenarios are defined on the basis of these data sets.

4.1. Model detergents

The PLA considered 4 different detergents in their analysis, which represent formulations from the 1990s. They were chosen to describe different washing agent concepts. In the PLA these detergent formulations have been analysed as they are sold and enter the washing machine. This is warrantable for an LCA which mainly looks at the production site. However, if the fate of detergent ingredients in surface waters is to be calculated, detergent formulations as they are expected to enter the sewerage system are required. Therefore, the formulations given in Table 4.1 comprise two percentages for each substance, one as it enters (columns ‘in’) and the second as the ingredient is assumed to leave the washing machine (columns ‘out’). Transformations are based on the molecular weights. Here, sodium perborate is substituted by boron (7%), sodium percarbonate is included in the sodium carbonate fraction (68%), and TAED is replaced by DAED (63%). In addition, it is considered that half of the optical brightener remains on the textile (Richner, 2000). These percentages are further described in section 4.5. In the table these changes are marked in bold face. It should be noted that the release of the sodium kations taking place during the washing process is not reflected in Table 4.1 and in the calculations. This is due to the fact that the toxicological information used refer to the salts.

The heavy-duty detergent represents the traditional detergent which is still on the market. The compact heavy-duty detergent has an average formulation of compact powder detergents which are currently widely in use. The tandem system consists of two detergents: a compact heavy-duty and a compact colour detergent, by assuming that 85% of the total laundry is coloured, i.e. it needs no bleaching. Finally, the 3-component system consists of three separate powders, a basic detergent, a bleaching agent, and a water softener. Depending on the types of laundry and water hardness, an optimal formulation can be obtained. The used formulation is based on the assumption of 85% colour laundry and an average water hardness for Germany. It was defined by the German Federal Environmental Agency (*'Umweltbundesamt'*, UBA). Consensus was reached among the participating stakeholders regarding this formulation (Grießhammer et al., 1997, p. 50). Water content has not further been investigated in the PLA, neither is this being done within this thesis.

Table 4.1.: **Model detergents as defined in the PLA (in) and as they are discharged into the sewerage system (out) (%)**

	Heavy-duty		Compact heavy-duty		Tandem system		3-component system	
	in	out	in	out	in	out	in	out
Recom. Dosage (g)	146	146	89	89	86.45	86.45	73.7	73.7
LAS	6.9	6.9	5.8	5.8	7.7	7.7	0	0
AS	3.1	3.1	2.8	2.8	3.8	3.8	6.1	6.1
Soap	0.5	0.5	0.4	0.4	0.9	0.9	2.6	2.6
AE	3.7	3.7	4.5	4.5	7.5	7.5	11.5	11.5
Zeolite A	20.3	20.3	20.7	20.7	29.7	29.7	40.2	40.2
Polycarboxylates	3.6	3.6	3.8	3.8	4.6	4.6	0	0
Sod. silicates	3.1	3.1	3.3	3.3	2.5	2.5	4.3	4.3
Sod. sulphate	19	19	2.4	2.4	3.8	3.8	0.1	0.1
Sod. citrate	0	0	1.7	1.7	5.2	5.2	0.5	0.5
Sod. carbonate	11.9	11.9	16.6	16.6	15	15	**17.8**	**19.3**
Sod. percarbonate	0	0	0	0	0	0	**2.2**	**0**
Sod. perborate/Boron	**19.1**	**1.3**	**21.1**	**1.5**	**3.3**	**0.2**	0	0
TAED/DAED	**0.8**	**0.5**	**3.8**	**2.4**	**0.6**	**0.4**	**0.4**	**0.25**
DAS-1	**0.12**	**0.06**	**0.15**	**0.08**	**0.02**	**0.01**	0	0
CMC	0.2	0.2	0.4	0.4	0.3	0.3	0.5	0.5
PVP	0	0	0	0	0.4	0.4	0	0
Water	remainder							

4.2. Model households

Three model households or use habits were defined in the PLA. They were developed with regard to households, whereas in this thesis the washing habits are needed with respect to capita. This transformation is based on the average household size in Germany, which is 2.26 (Grießhammer et al., 1997, p. 153). The three use habits are given in Table 4.2.

The Wishy-Washy use habit is defined to reflect average German washing habits based on consumer statistics. The two other habits, Smart and Scrubbed, represent a realistic span around this average. In the PLA, use habits also include assumptions about washing temperatures and the use of dryers, which is necessary for determining energy consumption. Further explanations of these assumptions are given in the PLA. Within the GREAT-ER product mode, these further assumptions are not relevant.

Table 4.2.: **Model use habits as defined in the PLA (per person)**

	Smart	Wishy-Washy	Scrubbed
Total annual laundry (kg)	163.04	217.39	217.39
Laundry per wash (kg)	4	2.75	1.75
Dosage (g)	72.3	103	175.1
Detergent	3-component system	Compact heavy-duty	Heavy-duty

4.3. Study areas

The PLA considers German conditions for detergents and use habits. Therefore, a German catchment is primarily used for the case study in this thesis. However, at the beginning of this thesis only the Itter catchment was included in the GREAT-ER database, which is a very small catchment, as was shown in section 2.3. For this reason, it was decided to integrate a further German region into the GREAT-ER database. Since monitoring data of detergent ingredients in the Rur river and its tributaries exist, the Rur river basin has been chosen as main study area. The monitoring data serve to judge the quality of the catchment integration. The Rur river basin is located in Western North Rhine-Westphalia and covers an area of approximately 2,500 km^2. Its integration is discussed in detail in the following chapter, whereas the capability of GREAT-ER to predict realistic concentrations of detergent ingredients in this catchment is analysed in chapter 6.

Other catchments are taken into account in section 7.3, since in this section the variability of the results due to changes in the catchment characteristics are analysed. The catchments and further use habits that are based on European detergent consumption statistics (Gutzschebauch, 1999) are described there.

4.4. Effect data

Effect data are required in order to calculate product risk ratios and critical lengths. As these are used to aggregate the different detergent ingredients, they have to be comparable. Therefore, data from an existing database compiled for a similar purpose are preferred, since this ensures data consistency. In addition, in order to estimate hypothetical product risk ratios, no-effect concentrations or predicted no-effect concentrations are necessary instead of acute data, while the CL estimation may in principle also be done with any other consistent effect data set. The DID-list developed in the context of the European Union scheme for the award of an ecolabel for detergents (European Union, 1999a) is suitable for this. A manual was written for guidance on how to use the data (European Union, 1999c).

In this database, two entries for each substance reflect toxicological information. One field contains (preferably) a measured NOEC value, while the second field contains the value to be used for calculating the critical dilution volume (CDV) criterion of the evaluation scheme, called *'Long Term Effect'* (LTE). Depending on the toxicological data given in the NOEC field, an extrapolation procedure is performed to assign the data of the different substances' equivalent meanings, which are the LTE concentrations (European Union, 1999a). This extrapolation procedure is less conservative than the effect assessment procedure as laid out in the TGD (Commission of the European Union, 1996b).

According to the manual (European Union, 1999c, p. 15), adjustments have to be performed for the two substances boron and zeolite A. These transformations are explained in section 4.5.

4.5. Considered substances

The choice of investigated substances is determined by the model formulations given in the PLA. For these substances different kinds of data are required for the product mode calculations. Unlike for GREAT-ER verifications, actual emission data are not needed in the product assessment. These may be used in the interpretation of results in order to determine the actual likelihood of the different scenarios, but are not necessary input parameters. Physico-chemical parameters are required, as for all GREAT-ER calculations. For calculations performed here, i.e. mode 1 for WWTP and rivers, and mode 2 for sewers, only percentual elimination efficiencies for the sewerage systems and WWTPs, as well as first-order in-stream removal rates for surface waters are necessary. In addition, toxicological information given in the DID list is used for the calculation of both CL and PRR_x.

All values chosen for the substance data are given in the following sections. They are subdivided according to the DID list (European Union, 1999a), which relates to the functions of the ingredients. The fate-related data are derived from a literature review while the toxicological information is taken from the DID list. In this section, the data and short explanations are provided for all considered substances. A tabular overview of the substance data is given in appendix A.1.

4.5.1. Anionic surfactants

There are many different anionic surfactants, of which three were considered in the PLA (Grießhammer et al., 1997), i.e. linear alkylbenzene sulfonates (LAS), alcohol sulphates (AS), and soap. The main function of surfactants is to unhinge dirt from the laundry and to keep it in the water column, i.e. to inhibit the redeposition of the particles on the textiles. In most detergents the latter is assisted by carboxymethylcellulose (CMC). In addition, soap also functions to prevent the creation of foam (Vollmer and Franz, 1994).

LAS

A huge number of studies that examine different aspects of toxicity, degradability, sorption, and use exist for LAS. Within the GREAT-ER project, simulations with LAS were carried out, from which necessary data could be obtained. In the product assessment calculations, the Itter data set is used (see section 2.3.3). In sections 6.1.3 and 6.3.3 it is shown that this data set is also applicable in the Rur catchment. For this reason, the Itter data set, given in the following, is used: 25% elimination in sewers and 98% in activated sludge type WWTPs, of which 20% is assumed to be eliminated in the primary settler (Matthijs et al., 2000). This latter value is an average value of measured efficiencies reported in the respective study. In addition, an in-stream removal rate assumed to be uniformly distributed between 0.03 and 0.35 h^{-1} is used. For trickling filter type WWTPs, a total elimination of 85% is assumed (ECETOC, 2000). Again, 20% is considered to be already eliminated in the primary settler, which is therefore the value used for WWTPs that only have a primary settler. The toxicological information given in column LTE of the DID list is 300 μg/l.

AS

For AS, only a few measured kinetics exist. The comparison of GREAT-ER results derived from the Rur 2000 data set and monitoring data revealed that a similar substance data set as for LAS results in realistic concentrations. Although some authors report a better elimination behaviour for AS than for LAS in both WWTP and rivers, with respect to the GREAT-ER calculations performed in the Rur catchment (see section 6.3.3) the same in-stream removal rate is used as for LAS. Regarding WWTP behaviour, 35% removal in the primary settler, 98.5% total removal in activated sludge type, and 88% in trickling filter type plants are chosen (see also Matthijs et al. (2000) and Painter (1992)). Sewer removal is assumed as for LAS, i.e 25%. In the PLA and in this thesis, AS made from palm oil is considered, i.e. a fatty alkohol sulphate (FAS). The appropriate LTE value for FAS is 550 μg/l.

Soap

Even fewer data are available for soap than for AS. The only study known and used is the Dutch environmental risk assessment of detergent chemicals (AISE/CESIO, 1996), the results of which were also published by Matthijs et al. (2000), Feijtel et al. (2000), and Van de Plassche et al. (2000). Unlike for LAS and AS, no removal of soap occurs in the sewers. The Dutch measurements even identified a concentration increase occurring in the sewers, which is explained by the hydrolysis of fats and oils. In the WWTPs, removal efficiencies of 45% for the primary settler and 98% in the activated sludge tanks are assumed, which give a total WWTP removal efficiency for activated sludge plants of 98.9%. This is consistent with the values given by Matthijs et al. (2000, a mean of 99.0%). For trickling filter type plants, a total removal of 91% is assumed, as a better elimination than for LAS can be expected. This assumption is based on test results given by Schöberl et al. (1988), which show that in general soap is degraded better than LAS. The reported results from screening tests on total degradability always gave higher values for soap than for LAS. A similar reasoning was applied for in-stream removal. As soap is believed to be degraded faster than LAS, a uniform distributed rate ranging between 0.06 and 1.71 is used. Due to this large span, the uncertainty related to this parameter is partly reflected.

Concerning aquatic toxicity, the LTE concentration for soaps with a chain length between 12 and 22 C-atoms is 1.6 mg/l.

4.5.2. Nonionic surfactants

In current laundry detergents in Europe mainly alcohol ethoxylathes (AE) are used. Further nonionic surfactants formerly used in Europe and still used in the US are alkylphenol ethoxylates. Due to the persistence and estrogenic activity of their metabolites (Destaillats et al., 2000), these were replaced in European detergents by AE. More recent nonionic surfactants are based on renewable resources, e.g. alkyl polyglucoside (APG). These proved to be an alternative (Hirsinger and Schick, 1995, Steber et al., 1995), but are not (yet) commercially relevant. For this reason, in both the PLA and in this thesis AE is the only nonionic surfactant considered.

Behaviour of AE in sewers, WWTPs, and rivers is the subject of several studies. In section 6.3.4, these studies, e.g. Holt et al. (1992), AISE/CESIO (1996), Steber (1997), and Marcomini et al. (2000), are analysed with respect to the Rur monitoring data of 2000. Based on this analysis an in-stream removal rate which is uniformly distributed between 0.012 and 0.055 h^{-1} (Marcomini et al., 2000), a sewer removal efficiency of 42% (AISE/CESIO, 1996), and a WWTP elimination efficiency of 99% in activated sludge plants are assumed. 25% of this total WWTP removal is assumed to occur in the primary settler (Matthijs et al., 2000). In trickling filter plants a total removal of 88% is used (AISE/CESIO, 1996, Holt et al., 1992), which also includes 25% elimination in the primary settler.

A petrochemical-based AE of chain lengths 12 to 14 with 7 ethoxylate groups is considered in the PLA (Grießhammer et al., 1997, p. 50). The appropriate entry from the DID list has an LTE concentration of 0.24 mg/l.

4.5.3. Builders

Builders are next to surfactants main ingredients of detergents. In European supercompact powders they represent one-half of the formulation (Bauer et al., 1999). Their main purposes are to adjust the pH-value, to prevent hydrophobic particles from redeposition on the laundry, to reduce the water hardness, and to facilitate removal of dirt from textiles. In addition, some builders are able to assist the bleaching process (Bauer et al., 1999) and in some powder detergents they are used to keep it powdery in order to permit longer storage. This latter application is also achieved by sodium sulphate, which is listed in accordance with the DID list in section 4.5.6.

During the eighties, phosphate compounds, mainly pentasodiumtriphosphate, were used. However, due to its contribution to eutrophication phosphate was replaced in most European countries by a combination of zeolite A, polycarboxylates, citrate, sodium carbonate, and (mainly sodium) silicate.

Zeolite A

Zeolites are either natural or synthetic crystalline aluminosilicates. The name came into being from an observation made in 1756 by a Swedish amateur mineralogist. He discovered that some minerals release a large amount of water when heated. He called these minerals zeolites, which is Greek meaning boiling (zeo) stones (lithos) (Christophliemk et al., 1992). In the second half of the seventies, zeolite A, a synthetic sodium-based zeolite, began to be used in detergents as a water softener, which is achieved by ion exchange. It is currently used in almost all phosphate-free laundry detergents.

Different studies examined the behaviour of zeolite A emitted via the wastewater path resulting from use in detergents. Field studies concluded that no sedimentation occurs in the sewerage systems (Christophliemk et al., 1992, ZEODET, 2000). For this reason, no elimination in the sewers is assumed in the calculations. Concerning fate in the WWTPs, different elimination efficiencies were observed that in most cases were above 90%, e.g. 96% according to ZEODET (2000). The dominant elimination pathway is transfer to sewage sludge (Bauer et al., 1999, Christophliemk et al., 1992). Kurzendörfer et al. (1997) report different elimination efficiencies in the sand trap and the primary settler, i.e. from 21% to 80%. Reported elimination efficiencies in the activated sludge tanks are 89% and 77-87%, while in trickling filter plants 81% removal was measured for biological treatment (Kurzendörfer et al., 1997). Therefore, 67% removal in the primary settler (Christophliemk et al., 1992), 70% in the activated sludge plant, and 42% in trickling filter plants is assumed, leading to total removals of 90 and 81% respectively for these types of plants.

Reported values for in-stream removal indicate no or only very slow elimination, which is then due to hydrolysis (ZEODET, 2000, Kurzendörfer et al., 1997). Therefore, a conservative approach is followed by assuming no in-stream removal. This will be kept in mind for the interpretation of the results. In addition, this will be changed in the assessment of the inorganic compounds conducted in section 7.4.

An entry for zeolite A with an LTE concentration of 120 mg/l is given in the DID list. According to the manual (European Union, 1999c) this value should not directly be set in relation with the zeolite A content in the detergent; the percentage has to be reduced by a factor of 0.79, as was mentioned above. No explanation is given in the manual, but it seems plausible that this correction is due to the fraction of water bound in the crystalline structure. A molecular weight-based revision supports this hypothesis, although it gives a deviation of 1 percent: Based on the molecular formula for zeolite A $Na_{12}[(AlO_2)_{12}(SiO2)_{12}] \cdot 27H_2O$ the cristalline water accounts for 78% of the molecular weight. Nevertheless, the correction factor given in the manual of 0.79 is considered in the product assessment.

Polycarboxylates

Polycarboxylates used in detergents are mainly water-soluble linear polymers. They are used as co-builders in conjunction with zeolite A in order to bind those ions that have the potential to increase water hardness.

Behaviour in wastewater and in WWTPs has been investigated in some studies. Both Schöberl and Huber (1988) and Opgenorth (1992) cite studies reporting elimination efficiencies in biological WWTPs above 90%. Hennes (1991) reports field studies indicating removals of 97 to 98%. Based on this, a uniform distribution between 91 and 97% is assumed for total removal in the sewerage system and activated sludge WWTP. As this elimination is partly also due to degradation, though mainly due to sorption, a lower elimination efficiency, i.e. 85%, is assumed for trickling filter plants. From these total removal figure, 18% are considered to occur in the primary settler (Opgenorth, 1992). No studies have been found related to fate in the sewerage systems. With respect to WWTP efficiencies, some removal seems plausible, but as no data could be found in the literature, the conservative approach is followed and elimination in the sewerage system is neglected.

A similar approach is used concerning in-stream removal. Some authors state possible biodegradation in surface waters, which is then expected to be slow (Opgenorth, 1992). However, available information is only scarce. For this reason, despite potential biodegradation, in order to follow the conservative approach no in-stream removal is assumed. Again, this will be kept in mind for the interpretation if the polycarboxylates turn out to be relevant.

Toxicity can be regarded as low. The LTE concentration is 124 mg/l and thus comparable to the toxicity of zeolite A.

Citrate

Citrate is a *"prime example of an environmentally acceptable detergent builder"* (Hoyt and Gewanter, 1992). It has a ubiquitous natural occurrence and can be found in most organisms, where it is a common metabolite. In detergents it functions as a water softener.

Biodegradation of citrate in WWTPs and in rivers has been investigated. Concerning WWTPs, values ranging from 96 to 99 and from 67 to 100% were reported in different studies for biological treatment (Hoyt and Gewanter, 1992). As no sorption occurs, this is only due to biodegradation. No studies were found concerning sewers. But since biodegradation may also occur during transport in the sewerage system, an elimination efficiency of 25% was assumed, which is the same value as for the anionic surfactants LAS and AS. In addition, in biological WWTPs, both activated sludge and trickling filter types, a uniformly distributed efficiency ranging from 96 to 99% is assumed (Hoyt and Gewanter, 1992, p. 237). However, based on Hoyt and Gewanter (1992, p. 238) no elimination in the primary settler is considered.

Biodegradation also occurs in surface waters. Kinetics with half-lives ranging from 0.2 to

3.5 hours are reported by Hoyt and Gewanter (1992). From these studies, the upper value, which corresponds to a rate of 0.198 h^{-1}, is used.

The LTE concentration given in the DID list for citrate is 85 mg/l. Beyond this concentration toxic effects may occur due to a pH-reduction caused by citrate (Schöberl and Huber, 1988).

Sodium silicate

Sodium silicates are used in laundry detergents in order to optimise the alcalinity, to prevent corrosion of the machine's metallic parts, and to keep the detergent powdery. In the aquatic environment, sodium silicates exist in ionic forms.

Studies of elimination behaviour in wastewater or in surface waters are very scarce. Falcone and Blumberg (1992) state that biochemical weathering processes have the potential to decompose silicates, but that these processes are not yet fully understood. Pulli (1997) assumes no elimination in wastewater or rivers. As biochemical weathering processes are considered to be rather slow compared to the residence time in a typical catchment, the approach assuming no elimination is followed here. This is confirmed by studies reported by Schöberl and Huber (1988).

The LTE concentration given in the DID list is 1 g/l, which demonstrates that no toxic effects are likely to occur from the use of silicates in detergents.

Sodium carbonate

Sodium carbonate emissions into the sewerage system resulting from use in laundry detergents may occur due to two functions. If sodium percarbonate is used as a bleaching agent, then this is transformed to sodium carbonate during the washing process and thus emitted as dissolved sodium carbonate. In addition, sodium carbonate itself serves to adjust an optimal pH-value.

The salt is dissolved in water solution. Their ionic parts remain stable during the entire wastewater path. Elimination does not occur in the sewers, nor during wastewater treatment. Also no in-stream removal occurs. For this reason, the only information needed is the toxicological information given in the DID list, i.e. 250 mg/l as LTE concentration.

4.5.4. Bleaching agents

Two main options exist for chemical bleaching. Either sodium perborate tetra- or monohydrate or alternatively sodium percarbonate is used. These bleaching agents are typically applied together with the bleaching activator tetraacetylethylendiamine (TAED), which allows for an effective bleaching process evan at lower temperatures, i.e. below 60°C. The bleaching agents alone are only active at temperatures above 60°C.

Sodium perborate tetrahydrate

During the washing process sodium perborate tetrahydrate is transformed to borate. During transport in the sewerage system and the WWTPs no elimination occurs. Therefore, the total amount of borate present in the detergent enters the surface waters, where no elimination occurs either. As in environmental monitoring boron rather than borate is generally measured, boron simulations are conducted in the case study. The content of boron in the detergent is derived from the molar mass. The only necessary parameter for the product mode assessment is therefore the toxicological information, which is given in the DID list. An LTE value of 6 mg/l is given for borate. However, the manual for applying these criteria stipulates the use of a correction factor, as the given LTE value refers to sodium metaborate ($NaBO_2$). In addition, boron is used in the GREAT-ER simulations rather than perborate. For these reasons, a molecular weight-based adjustment of the LTE concentration has to be done (factor 6.09) (European Union, 1999c).

Sodium percarbonate

As with sodium perborate tetrahydrate, sodium percarbonate also undergoes a transformation process during the bleaching process taking place in the washing machine. It enters the sewerage system as dissolved sodium carbonate. In the product formulation the percentage of sodium percarbonate is therefore added to the sodium carbonate fraction based on molecular weight. The transfer factor of 0.68 is identical to the correction factor given for the ecolabel calculation (European Union, 1999c).

No elimination occurs for sodium carbonate, nor for the ions. Therefore, the only necessary parameter is the LTE concentration for sodium carbonate as given in the DID list, i.e. 250 mg/l.

TAED

The following information about tetraacetylethylenediamine (TAED) and its metabolite diacetylethylendiamine (DAED) is extracted from Gilbert (1992). In order to reduce energy use during laundry processes, TAED is added to the detergent formulation to enable an effective bleaching even at lower temperatures. In addition, TAED possesses antimicrobial properties which deliver significant hygiene benefits at low temperatures, which could otherwise only be obtained in a boil-wash. One disadvantage of TAED is the fact that the unwanted bleaching of coloured clothes may occur at lower temperatures. This can only be avoided by separating coloured and white laundry.

During the washing process, TAED undergoes perhydrolysis, leading to DAED, which enters the sewerage system. Therefore, GREAT-ER calculations are carried out for DAED instead of TAED, with a percentage reduced according to the molecular weights, giving a reduction of 63%. Since studies show a comparable toxicity of TAED and DAED, the toxicological value given for TAED in the DID list can directly be applied to DAED. In addition, TAED and DAED show similar fate properties concerning biodegradability in sewers, WWTPs, and finally in surface waters.

Both TAED and DAED are highly water soluble compounds with low octanol-water partitioning coefficients limiting its likelihood of sorption to sludge or sediment. However, high elimination efficiencies were detected in WWTP measurements, which are due to biodegradation. For this reason, a uniform distribution between 96 and 99% was assumed as the total removal efficiency for sewer systems and WWTPs. However, in the primary settler no removal is assumed. This is conservative since Gilbert (1992) only reports that no DAED was found in sewage sludges, However, no information is available concerning elimination in the primary settler step.

No degradation kinetics were reported with regard to in-stream removal. Therefore, the methodology of the EUSES model is used, which uses a half-life of 15 days for readily biodegradable substances. This is most probably a too conservative estimate, compared with substances for which kinetics were measured, e.g. LAS. If DAED proves to be significant in the product assessment, these conservative assumptions will be kept in mind. The LTE concentration given in the DID-list for TAED is 500 mg/l.

4.5.5. Optical brighteners

Two different optical brighteners or flourescent whitening agents (FWA), are used in detergents, which are both included in the DID list, i.e. FWA 1 and FWA 5. FWA 1 is a disodium 4,4'-bis (4-anilino-5-morpholino-1,3,5-triazin-2-yl)amino stilbene-2,2'-disulfonate (DAS-1), while FWA 5 is a disodium 4,4'-bis(2-sulfostryryl)biphenyl (DSBP). According to Richner (2000), 85% of optical brighteners in German detergents consist of FWA 1, while only 15% are FWA 5. Thus, as FWA 1 is the more important optical brightener, FWA 1 is used in the product mode calculations. This leads to a slight overestimation of the contribution of the optical brighteners, since FWA 1 is more toxic than FWA 5 (according to European Union, 1999a, by about a factor of 3) and because FWA 5 degrades faster in rivers than FWA 1 (Poiger et al., 1999). Their behaviour in WWTPs are comparable (Kramer, 1992). It should be noted that FWA 5 was used in the PLA. However, due to its minor market share, it is not used in this analysis.

Fate behaviour in WWTPs is mainly determined by sorption to sludges, while Poiger et al. (1999) determined sorption to sediments and degradation by photolysis as elimination pathways from the surface water column. Both measured elimination efficiencies and in-stream removal rates vary throughout the different studies. The total elimination efficiency of 81% for sewers and WWTPs (both activated sludge and trickling filter type) can be considered as conservative, regarding the range of reported values (Kramer, 1992). The value is taken from Pulli (1997) and is based on unpublished information from Ciba Geigy. 55% of WWTP removal is assumed to take place in the primary settler (Kramer, 1992). For in-stream removal, a medium value was chosen, i.e. 0.0108 h^{-1}, which is given as a rate constant under sunny conditions that should not be expected to occur under cloudy skies. However, as faster values are also reported (Pulli, 1997) and sorption also usually occurs (Poiger et al., 1999), this value can be regarded as an average value.

The prominent property of optical brighteners is their ability to fluorescence. This is the ability to absorb UV-light and to emit it as blue light, which compensates the unwanted yellow appearance of laundry and gives the colours more brightness. Their purpose is therefore not to clean textiles but to remain on the textile. The percentage of FWAs remaining on the textiles after the laundry process may vary to a considerable degree, i.e. Kramer (1992) gives values of between 20 and 95%. According to Richner (2000), 50% is a reasonable mean value. This value is therefore used in the calculations. This percentage is considered in the product formulations since these are given as they enter the sewerage system, i.e. the percentage according to the PLA is reduced by a factor of 0.5.

4.5.6. Miscellaneous

Besides the main detergent components surfactants, builders, bleaching agents, and optical brighteners other substances are also used in detergents. Some of them are considered in the PLA. These are listed here as miscellaneous, which is analogous to the subdivision given in the DID list.

Polyvinylpyrrolidon

Polyvinylpyrrolidon (PVP) is used in detergents for coloured laundry. It prevents colours fading between different textiles. Information regarding its environmental fate properties is very scarce. The DID list classifies PVPs as neither aerobically nor anaerobically degradable. Therefore in-stream removal and removal in the sewerage system is not assumed. On the contrary, a 25% elimination efficiency for both activated sludge and trickling filter WWTPs is assumed in the calculations, which is based on information provided by Taylor (1999). Since no further information related to the fate of PVP in WWTPs could be obtained, it is assumed that half of the removal occurs in the primary settler. As the fate-related parameters are considered highly uncertain, this will have to be further analysed, if PVP turns out to be relevant.

According to the toxicological information given on the DID list PVP does not pose a significant hazard, since the LTE concentration is 100 mg/l.

Carboxymethylcellulose

Carboxymethylcellulose (CMC) is used to inhibit the particles present in the washing liquid during the washing process from redepositing onto the laundry. Like polycarboxylates, CMC belongs to the group of water-soluble polymers which can either be natural, synthetic or semisynthetic. CMC belongs to the latter group.

According to Schöberl and Huber (1988) and Bafelaan et al. (1992), biodegradation may occur in both WWTPs and in rivers, which is, however, rather slow and only partial. Results reported in Schöberl and Huber (1988) from EPA-activated sludge tests are used in the calculations. This test gave an elimination efficiency of 27% for activated sludge plants. No data are available for trickling filter. But since the removal is most probably due to biodegradation, a lower efficiency is assumed, i.e. 20% was arbitrarily chosen. No elimination is assumed in the primary settler. However, no studies were found supporting or rejecting this thesis. The choice is based on the water solubility of CMC and on Bafelaan et al. (1992), who state that only degradation but no sorption occurs. Concerning in-stream removal, a conservative approach based on Schöberl and Huber (1988) is followed by assuming no in-stream removal. This choice may be seen as too conservative, since Bafelaan et al. (1992) report degradation pathways. For this reason, this potential overestimation of CMC will be borne in mind during interpretation if CMC turns out to be relevant.

All test data available for CMC indicate very high concentrations at which effects occurred. This is documented in the DID list, in which the LTE concentration is 250 mg/l.

Sodium sulphate

The inorganic salt sodium sulphate is used to increase the dryness of the detergent powder, which facilitates better storage and dosage of the powder (Grießhammer et al., 1997, appendix p. 59). Sodium sulphate is dissolved in water. The ions are neither eliminated in wastewater nor in surface waters (Schöberl and Huber, 1988), limiting the necessary data to the toxicological information given in the DID list. The LTE concentration of 1 g/l shows that it is not relevant in terms of aquatic toxicity. The use of sodium sulphate is controversial due to the fact, that it increases the salt content in the freshwaters. As more recent detergent formulations do not require sodium sulphate, although it is still used in others, this debate is not yet over. In section 7.4 this question is evaluated with regard to the scenarios defined in the case study.

5. The Rur catchment - Integration into the GREAT-ER model

5.1. Introduction

As was described in section 2.3, the Itter catchment was incorporated as the first German study area into the GREAT-ER system during its development phase. However, in order to assess the aquatic ecotoxicological impacts of household laundry using the GREAT-ER product mode, the Itter catchment is considered as too small a catchment. Since the incorporation of further catchments from different parts of Europe was one aim following the GREAT-ER development phase, the Rur catchment in Western North Rhine-Westphalia was chosen as a further German study area. The prime reason for this catchment was the availability of monitoring results collected by Henkel KGaA between 1993 and 1995 (Schröder, 1995a,b). A comparison of monitoring and simulation results allows to calibrate catchment-specific substance data sets to be used in the product assessment as well as to check the quality of the incorporation of a new catchment.

In this chapter, the integration of the Rur catchment into the GREAT-ER system is described, which also includes the development of a simple hydrological model. Because the discharge site data changed during the nineties, two data sets were developed. The first considers the situation in 1993, called Rur 1993, while the second reflects newest available data, called Rur 2000. However, the difference is only with respect to the discharge site data. Since hydrological information is based on long-term statistics, the development of two different hydrological data sets is not considered necessary. Besides the discharge site data also the monitoring data, which are described by their mean values and the span of data, are differentiated according to the years of sampling. Monitoring data sampled in 1993 are available for the detergent and cleaning agent ingredients boron, LAS, nitrilotriacetate (NTA), and EDTA. In the following chapter 6, results of GREAT-ER simulations calculated for the Rur catchment are shown together with the monitoring results in order to judge the quality of the incorporation and the capability of the GREAT-ER model to predict concentrations that are in the range of measured concentrations[1].

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[1] The integration and the simulation results using the 1993 data set were submitted for publication (Schulze and Matthies, 2001).

5.2. The Rur river basin

The Rur river basin has an area of approx. 2,500 km^2. It discharges wastewater for about 1 million inhabitants, which is increased by industrial discharges contributing wastewater for an additional equivalent of 900,000 inhabitants. The largest city is Aachen/Aix-La-Chapelle. The upper courses of the Rur and its tributaries are comparable to low mountain rivers, whereas the lower courses are situated in a flat region where significant anthropogenic impacts occur. The border between these two parts is marked by large water reservoirs, e.g. the ‘Rurtalsperre’ which is one of the largest in Germany. These are partly used as drinking water reservoirs. Nonetheless, smaller discharges are located upstream from the water reservoirs, e.g. at Monschau.

The most relevant discharges concerning detergents and household cleaning products are Düren WWTP (River Rur) and Aachen-Soers WWTP (River Wurm). In the upper part of the study area, anthropogenic impacts are only moderate, while in the lower parts they lead to a significant impact on the water quality (Schröder, 1995a). However, due to improvements performed by the local water authorities ‘*Wasserverband Eifel-Rur*’ (WVER), discharge loads into the Rur and its tributaries were significantly reduced during the nineties (see, for example, WVER, 1996). Monitoring data collected by the North Rhine-Westphalia State Environmental Agency (‘*Landesumweltamt*’, LUA) show similar findings (Landesumweltamt Nordrhein-Westfalen, 1997).

5.3. Data collection and assembly

5.3.1. River network

The river network must be given in vector-type data, since topological information such as confluences or bifurcations are used by the model. The data must be given in line-format, i.e. a polygon representation of a large river would need to be transformed in a line feature. For Germany, the Federal Environmental Agency (UBA) has digitised the *Feines Gewässernetz Deutschland*, which is an extension of a data set created by the Federal Agency for Cartography and Geodesy (‘*Bundesamt für Kartographie und Geodäsie*’, BKG). The level of detail of the river network is comparable to a 1:200 000 map (Treffler, 1999).

For use in GREAT-ER, some errors existing in the river network had to be removed. In addition, some of the line segments had to be flipped, i.e. their direction had to be changed such that all line segments are directed downstreams. In addition, the number of line segments was increased by splitting existing ones. This increased segmentation is not of importance for the calculations as such, but visualisation of the results becomes more detailed. However, the greater number of river stretches increases simulation time.

The lengths of stretches should not be too variable, since otherwise the aggregation of results across river stretches becomes biased. For this reason, the lengths are mostly shorter than 1000 metres, only 6 of the 3187 stretches are longer. Finally, the data set has to be provided in geographic projection. The river network together with the water reservoirs and discharge as well as monitoring sites of the 1993 campaign conducted by Henkel KGaA are shown in Figure 5.1.

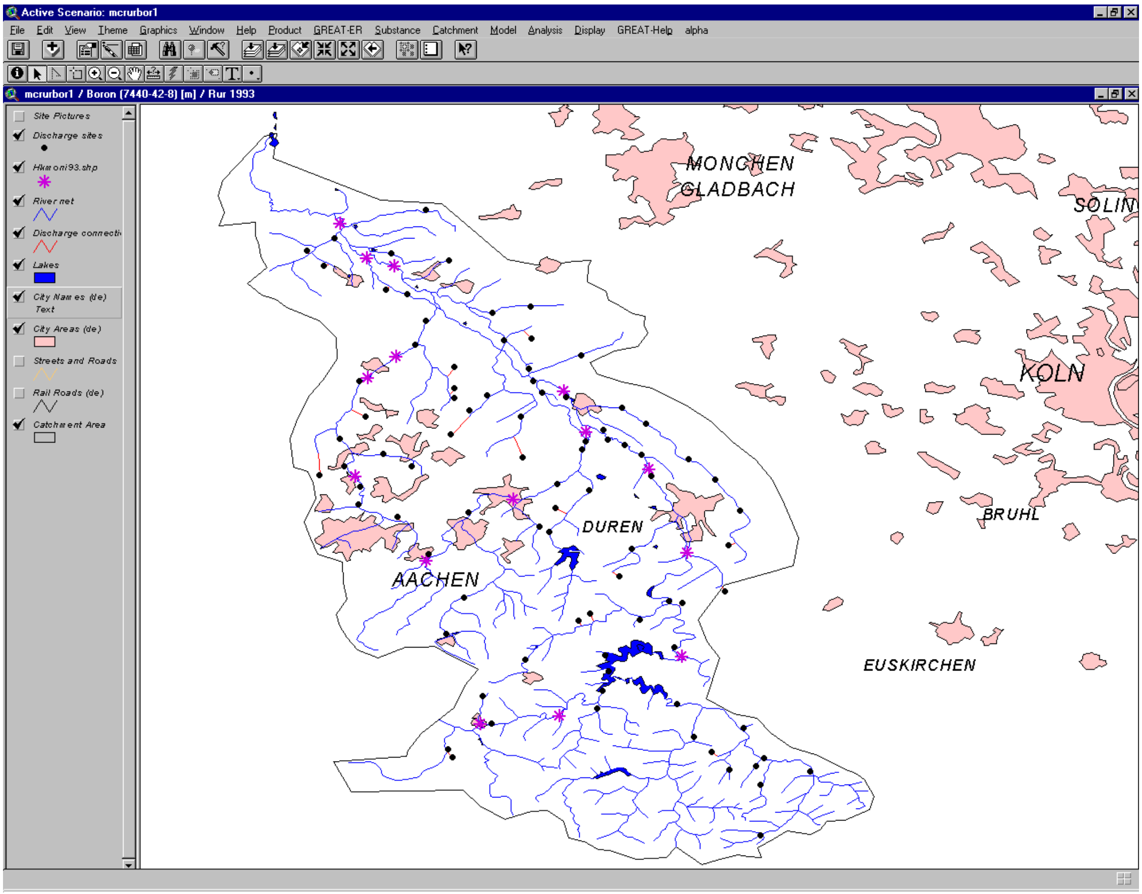

Figure 5.1.: **The Rur river network.** The river stretches, water reservoirs (polygons), discharge (points) and monitoring sites (stars) in the GREAT-ER 1.0 environment. Data source: UMPLIS-Umweltbundesamt.

5.3.2. River attributes

For each river stretch GREAT-ER requires flow distributions, lengths in metres and flow velocities. The water depths are only needed, if the elimination processes volatilisation and sedimentation are to be modelled explicitly. This is not the case for GREAT-ER mode 1 calculations being performed in the Rur catchment.

Flow

Flow data are the most important river attributes. GREAT-ER assumes the annual distribution of the mean daily water flows at a site to be log-normally distributed. Under this assumption, the hydrological situation in a stretch can be described by the mean and the 95$^{\text{th}}$ percentile low flow, i.e. the flow that is exceeded for 95% of the days. Therefore, these two values, in the remainder referred to as Q_m and Q_5, must be given for each stretch. However, in general measured flow statistics are only available at the gauging stations. Hence, flow statistics at ungauged sites need to be calculated using appropriate models. For the Rur catchment, a model has been developed for this purpose, which is explained in section 5.4.

Flow data at the gauging stations are provided by two sources, namely the WVER and the regional section of the LUA, the *'Staatliches Umweltamt'* (StUA) Aachen. From these sources, both mean daily flow data for some gauging stations and aggregated long-term statistical main values for all gauging stations, among them the necessary Q_m and Q_5, and the corresponding water depths are obtained. These statistical data are based on samplings over differing lengths of time, i.e. between 25 and 50 years.

Stretch lengths

The lengths can be derived from the digital river network data set. This introduces an error, the magnitude of which depends on the level of detail of the river data set. To quantify this error, the lengths derived from the river network have been compared to data from public authorities. Attribute data of the gauging station data provided by the LUA include the gauging station's distance to the mouth of the river in which it is located. Thus, for each of the main rivers Rur, Wurm, and Inde the distances between the upstream and the most downstream gauging stations can be calculated from these given data. The difference can be compared to distances between the two points on the basis of the river network.

Table 5.1.: **River lengths derived from GIS vs. data from public authorities**

River	From-gauging station	To-gauging station	Estimated from ... GIS	given data	Deviation (%)
Rur	Zerkall	Stah	65.21 km	68.97 km	5.45
Wurm	Kalkofen	Randerath	33.68 km	35.60 km	5.39
Inde	Kornelimünster	Kirchberg	27.45 km	29.56 km	7.14

For the Wurm river, the length derived from the river network is 5.39% shorter than the given value. Differences for the Inde and Rur rivers are 7.14% and 5.45% respectively (see Table 5.1). In the case of the Rur river, the most upstream gauging station below the water reservoirs is used. With respect to the limited influence of river lengths on the simulation results, which is due to the exponential decay function, this error is acceptable. Thus, river lengths as derived from the digital river network are used.

Flow velocity

Analogously, the mean and 95th percentile flow velocities are needed for each stretch. If no measured flow velocities are available, regression equations deriving flow velocities from flow data can be used, e.g. as proposed by the Institute of Hydrology (1995). There are alternatives that also consider other parameters, which have been analysed and compared by Klepper and den Hollander (1999). However, these regression equations were developed for specific catchments in specific areas and are not validated for other regions. Even more important is the fact that hydraulic constructions, such as water reservoirs in the Rur catchment, decrease the applicability of such approaches. For this reason, measured flow velocities are used whenever possible.

In the Rur catchment, flow velocity data are only available for the main river below the water reservoir Rurtalsperre. These were provided by the WVER. For these sections, measured mean and 95th percentile low flow velocities can directly be used, while for the other stretches velocity is estimated from flow, using the approach proposed by the Institute of Hydrology (1995). A comparison of measured and calculated flow velocities in the lower parts of the Rur river is given in Table 5.2.

Table 5.2.: **Measured vs. calculated flow velocities in the lower courses of the Rur**

Section	Measured mean velocity	Calculated mean velocity
Heimbach - Zerkall	1.46 m/s	0.51 m/s
Zerkall - Obermaubach	0.56 m/s	0.53 m/s
Obermaubach - Düren	1.51 m/s	0.54 m/s
Düren - border	1.01 m/s	0.63 m/s

The deviations between measured and estimated flow velocitites are rather large. However, the results suggest that by using the regression approach mainly underpredictions occur, leading to higher predicted residence times in the river stretches. On the contrary, the underestimated river lengths, given above, reduce residence time. Thus, the underestimated river length partly compensates the overestimated residence time.

5.3.3. Discharge site data

Concerning the discharge situation, GREAT-ER needs information about the connected population, industrial equivalents, the mean waste water flow, i.e. the water quantity per time emitted, the type of wastewater treatment, and optionally the separation of the flow into domestic, industrial and runoff parts. For the Rur catchment, these data have been provided by the LUA and the WVER separately for each year since 1993. In the Rur catchment, all discharge sites are of the activated sludge type (WVER, 2000).

An investigation of the data revealed that the number of discharge sites decreased from 1993 to 2000, which is due to current and past activities of the WVER, which is closing smaller and less efficient WWTPs. These activities are further described in the annual reports (WVER, 1996). Hence, two data sets have been developed. One data set reflects the situation in 1993, while the other reflects the situation in 2000.

5.3.4. Monitoring data

Monitoring data from three different sources are available, two of which could be used for evaluating the model's accuracy. In 1993, Henkel KGaA conducted a monitoring programme aimed at the determination of steady-state concentrations for LAS, boron, and orthophosphate concentrations in the Rur river and its main tributaries. Data from 15 sampling sites were collected (Schröder, 1995b). These locations are shown in Figure 5.1. From 1993 to 1995, Henkel carried out a second monitoring programme in the Rur catchment (Schröder, 1995a). The purpose of this monitoring campaign was the determination of instream removal rates for selected anionic surfactants below the discharges of the two municipal wastewater treatment plants Monschau and Düren WWTP. Since in this second monitoring programme data were only collected in river stretches below these discharges, they are not used for comparison with the simulation results.

The LUA performs different long-term monitoring programmes, the main results of which are regularly published in the water quality reports (Landesumweltamt Nordrhein-Westfalen, 1997). On request, monitoring data for about 150 parameters from 1990 onwards, comprising biological, physical, and chemical water quality parameters as well as different single substances and sum parameters for anthropogenic substances, e.g. surfactants or adsorbed organic halogens, could be obtained in digital format. These data have been introduced into the GREAT-ER system. However, both the number of sites and the number of samples per site vary considerably between the substances. For example, pesticides are only measured a very few times, whereas standard parameters such as TOC or BOD are measured regularly[2]. In this thesis, monitoring data for EDTA, NTA, and boron were used.

In addition, the WVER conducts a water quality monitoring programme, which is much smaller regarding size and amount of data than the LUA programme. In this programme, about 30 parameters at 17 sites are measured between two and four times a year. As these are mainly metals and sum parameters, the data were not applicable for evaluating the accuracy of GREAT-ER.

[2]Therefore, Avenue scripts have been developed for easier visualisation in the GREAT-ER software.

5.3.5. Additional background data

Additional background maps can provide an insight into the study area for those who are not familiar with the region. For the Rur catchment, site pictures taken at the monitoring stations as well as a map of the water reservoirs are available (see Figure 5.1). Also, as for all GREAT-ER catchments, the freely available Digital Chart of the World data were included in the Rur catchment data.

In addition, the water quality data mentioned above provide background information. All monitoring data have been incorporated into the GREAT-ER system. They can be directly loaded using the 'Additional background data' menu item.

5.3.6. Substance data

Substance data can be divided into the categories emission data, parameters determining fate behaviour, and effect data. The latter are not required for GREAT-ER calculations, but are used in the GREAT-ER product mode.

Actual emission data are necessary for risk assessment and also for the comparison of monitoring and model results. For detergent ingredients, emission data are published annually by the German manufacturers associations IKW and TEGEWA. The only river fate-related parameter required for GREAT-ER mode 1 calculations is an aggregated first-order instream removal rate, which represents all processes contributing to the substance's elimination from the water column. Further input parameters quantify percentual elimination efficiencies in the sewerage system and the sewage treatment plant.

5.3.7. Generation of a GREAT-ER data set

The different kinds of geographic information are kept in a well-defined format in the GIS, which is described in ECETOC (1999a). This format considers the topological relations between the different geographical objects such as river stretches and discharge sites. Since this format is quite complex and the data sets may be very large, scripts have been developed by Wagner (1999) to facilitate the generation of GREAT-ER data sets.

5.4. Hydrological modelling

The aim of hydrological modelling in this thesis is the derivation of Q_m and Q_5 values for each river stretch from the information given at the gauging stations. Different approaches have been proposed that vary from process-based models to easier empirical approaches. Aschwanden (1995) investigated several of these approaches with respect to conditions in Switzerland. As the flow regimes in Switzerland are uplands, the findings are not applicable to the Rur catchment, whose lower courses are situated in lowlands. However, the study provides a good overview of the field.

Complex hydrological models attempt to model all ongoing processes, which requires a large amount of data concerning land use, soil types, precipitation, and climatic data (e.g. the Soil Moisture Routing model, SMR, Frankenberger et al., 1999). Other models are based on a phenomenological black-box structure using a regression-type analysis (Dyck, 1980a,b). In the first case, the uncertainties of all the processes, e.g. the actual evapotranspiration, and the high detail of required data, e.g. digital elevation models and precise land use information, have to be considered, which typically leads to the calibration of the model using existing measured data from the gauging stations. Given the intention to integrate large European catchments into the system, full hydrological modelling is at present beyond the scope of the GREAT-ER system. Since currently only the flow data within the rivers are needed, it is also not necessary. For this reduced purpose, empirical or statistical approaches can be used[3].

The method developed in this thesis consists of two steps: a nonlinear regression followed by a local refinement. Theory and results obtained for the Rur catchment are given. It should be noted that, since the measured hydrological data used are based on long-term statistics, there is no need to derive different data sets for different years. For this reason, the same hydrological information is used in the 1993 and 2000 data sets.

5.4.1. Nonlinear regression

Both Rodriguez-Iturbe and Rinaldo (1997) and Dyck (1980b) give a general relationship between the flow at a location and the corresponding subcatchment size, which most often follows the equation

$$Q = c_1 \cdot A^{c_2}$$

where Q is the flow and A is the size of the subcatchment. Regarding mean flow, c_2 is typically between 0.5 and 1 (Aschwanden, 1995, p. 37), whereas Demuth (1993, p. 110) proposes a linear relationship between Q and A, i.e. $c_2 = 1$. Dyck (1980b) also gives a relationship between the accumulated river length at a location, $Accumulu$, and the corresponding subcatchment size A, following the equation

$$A = c_3 \cdot Accumulu^{c_4}$$

These two equations can be combined leading to

$$Q = c_5 \cdot Accumu^{c_6}$$

with $c_5 = c_1 \cdot c_3^{c_2}$ and $c_6 = c_4 \cdot c_2$. The advantage of using the accumulated river length instead of the subcatchment size directly is the fact that the sizes of the subcatchments are only known at the gauged sites and not at the ungauged sites, whereas the accumulated river lengths can be calculated for all river stretches without further input data from the

[3] The difference between empirical and statistical approaches is explained by Demuth (1993).

river network. Deriving subcatchments for any stretch is typically based on a digital elevation model, which was not available for the Rur catchment in a sufficient resolution.

Relationship between accumulated river length and subcatchment area

The hypothesis of the relationship between accumulated river length and subcatchment size was tested for the gauging stations in the Rur catchment. In Figure 5.2 this relationship is plotted. The regression equation is $A = 1.662 \cdot Accumu^{1.0414}$, with $r^2 = 0.983$. The regression was performed using the software SPSS$^{\mathrm{TM}}$ (SPSS Inc.).

In the Rur catchment some artifical channels exist in which gauging stations are operating. In this plot, these gauging stations have been omitted, since in general these do not have a catchment area. A similar plot can be derived for the well-established relationship between subcatchment area and flow.

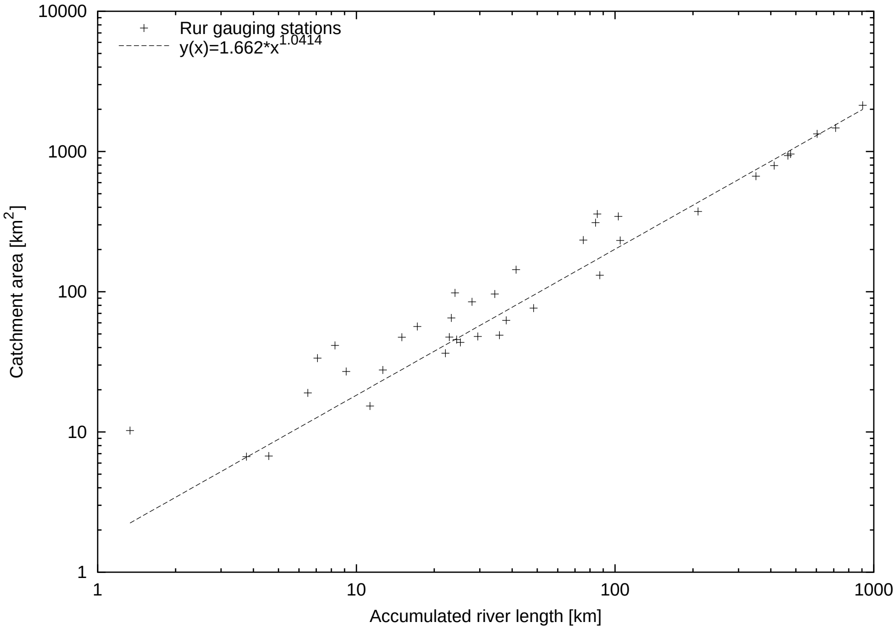

Figure 5.2.: **Relationship between accumulated river length and subcatchment size**

Application of the regression in the Rur catchment

In order to perform the regression, each gauging station was assigned to a river stretch, since the GREAT-ER model is based on information on a river stretch basis. Then, the accumulated river length was calculated for each river stretch using standard GIS methods, thus establishing the relationship between gauging station data and the accumulated river length. After this preparation, the nonlinear regression was conducted. The regression was done twice to determine relationships for the two required values, Q_m and Q_5. Following the regressions, the derived equations were applied to all river stretches, thus giving a consistent preliminary flow profile containing Q_m, and Q_5 for all river stretches in the catchment.

It should be noted that Demuth (1993, p. 111) states that this approach can primarily be applied for deriving mean flows. Concerning the more extreme low and high flow relationships he states that such an approach may be applied, but that deviations may occur. Verdonck et al. (1999) applied this approach in the Rupel catchment (Belgium). However, studies judging the goodness of this application are not yet available.

The nonlinear regression was performed following the equation from above and using the Levenberg-Marquart algorithm, leading to:

$$Q_m = 0.000116 \cdot Accumu^{0.8884}$$

$$Q_5 = 5.565 \cdot 10^{-7} \cdot Accumu^{1.2311}$$

In this analysis, $Accumu$ was given in metres, whereas the flows are calculated in m^3/s. The fact that the exponent for the second equation is greater than 1 while it is smaller than 1 for Q_m was observed in other catchments as well, e.g. in the Ruhr and Lahn catchments in Germany (unpublished) and in the Rupel catchment in Belgium (Verdonck et al., 1999). This outcome suggests that flow distributions are more dense downstream. In the case of the Rur this is not surprising since due to the huge water reservoirs and the controlling of the water flow by the WVER, flows in the downstream parts are less variable. r^2 was 0.98 for both equations. The mean of the square residues are 0.587 m^3/s for the Q_m and 0.182 m^3/s for the Q_5 equation.

5.4.2. Local refinement

Limitations of this simple approach are obvious. Deviations may occur due to natural variations such as rainfall, soil type, or vegetation, as well as due to anthropogenically influenced disturbances of natural water flows, such as land use and hydraulic constructions. Especially the latter factor makes accurate flow predictions based on physical models very difficult, as such site-specific deviations from natural conditions would have to be included in a process-based model.

The goodness of the regression may be judged by comparing calculated and measured Q_m and Q_5 values at the gauging stations. These deviations, expressed as a ratio between calculated and measured flows, are called local adjustment factors (LAF) and are plotted in Figure 5.3 against the accumulated river length.

The plots show that in the lower courses deviations are generally small, whereas in the upper courses larger deviations occur. This shows that the regression gives better results in the more downstream section. It implies that in the catchment areas near gauging stations with an LAF far away from 1, the need for local adjustment is higher. From the plots it may therefore be concluded that when only intending to perform GREAT-ER calculations in the lower courses, the regression alone may be sufficient, but if intending to perform simulations in the entire catchment and therefore also in smaller subcatchments, as it is the case here, the regression is insufficient. The local refinement procedure, which performs an adjustment of the results given by the regression, was developed for this reason. The local refinement procedure has been implemented using the GAWK scripting language, due to which it could be integrated into the existing GREAT-ER preprocessing routines developed by Wagner (1999).

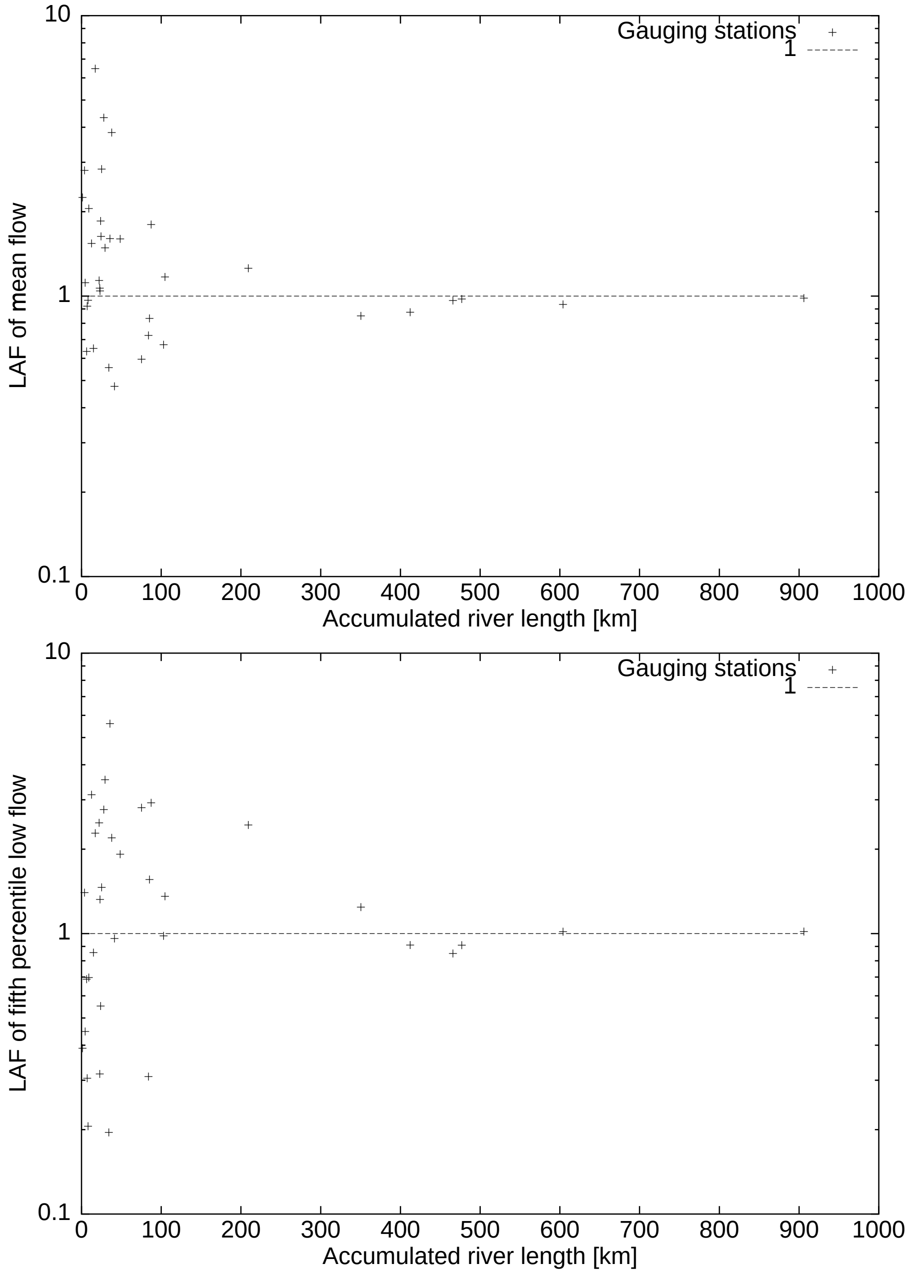

Figure 5.3.: **Local adjustment factors for Q_m and Q_5** as functions of the catchment area. The y-axis is logarithmic to better demonstrate deviations from LAF = 1, which indicates an agreement between measured and calculated values.

Calculation and application of local adjustment factors

The discrepancy between estimated and measured flow at each gauging station for both Q_m and Q_5 can be quantified as a ratio of estimated and observed flow, which are the LAFs determined for both Q_m and Q_5.

$$LAF_{\mathrm{m}}(GID) = Q_{\mathrm{m,regr}}(GID)/Q_{\mathrm{m,meas}}(GID)$$

$$LAF_5(GID) = Q_{5,\mathrm{regr}}(GID)/Q_{5,\mathrm{meas}}(GID)$$

where GID is the gauging station's ID. These LAFs are now assumed as also being representative for the ungauged river stretches near this station. Thus, in a second step the regression-estimated mean and low flows in ungauged river stretches are adjusted by stretch-specific local adjustment factors ($LAF_{\mathrm{m,5}}$(SID)), which are based on the nearest gauging stations' LAFs.

Nearest gauging stations of a stretch are defined as the next gauging station in downstream and in upstream direction. From these two values, the LAF for an ungauged stretch is derived. If a stretch has only one nearest gauging station, which usually occurs at the sources and near the mouth, then the LAF at the ungauged site equals that at the nearest gauging station. Therefore, if only one nearest gauging station exists, adjusted flows are calculated as follows

$$Q_{\mathrm{m,adj}}(SID) = Q_{\mathrm{m,regr}}(SID)/LAF_{\mathrm{m}}(nGID)$$
$$Q_{5,\mathrm{adj}}(SID) = Q_{5,\mathrm{regr}}(SID)/LAF_5(nGID)$$

where SID depicts the stretch ID and nGID is the nearest GID.

If a river stretch has nearest gauging stations up- and downstream, their influence is weighted by the inverse-distance method, i.e. the shorter the path from the actual river stretch along the river network to a gauging station, the more important the gauging station is considered to be. This is done by first calculating adjusted flows according to both gauging stations and then deriving the final flow by taking the inverse-distance-weighted mean of these two flows. Again, this is executed for Q_m and Q_5 separately, i.e.

$$Q_{\mathrm{m,adj}}(SID) = \frac{d_d}{d_d + d_u} \cdot \frac{Q_{\mathrm{m,regr}}(SID)}{LAF_{\mathrm{m}}(nGIDu)} + \frac{d_u}{d_d + d_u} \cdot \frac{Q_{\mathrm{m,regr}}(SID)}{LAF_{\mathrm{m}}(nGIDd)}$$

$$Q_{5,\mathrm{adj}}(SID) = \frac{d_d}{d_d + d_u} \cdot \frac{Q_{5,\mathrm{regr}}(SID)}{LAF_5(nGIDu)} + \frac{d_u}{d_d + d_u} \cdot \frac{Q_{5,\mathrm{regr}}(SID)}{LAF_5(nGIDd)}$$

d_d and d_u depict the distance from the start of a stretch to the nearest downstream and upstream gauging stations respectively. Analogously, nGIDu and nGIDd are the IDs of the respective gauging stations.

Processing of confluences and bifurcations

Finding the nearest gauging station is not always trivial, since complex situations, as for example given in Figure 5.4, need to be processed. In the case of the absence of bifurcations, the nearest downstream gauging station can directly be found by tracing down the river network. If bifurcations exist, the nearest gauging stations in both wings are searched for by starting at the bifurcation stretch and tracing down in both wings. From these two gauging stations, distance-weighted LAF_m and LAF_5 values for a new virtual gauging station located at the bifurcation stretch are calculated. The bifurcation is then considered as the nearest gauging station. The length of the path from the actual stretch to the bifurcation is used as the distance.

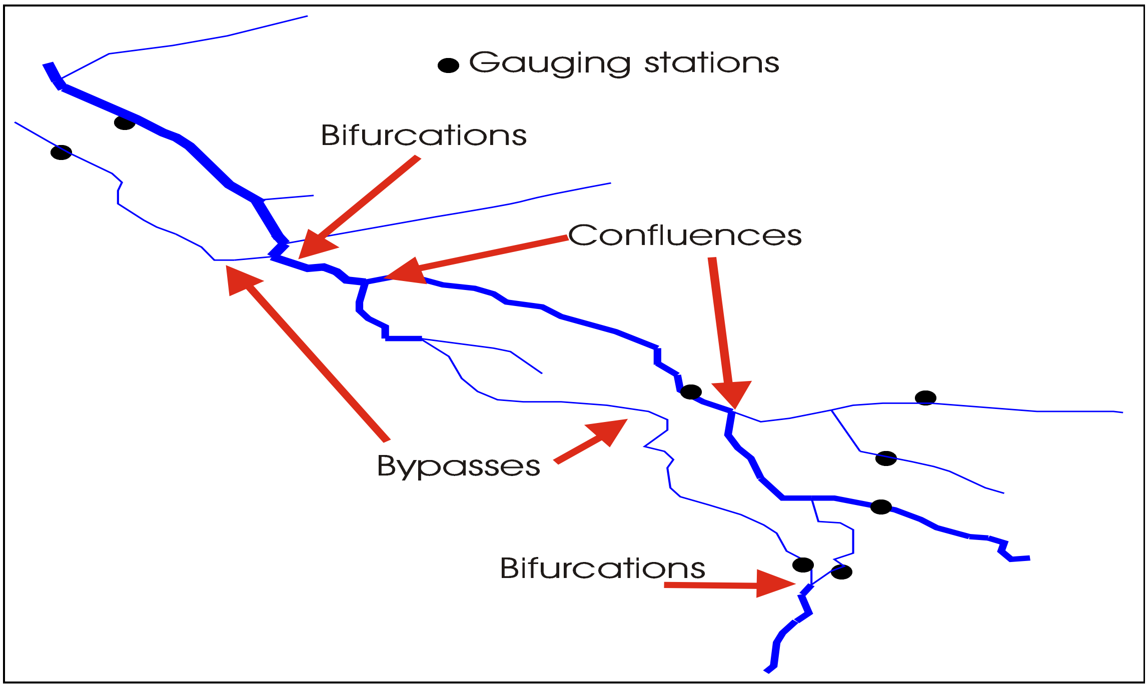

Figure 5.4.: **Complex topological situation**

A similar method is applied to find the nearest upstream gauging station. Instead of bifurcations, confluences need to be solved. These occur much more often than bifurcations. Therefore, a slightly different strategy is used to find the nearest upstream gauging station of each river stretch, which increases the speed of the algorithm.

Firstly, for each gauging station all downstream confluences are searched for. This downstream search stops when the next gauging station in the downstream direction is found. Within this step, the information about the nearest upstream gauging station is stored for each confluence. Thus, afterwards the nearest upstream gauging station and its distance are known for each confluence. With this information, the nearest upstream gauging station and its distance can be calculated for each stretch, since in such a search either a next gauging station or a next confluence is found. The quality of the results is further improved by some plausibility checks and manual improvements, which can be done by defining further virtual gauging stations.

Consideration of discharges

The LAF considers all deviations between measured and regression-estimated flows occurring at the gauging stations, regardless of whether they are of natural or anthropogenic origin. Therefore, discharges from WWTPs are included only implicitly, but not explicitly.

For large plants with only a small stream dilution factor (SDF, Feijtel et al., 2000), which is defined as the ratio of mean effluent flow divided by the mean flow of the receiving stretch, this may lead to unrealistic results in the stretches directly above and below these discharges, which in fact occurred for some plants.

To solve this problem, the SDFs have been calculated for all WWTPs. If an SDF is smaller than 10, the mean discharge flow of that plant is considered as not being negligible. In such a case, virtual gauging stations have been defined in the receiving stretch as well as in the stretch directly upstream of the discharge. The difference in the flows at the stations equals the mean effluent flow of the discharge site. Due to this construction, the difference in water flow up- and downstream of the discharge is appropriately considered.

5.4.3. Results obtained in the Rur catchment

In Figure 5.5, the Q_m and Q_5 flow profiles of the main river are given together with the gauging station's data. The Rur river was chosen as an example; analogous plots have been obtained for the other rivers. It can be seen that at the gauging stations, observed and measured flows are identical, which follows directly from the construction. In the other stretches, the flow profile gives a consistent picture. In addition, realistic flow increases due to confluences can be identified.

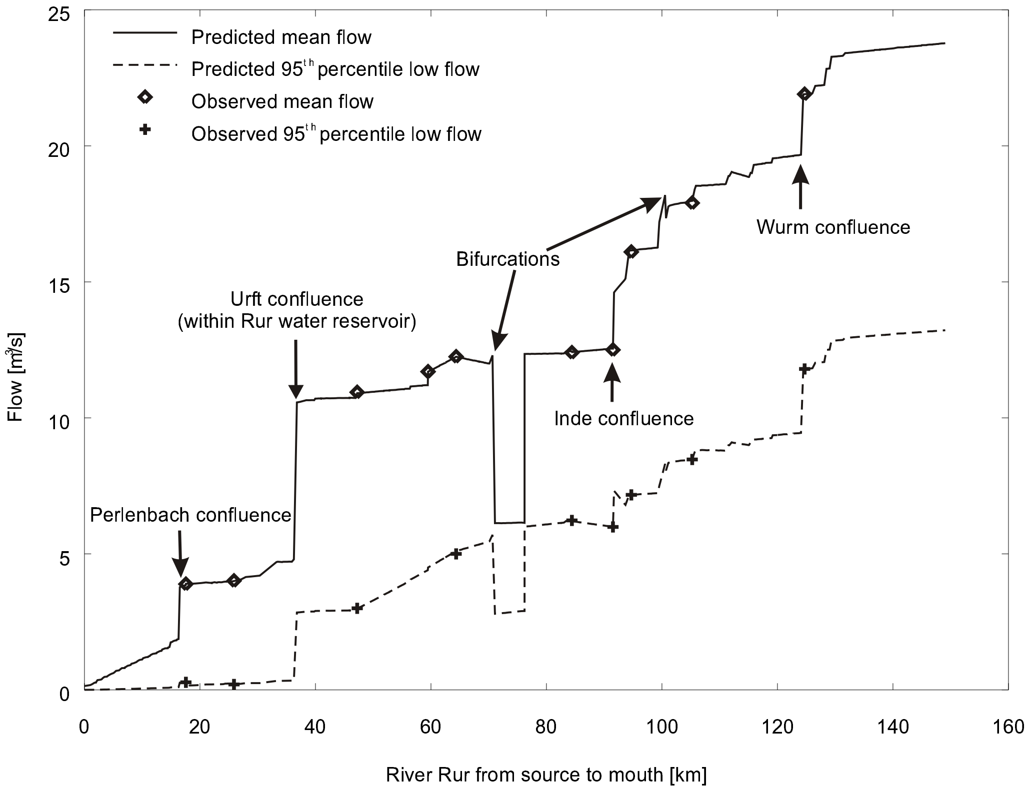

Figure 5.5.: **Calculated and observed flow profile in Rur catchment**

5.4.4. Discussion of methodology

Hydrological modelling in the context of the GREAT-ER model aims at deriving values which describe the annual flow variability in a river stretch under the assumption that these are log-normally distributed. An understanding of hydrological processes is not the aim of this modelling. Therefore, process-based models may be replaced by empirical ones, which may be extended by GIS techniques to account for local to regional variations.

The proposed methodology applies the relationship of catchment area and flow as a basis. From this starting point, improved predicted flows are derived by considering local variations given as a deviation of observed and estimated flow. Due to this and the consideration of discharges, this approach uses all existing information for deriving flow data.

The goodness of this approach depends on the density of the gauging stations. The more gauging stations exist, the better the results are expected to be. Deviations from measured flow statistics cannot be calculated, since at the gauged stretches the calculated flows equal the measured ones, due to this construction. A further check of the hydrological data, apart from plots such as the one given in Figure 5.5 may be done with the help of boron simulations. Due to its conservative fate behaviour, boron may be used to judge the consistency of the hydrological data. This was shown in section 2.3 using the Itter catchment as an example.

There is one aspect omitted compared to existing hydrological models such as MICROLOWFLOWS (Institute of Hydrology, 1995): Water abstractions are not explicitly considered. However, comparisons of measured flows at the gauging stations indicate that water abstractions do exist. Nevertheless, it was decided not to consider water abstractions explicitly, since the hydrological data derived from this model are to be used within the GREAT-ER model. Because the current data structure in GREAT-ER does not allow for an adequate consideration of water abstractions within the fate modelling of substances, their explicit consideration in the hydrological modelling does not improve the hydrological information used in the GREAT-ER model. This is explained in the following reasoning.

If in GREAT-ER the flow decreases at a transition from one stretch to another due to water abstraction, the concentration of a simulated substance, assuming an inert compound, would increase due to the mass balance performed at the start of the stretch. This is of course unrealistic, since drawing off water also eliminates a fraction of the substance load from the river, i.e. the concentration would remain constant. This GREAT-ER-inherent problem cannot be solved within the current data and model structure. Accounting for this process would require simultaneous modelling of the hydrology and the environmental fate of the active substance, thus implying a reconstruction of the core GREAT-ER model. Regarding the intended application of the model, which was originally environmental risk assessment of chemicals, and which in this thesis is a comparative assessment of detergents, not considering water abstractions does not lead to model restrictions.

6. GREAT-ER simulations in the Rur catchment

In order to judge the goodness of the incorporation of the Rur data sets into the GREAT-ER system, simulation results are compared to existing monitoring data from 1993. The conformity of measurements and predicted concentrations is called accuracy. In addition, in May 2000 a further monitoring programme was conducted, the results of which were used to judge the accuracy of simulations applying the Rur 2000 data set. The second purpose of this monitoring programme is to calibrate catchment-specific substance input parameters for the monitored detergent ingredients. The substances used in the 1993 simulations were again monitored, but also further detergent ingredients were included in the monitoring campaign.

In this chapter, first the accuracy of GREAT-ER predictions is judged on the basis of the 1993 catchment and monitoring data sets. Then, the 2000 monitoring programme is briefly described. Further simulation results are then presented that correspond to the year 2000 data set. Finally, conclusions are drawn. The comparison is made by comparing mean simulation results with the mean values of the monitoring data, whose spans of values are also plotted.

6.1. Results applying the 1993 data set

6.1.1. Number of Monte-Carlo shots

Another input parameter of GREAT-ER is the number of Monte-Carlo shots. Statistical theory claims that the statistical error of the probability distribution function decreases with an increasing number of shots. In addition, an increasing statistical error can be expected with an increasing number of distributed input parameters, due to the propagation of variance. Therefore, prior to performing simulations, an appropriate number of Monte Carlo shots has to be chosen.

In order to determine a reasonable number of shots, test simulations with different numbers of Monte Carlo shots are carried out and both mean and 90th percentile concentrations in all stretches are compared. In Figure 6.1, boron and LAS simulation results in the river Rur are shown. In the case of boron, only the catchment parameters were distributed, while in the LAS scenario, the in-stream removal rate (uniform between 0.03 and 0.35 per hour), the sewerage system elimination (uniform between 15 and 35%) as well as the two WWTP efficiencies for the primary settler (uniform between 10 to 20%) and the activated sludge tanks (uniform between 96 and 98%) are distributed. Thus, these two scenarios reflect extrema concerning the number of distributed parameters.

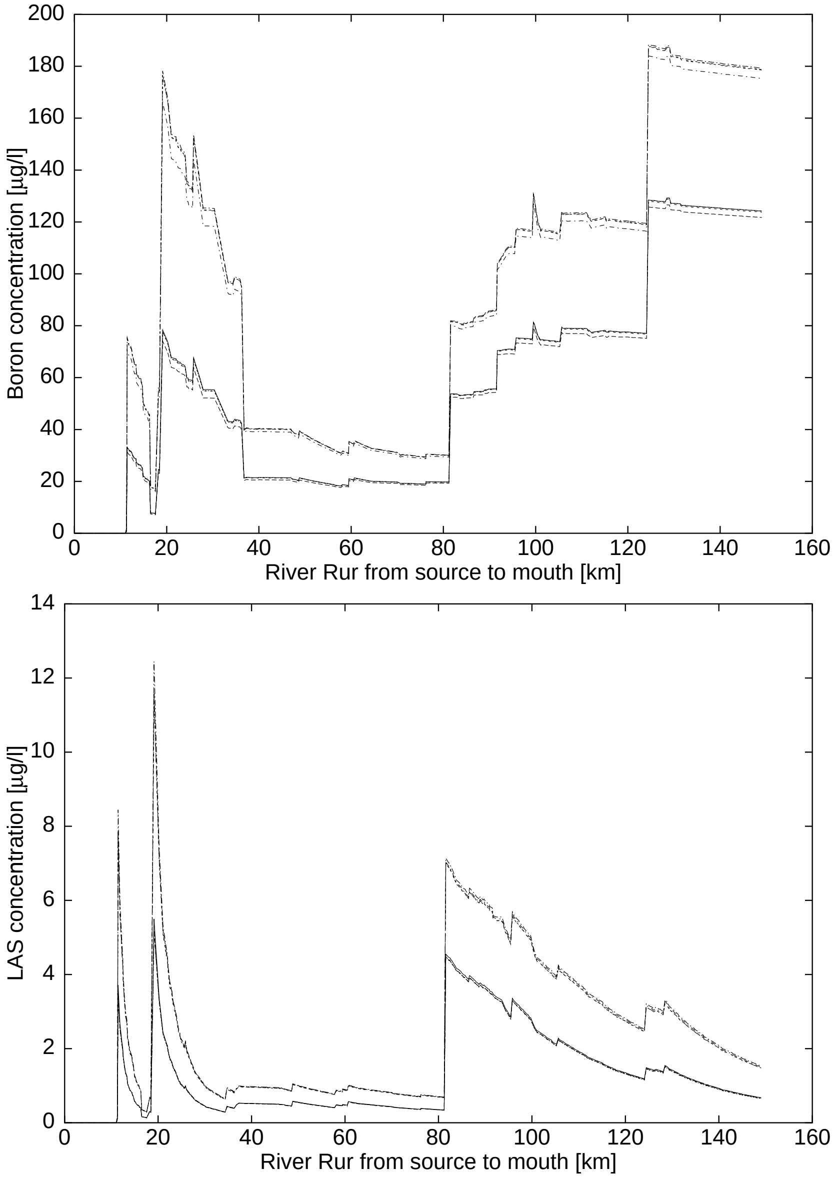

Figure 6.1.: **GREAT-ER results for different numbers of Monte-Carlo shots in the Rur river (boron and LAS).** Results are given for 1000, 2000, 5000, and 10,000 shots. The upper sequences of functions show the 90th percentiles, whereas the lower show the mean results.

In the case of boron, small differences in the results can be found. Facing other model uncertainties, e.g. regarding emission estimates, these are considered to be of only minor importance. Thus, a choice of 2000 Monte Carlo shots per simulation seems to be justified in the case of boron. In the case of a degradable substance such as LAS, for which all input parameters except the per-capita consumption are distributed, the variation of results is even smaller. This unexpected result is most likely due to in-stream removal, which lowers variations due to the exponential decay function. Equal results were derived for the other rivers in the Rur catchment.

Concluding, 2000 Monte Carlo simulations are sufficient for both substances. This value is therefore used in the remainder of this thesis.

6.1.2. Boron

In order to determine the quality of the catchment's integration into the GREAT-ER system, a substance that is not subject to transformation processes is best suited. As it was shown in section 2.3.3, this is the case for boron, which is used in detergents in the form of sodium perborate tetrahydrate as a bleaching agent (see sections 2.3.3 and 4.5). The only factors determining riverine boron concentrations are emission, dilution in the different stretches, and the geogenic background concentration.

Background concentration

Geogenic boron levels in the environment vary to a considerable degree. Metzner et al. (1999) report results from different countries, in which geogenic concentrations are below 0.1 mg/l, 0.1 to 0.3 mg/l, smaller than 0.02 mg/l or even 15.2 mg/l (Chile). For Germany, typical values of 0.01 to 0.05 mg/l are reported. In the Itter, 0.055 mg/l were measured and successfully applied in GREAT-ER simulations, see section 2.3.

For the Rur catchment, there are two ways in which to determine a background concentration. The fastest way is to directly use mean concentrations measured in the headwaters of the Rur catchment. A second method is to calculate the deviations between simulated and measured values by assuming a zero background concentration for all sampling sites. These differences can then be minimised to derive a background concentration. However, the second procedure requires that all anthropogenic sources are considered, which is most probably not the case, since not all emission sources are known and published. For this reason, the first method is used to determine the background concentration.

There are three sampling sites in stretches of the Rur catchment that are more or less free from anthropogenic impacts. Mean concentrations at these sites range from 0.026 to 0.11 mg/l. Since in GREAT-ER one background value for the entire catchment has to be entered, the mean value of 70 μg/l is used.

Simulation without additional input

As outlined above, 2000 Monte-Carlo shots were chosen. Boron consumption in detergents and cleaning agents for 1993 according to IKW (1994, 0.0893 kg per capita and year) is used as a basis. This originates from the use of 97,865 tons of sodium perborate tetrahydrate in these applications. The transformation is based on the fact that 7% of sodium perborate tetrahydrate is boron (Raymond and Butterwick, 1992). Since almost all samples were taken in the three rivers Rur, Wurm, and Inde, simulation results from these rivers are given. The mean of the simulated concentrations, together with all available monitoring data from 1993 are shown in Figures 6.2 and 6.3.

The first simulation shows that the agreement between measured and simulated mean concentrations is approximately a factor of 2. Therefore, the aim of GREAT-ER, i.e. a factor of 3 (Feijtel et al., 1997), is fulfilled for boron using national consumption data. In the Inde river, no general trend regarding over- or underpredictions can be observed. In the lower courses of the Wurm and Rur rivers, however, concentrations are mainly underpredicted. The most obvious reason for this is additional input from industry.

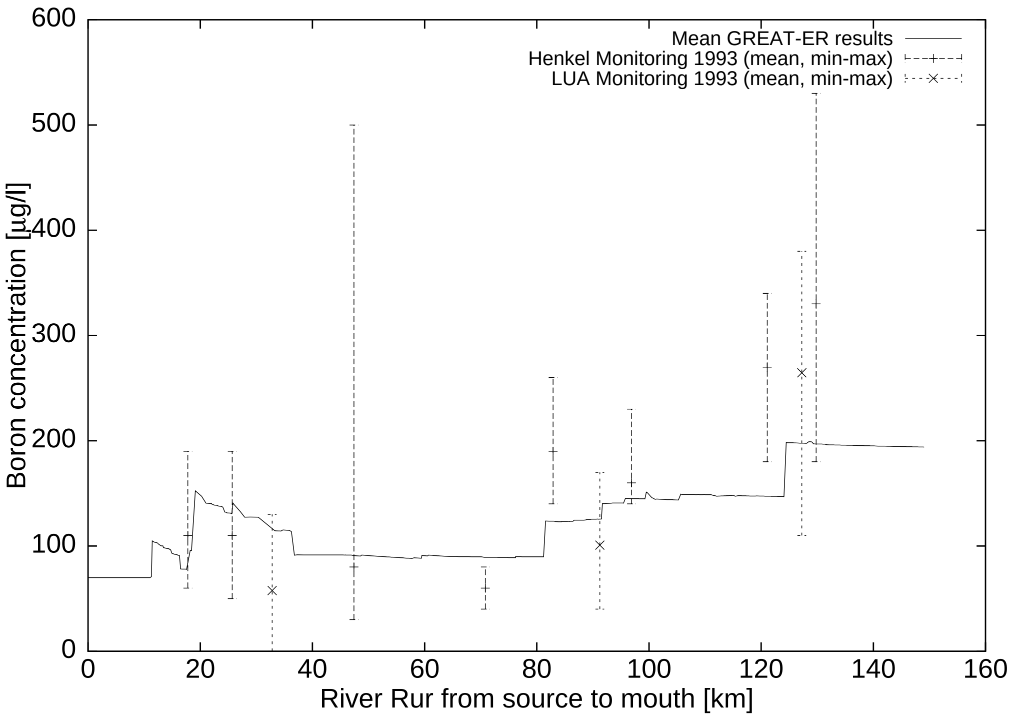

Figure 6.2.: **GREAT-ER results for boron vs. measurements (Rur river, 1993 data).** Emission is based on detergent consumption data.

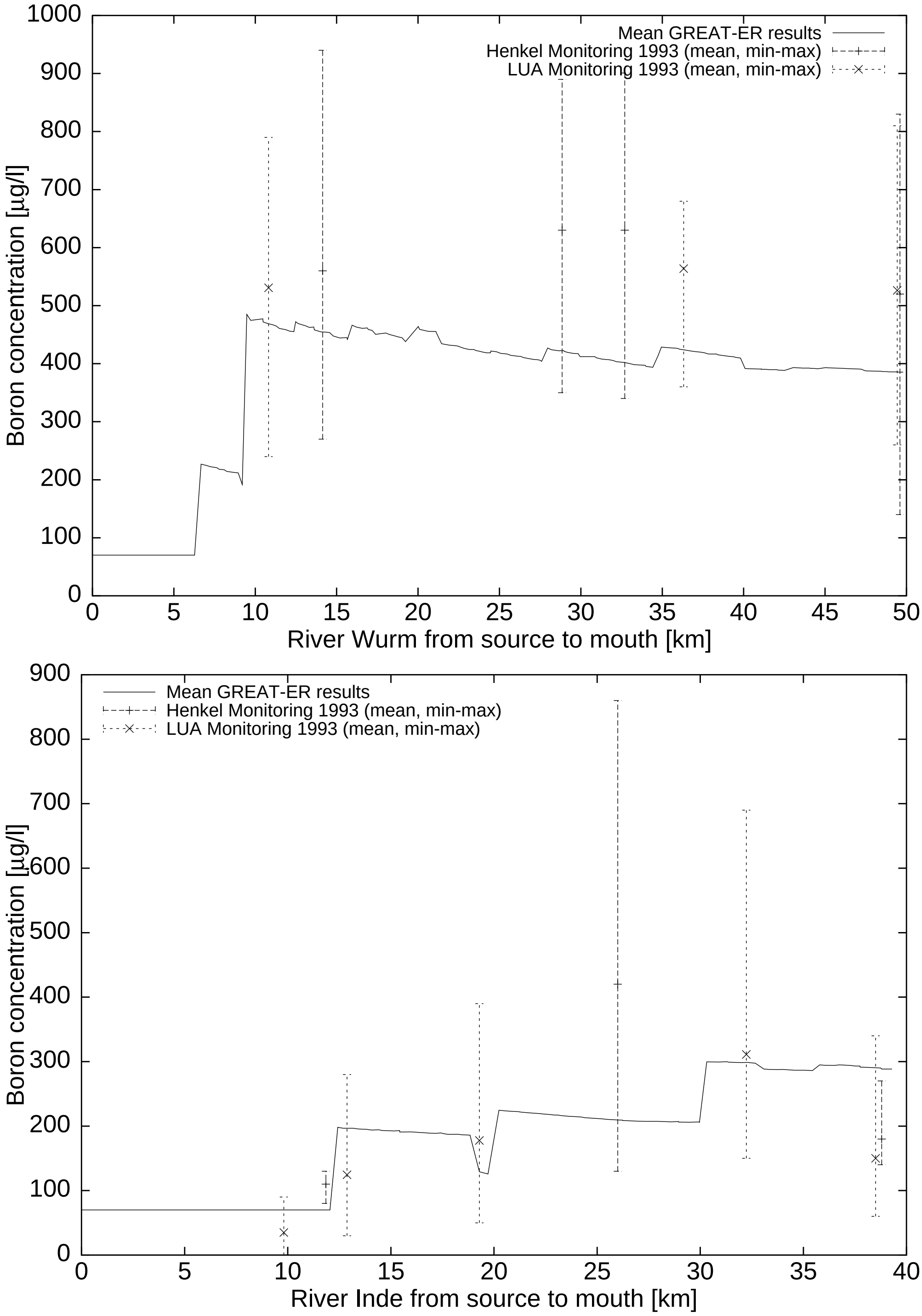

Figure 6.3.: **GREAT-ER results for boron vs. measurements (Wurm and Inde rivers, 1993 data).** Emission is based on detergent consumption data.

Simulation considering additional input

Since underpredictions occurred in the lower courses of the Rur and Wurm rivers, additional industrial emission sources were investigated. Two discharges that are potentially relevant for boron were identified. An indirect discharge into the Wurm river from photochemical industries occurs via Herzogenrath WWTP. Via Linnich WWTP an indirect discharge from the paper industry exists into the river Rur. Both branches are known sources of boron emissions (Metzner et al., 1999). However, actual boron loads for 1993 could not be determined. Therefore, two scenarios are calculated assuming additional boron discharge at these two plants, the loads of which were derived on the basis of the deviation between monitoring and simulation. In the first scenario, an additional input in the Wurm river is assumed, occurring at Herzogenrath WWTP. An annual boron discharge of 20 tons was determined by performing a mass balance at the next downstream sampling site. Figure 6.4 shows mean simulation results and the monitoring data.

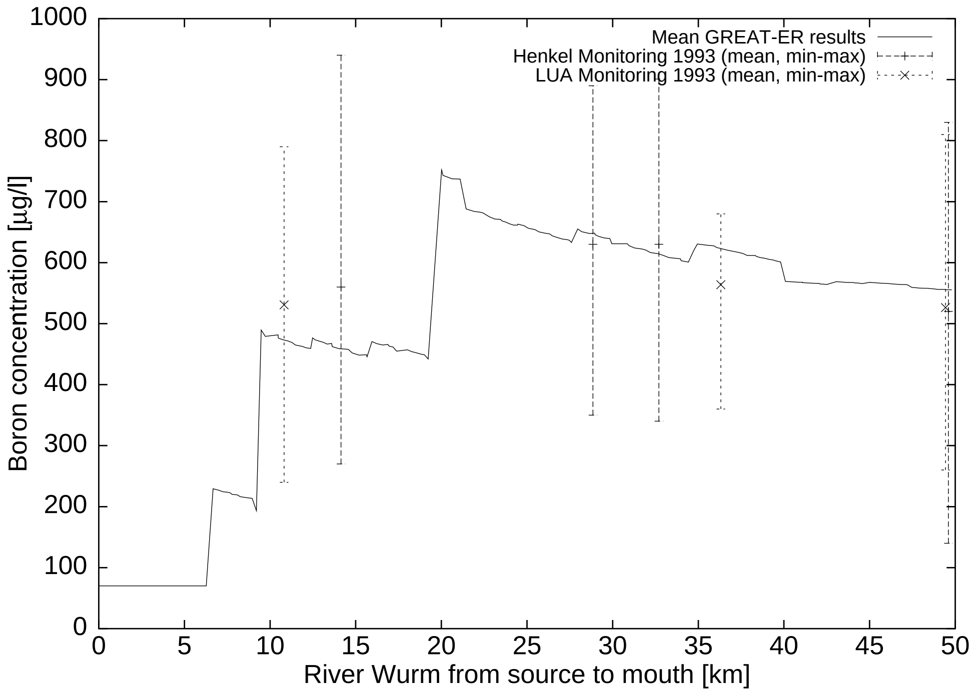

Figure 6.4.: **GREAT-ER results for boron vs. measurements (Wurm river, 1993 data).** Additional discharge of 20 t/a at Herzogenrath WWTP (near 20 km) was assumed.

Assuming an additional input at Herzogenrath WWTP, mean simulation results in the Wurm river are very close to the monitoring data. In the second scenario, an additional discharge into the Rur river is also considered, occurring with a quantity of 70 tons per year at Linnich WWTP. The results are shown in Figure 6.5. It can be seen that by assuming these two additional inputs, mean GREAT-ER results in the Rur river are close to the mean values of the monitoring data.

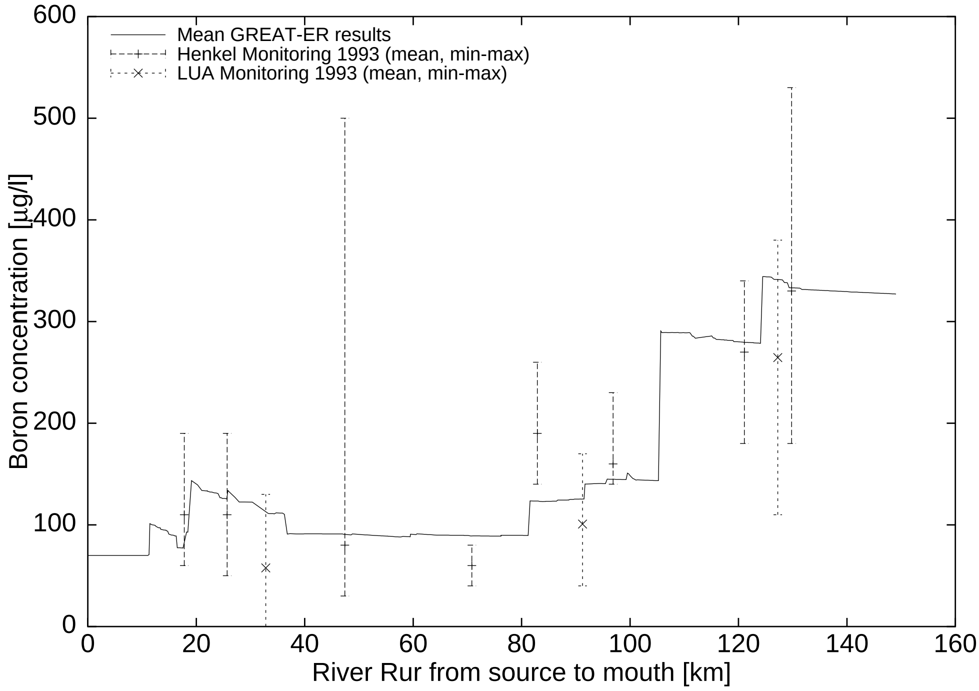

Figure 6.5.: **GREAT-ER results for boron vs. measurements (Rur river, 1993 data).** A second additional discharge of 70 t/a at Linnich WWTP (near 105 km) was assumed.

6.1.3. LAS

Another compound which could be compared to monitoring data is the anionic surfactant LAS. In contrast to boron, it is degradable and adsorbs to surfaces, i.e. sedimentation is a relevant process. Consequently, it also undergoes elimination processes in the sewerage system and in wastewater treatment plants. Different in-stream removal rates and wastewater treatment elimination efficiencies have been published to date, among others by Berna et al. (1989), Schröder (1995a), AISE/CESIO (1996), Schöberl (1996), Holt et al. (1998), Schröder and Reichensperger (1998), and Schröder et al. (1999), see also the Itter study (section 2.3).

In general, no geogenic LAS background concentration is expected. However, experiences from the Itter catchment revealed that also in headwaters of the Itter, which can be regarded as free from point sources, LAS concentrations of 5 μg/l were repeatedly measured. The same was observed in all other monitoring campaigns that were part of the first GREAT-ER phase, see the monitoring data on the GREAT-ER CD (ECETOC, 2000). LAS was also detected in the headwaters of the Rur catchment. Based on these findings, a background concentration of 3 μg/l is used for the LAS calculations, which is the mean of measured LAS concentrations in upper courses of the river Inde upstream from known discharge sites. The potential sources of these LAS loads are not known.

Calculation with default data sets

In section 2.3, two substance data sets were used and compared in the Itter catchment, called the ECETOC and Itter data sets. They are also applied in this catchment to investigate whether substance data sets can be transferred between different catchments.

Both data sets assume a sewer removal efficiency of 25% and an activated sludge plant efficiency of 98%, which gives a total elimination of 98.5% before entering the surface water. The ECETOC data set considers an in-stream removal rate of 0.06 per hour, which translates into a half-life of 12 hours, while the Itter data set considers a uniform distributed in-stream removal rate of between 0.03 and 0.35 per hour, which correspond to half-lifes of 24 and 2 hours respectively. Results obtained using the German LAS consumption data for 1993 (0.5757 kg per capita and year, IKW, 1994) and applying both data sets are shown in Figure 6.6.

As for boron, the 'factor of three' criterion is achieved. Moreover, at all sampling sites the simulation results lie in the range of the measured values. However, a general underprediction of the mean concentrations can be observed in the Rur river, while in the Wurm river the discharge at Aachen-Soers (near to 10 km) dominates the simulation results. This dominance is not directly observable in the measurements. However, the simulation results in the Wurm are not rejected by the monitoring data, since the nearest monitoring site is already 4 km downstream from the discharge, permitting biodegradation to occur. The underpredictions in the Rur may be caused by (i) too little consumption data, (ii) too high assumed wastewater treatment efficiencies or (iii) too high in-stream removal rates. Regarding the overpredictions in the Wurm river, explanation (i) can most probably be excluded, whereas explanations (ii) and (iii) can not be decided with this information alone. In addition, regarding the very low LAS concentrations, a simple first-order degradation rate might not be appropriate.

Concluding, GREAT-ER is able to predict observable LAS concentration profiles when using generic consumption data and substance data derived in other catchments.

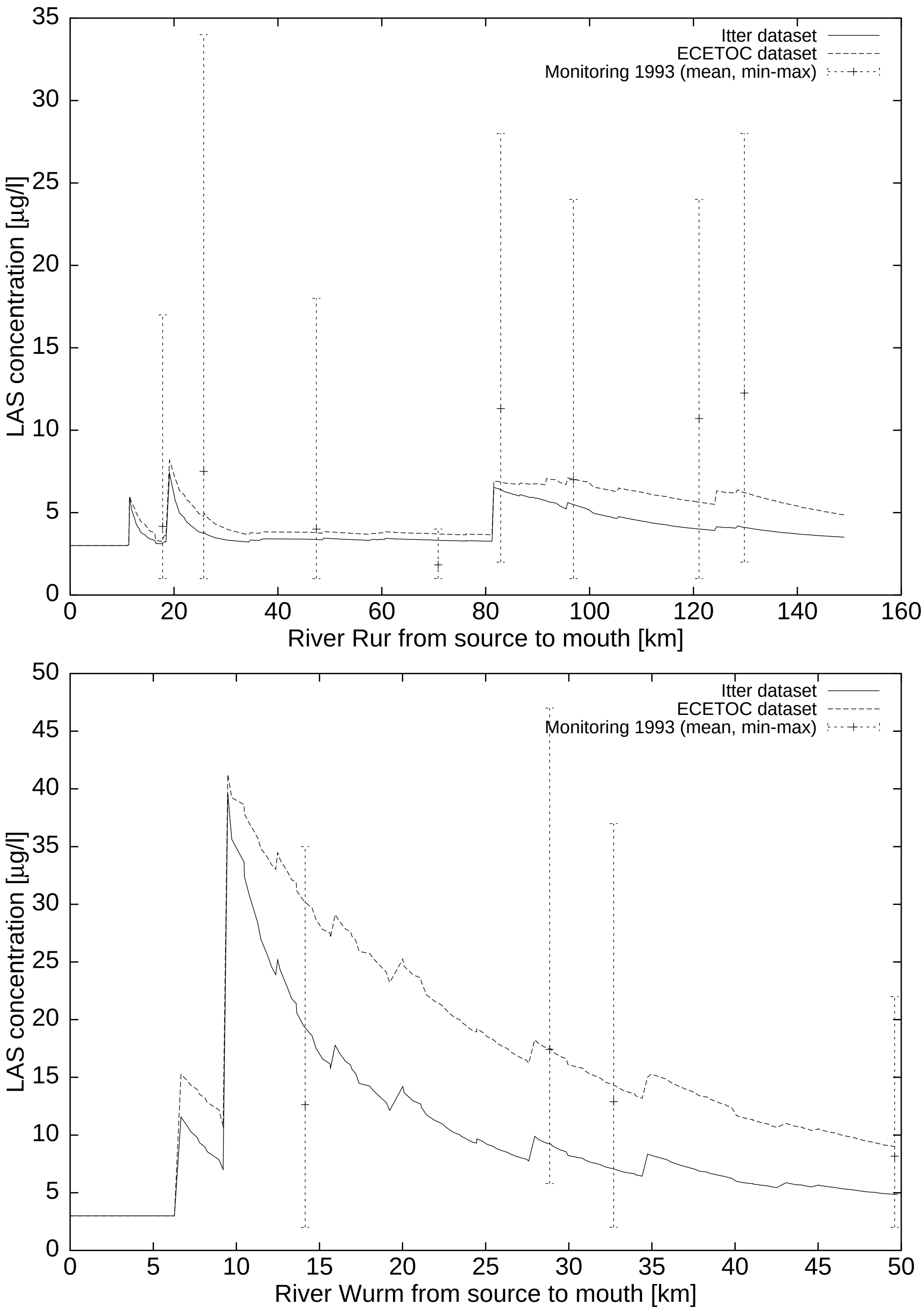

Figure 6.6.: **GREAT-ER results for LAS applying the ECETOC and Itter substance data sets vs. measurements (1993 data).**

6.1.4. NTA

In Germany, the use of NTA in household products such as detergents decreased during the nineties. Since the second half of the decade, NTA has been more or less replaced in household detergents. However, it is still used in different industrial applications, including industrial cleaning. In 1993, 2360 tons of NTA were used (CEFIC, 2000), of which 453.7 tons (calculated as nitrilotriacetic acid) were used in products underlying the German detergent and cleaning agents law (CEFIC, 2000, IKW, 1994). Both consumption data are used for simulations in order to determine the appropriateness of either data set. Since no information on the spatial distribution of the consumption is available, the 2360 tons are assigned uniformly distributed to the connected population. This implies the assumption that industrial activity is higher in more densely populated areas than in remote regions.

Substance data describing the fate of NTA can be found in the literature, e.g. Kuhn et al. (1987), Alder et al. (1990), Ulrich (1991), and Alder et al. (1997). An in-stream removal rate of $0.035\mathrm{d}^{-1}$ is used, which is based on in-situ measurements from the Greifensee (Ulrich, 1991), although in-stream removal rates in lakes and rivers are likely to differ. For the WWTP behaviour, a uniform distribution of between 95 and 98% is used as the total efficiency (comprising both the sewerage system and the wastewater treatment plant). This value is based on Alder et al. (1997, 1990). A report for NTA provided by the *GDCh-Beratergremium für Altstoffe* (BUA, 1986) cites other studies that reported elimination efficiencies for activated sludge type WWTPs of 84 and 88%. For this reason, in a third simulation a uniform WWTP elimination efficiency ranging from 84 to 88% is assumed to check these data, together with the emission data according to the total NTA consumption in Germany. Results of the three scenarios together with monitoring data are given in Figure 6.7.

Regarding the rivers Rur and Wurm, in the first two scenarios GREAT-ER underpredicts mean concentrations at all sites, while the model overpredicts at all sites in the third scenario. The same is true for the Vicht river except for its mouth. Regarding the Inde river, no trend can be observed. Nevertheless, by directly using the substance data from the literature the factor of three criterion is met when using the total NTA consumption. However, in the lower parts of the catchment the deviations are more or less a factor of 3. Keeping in mind the underlying assumptions concerning emission, improvements in the predictions can most probably be obtained by incorporating more detailed information concerning the use of NTA in the Rur catchment.

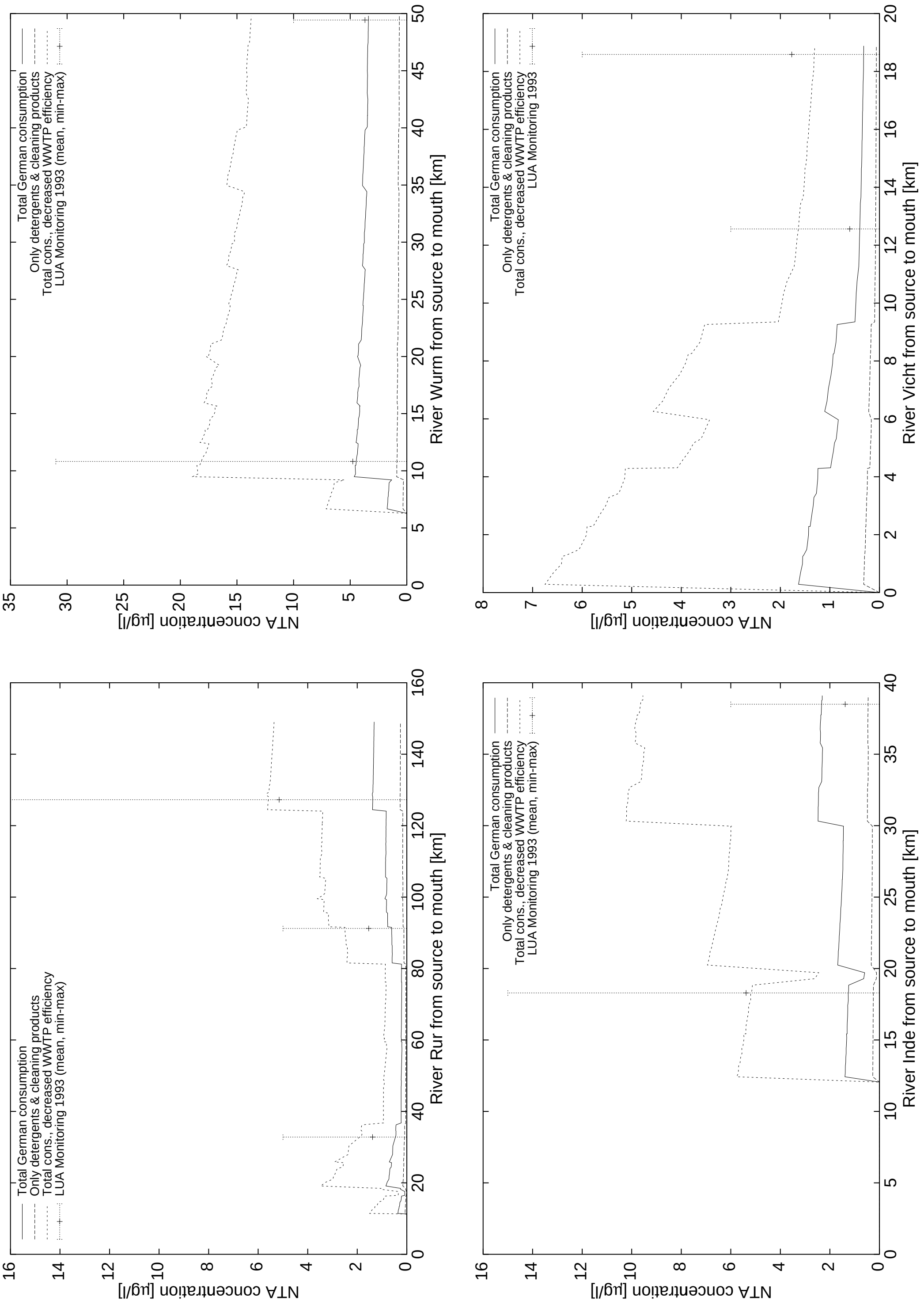

Figure 6.7.: **GREAT-ER results for NTA vs. measurements (1993 data sets).**

6.1.5. EDTA

Different kinds of uncertainty have to be taken into account when simulating EDTA. Firstly, consumption data of EDTA vary in different studies. As for NTA, CEFIC regularly conducts surveys of EDTA production and consumption in Europe (CEFIC, 2000). Results of these studies are also given in the BUA report (BUA, 1996) and partly by Gartiser (1997). The applications of EDTA in different branches are also given. A difficulty which causes uncertainty arises, similar to the case of NTA, in deciding which application can be translated into a per-capita basis, since only some information about the percentage of EDTA being discharged into water due to different applications is available (UBA, 1998). However, it is unclear whether a 'wide dispersive use' assumption is valid at all or for a certain percentage. Therefore, various scenarios were carried out, in which different uses of EDTA are transferred into the per-capita basis. A further uncertainty arises from the fact that only an (unknown) part of the EDTA masses listed are eventually used and discharged in Germany (UBA, 1998).

Removal efficiency in wastewater treatment is also a rather uncertain parameter. Many studies state that EDTA is not eliminated during wastewater treatment, for example Wolf and Gilbert (1992), Alder et al. (1990), and Alder et al. (1997). However, the BUA report (BUA, 1996) cites studies in which elimination efficiencies between 10 and 53% are reported. There are EDTA-specific elimination techniques which can be applied to increase wastewater efficiency. Nevertheless, because most of the studies conclude that EDTA is not eliminated in wastewater treatment, no removal is used as default.

The third uncertainty is related to in-stream removal. According to the literature, photolysis is the only significant removal process. However, it only occurs if EDTA is complex-bound with iron. Nowack and Baumann (1998) report that values from 20 to 90% of the EDTA present in effluents of wastewater treatment plants form a complex with iron.Thus, it is not surprising that measured in-stream removal rates vary from no elimination to a half-life of only a few days (Wolf and Gilbert, 1992). The BUA report (BUA, 1996) cites studies showing even biodegradability of EDTA under some conditions.

Based on these findings, two classes of scenarios were defined. Different consumption data by assuming fixed elimination behaviour, i.e. no elimination in the sewerage system and wastewater treatment and an in-stream removal half-life of 48 days, are investigated in the first set of scenarios. In the second class of scenarios, the influence of different in-stream removal rates are analysed by keeping the emission data constant. As for NTA, monitoring data for 1993 can be taken from the LUA monitoring campaigns for the four main rivers Rur, Wurm, Inde, and Vicht.

Varying consumption scenarios

Four scenarios have been defined which consider the different EDTA applications mentioned in the BUA (1996) report in the per-capita translation, i.e. different percentages of the total consumption in Germany in 1993 (4270 t, BUA, 1996) are used in the scenarios. In the first scenario only industrial and household cleaning products and cosmetics are considered (31%, C & C scenario). In the second scenario, photochemistry is also included (58%, C& C & P scenario). The third scenario also considers textile and galvanic industries (65%), while in the last scenario the total amount (4270 t, or 100%) is considered. The remaining 35% between the third and fourth scenario arise from agricultural use (3%) and from further applications including water purification (32%).

The first set of plots, shown in Figure 6.8, shows that EDTA concentrations are overpredicted in most cases. The factor of three criterion is only met when using the C & C scenario. The overpredictions may be caused by the fact that not all EDTA used in cosmetical applications enters the surface waters, which is mentioned by UBA (1998). However, this application accounts for only 3% of the total EDTA consumption, hence being responsible for 10% of the release in the C & C scenario. A second reason may have been due to removal processes either during wastewater treatment or in the surface waters themselves. Regarding the average residence time of water in the catchment, which is about one day from the Rurtalsperre to the catchment's outlet, 48 days is a slow elimination constant. This has been examined in the second series of EDTA-scenarios.

Varying in-stream removal rates

In the second set of simulations three further scenarios based on the C & C scenario were defined, i.e. assuming no photolysis (scenario B), a half-life of 1 day (scenario C) and a uniformly distributed half-life of between 1 and 48 days (scenario D). The results together with the original C & C scenario (half-life of 48 days, data set A) are shown in Figure 6.9.

Scenarios C and D give results that in most cases are in the ranges of the measured concentrations, while scenarios A and B overpredict. The statement made above that a half-life of 48 days is quite slow is proven here, as the differences between the results of the two last scenarios are only very small.

It is thus shown that only when assuming a significant photolysis rate in combination with the C & C scenario, EDTA predictions in the range of measured concentrations can be obtained. However, this also shows the sensitivity of the GREAT-ER model to parameters determining the release into surface waters, i.e. the production figures or the wastewater treatment assumptions. It can also be seen that the influence of in-stream removal cannot be neglected, but that it is compared to the release estimation bound.

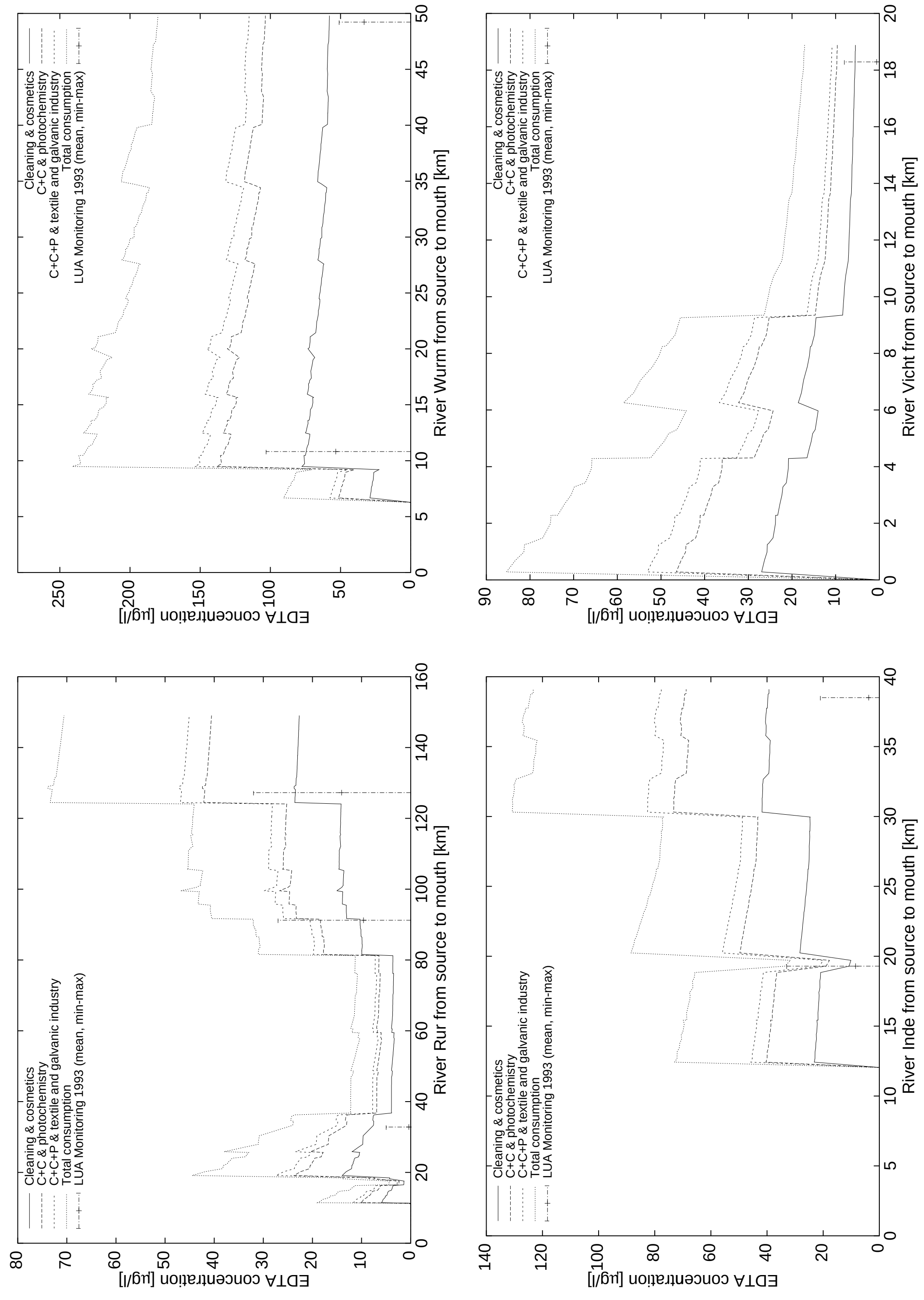

Figure 6.8.: **GREAT-ER results for EDTA assuming different consumption data vs. measurements (1993 data).**

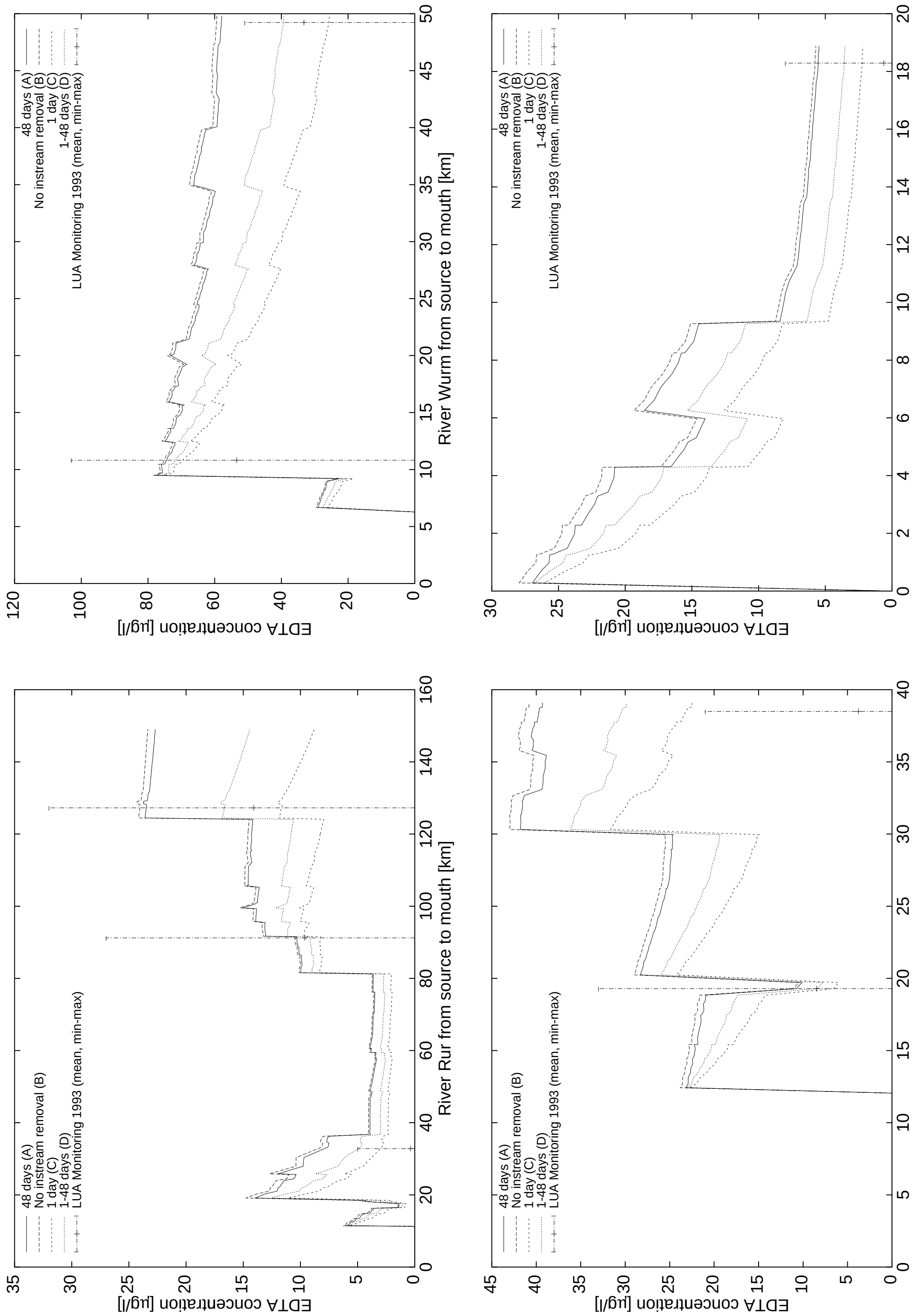

Figure 6.9.: **GREAT-ER results for EDTA assuming different photolysis rates vs. measurements (1993 data).**

6.2. Rur 2000 data set and monitoring

Future simulations beyond this thesis will most probably aim at portraying current situations. As newest discharge site data were available, a second data set with these data was also integrated into the GREAT-ER system. This second data set is characterised by efforts of the WVER to close smaller and less efficient WWTPs in favour of larger and more efficient WWTPs. Thus, the number of discharge sites has decreased. In order to verify this data set, a small monitoring programme was conducted in cooperation with Henkel KGaA, which was financed by the European Risk Assessment Steering Committee (ERASM).

As in the previous section, this verification is carried out by comparing the monitoring results with GREAT-ER 1.0 calculations based on 2000 monitoring and discharge site data. However, since emission data could only be based on newest available market data, which for the surfactants were from 1998 (TEGEWA, 2000) and for the other substances from 1999 (IKW, 2000), the comparison is subject to this uncertainty.

Because a general verification with the catchment data set was already conducted in the previous section, the model can now also be used to explain measured concentrations. This may aid the interpretation of monitoring data if only few monitoring data are available.

A further purpose of this monitoring is to determine input parameters for further detergent ingredients concerning in-stream removal and WWTP efficiency, as these are necessary for the product mode assessments. This purpose is relevant for the surfactants AS and AE. The Rur catchment is the first catchment for which two data sets from different years exist. For this reason, it can be investigated for the first time whether parameters such as background concentrations or wastewater treatment efficiencies, which were derived on the basis of discharge site, emission, and monitoring data from 1993, can be successfully applied in the 2000 modelling. This is conducted for boron, LAS, NTA, and EDTA.

In this section, the design of the Rur monitoring campaign is described. Then, the results of the monitoring programme as well as comparisons with GREAT-ER 1.0 results are given[1]. Finally, conclusions considering the whole chapter are drawn.

6.2.1. Choice of substances

The monitoring design comprises the selection of the monitoring sites, the frequency, and the number of parameters and substances to be measured. This decision is typically based on both the purpose and resources to reveal representative data of the catchment (Holt et al., 2000).

Since the current work in the Rur catchment aims at comparing potential aquatic ecotoxicological impacts due to the use of different laundry detergents by using the GREAT-ER

[1] An article having these contents has also been prepared (Schulze et al., 2001b).

software, the choice of substances was primarily focussed on detergent and cleaning agent ingredients. Further prerequisites for the choice of suitable substances were the expected environmental concentrations that should be at detectable levels, and the quality and quantity of information about the substance-specific emission data.

This led to the parameters and substances listed in Table 6.1. The list consists of typical water quality parameters, detergent ingredients such as boron as well as an- and nonionic surfactants, the chelating agents NTA and EDTA, and finally caffeine. Caffeine is a substance which may be regarded as 'down-the-drain'. However, its environmental emission pathways are not completely understood. Therefore, samples were taken to assess whether it can be found at detectable levels in the environment.

6.2.2. Choice of sampling sites

GREAT-ER estimates the spatial distribution of 'down-the-drain' chemicals in surface waters. Thus not only the hot spots are of interest but the whole range of more heavily and moderately loaded stretches, as well as almost unloaded stretches. The sampling sites are given in Figure 6.10. The risk of measuring an outlier is higher in very small rivers, because monitoring may reflect an extreme situation of only a short-term duration. Thus, main rivers are more suited. Due to technical restrictions, the monitoring programme was limited to the lower courses of the catchment, i.e. no samples were taken above the water reservoirs. Monitoring was performed on two sunny days in May 2000. The average water temperature was 17.2 +/- 1.3°C.

6.2.3. Sampling frequency

With the defined substances and sampling sites, the sampling frequency depends on the available resources. Composite samples over time were sampled. At each of the eight monitoring sites, 12 samples were collected over 24 hours using an automatic sampler in order to derive a mean daily concentration. At two sites, however, due to technical problems a composite of 2 and 3 samples respectively could only be attained.

6.2.4. Incorporation into GREAT-ER

A geographical data set was derived in which the locations and some attributes of the sampling sites are stored. The monitoring results were also added to this data set. The data were then transferred to a digital format accessible by the GREAT-ER software. The data set is kept as additional background information, due to which the data may be displayed within GREAT-ER's 'Easy-To-Use' mode. A further geographical data set was developed containing locations of those monitoring sites at which photographs were taken during the monitoring. The data and photographs can be loaded in GREAT-ER using the 'Show Site Pictures' entry in the 'Display' menu.

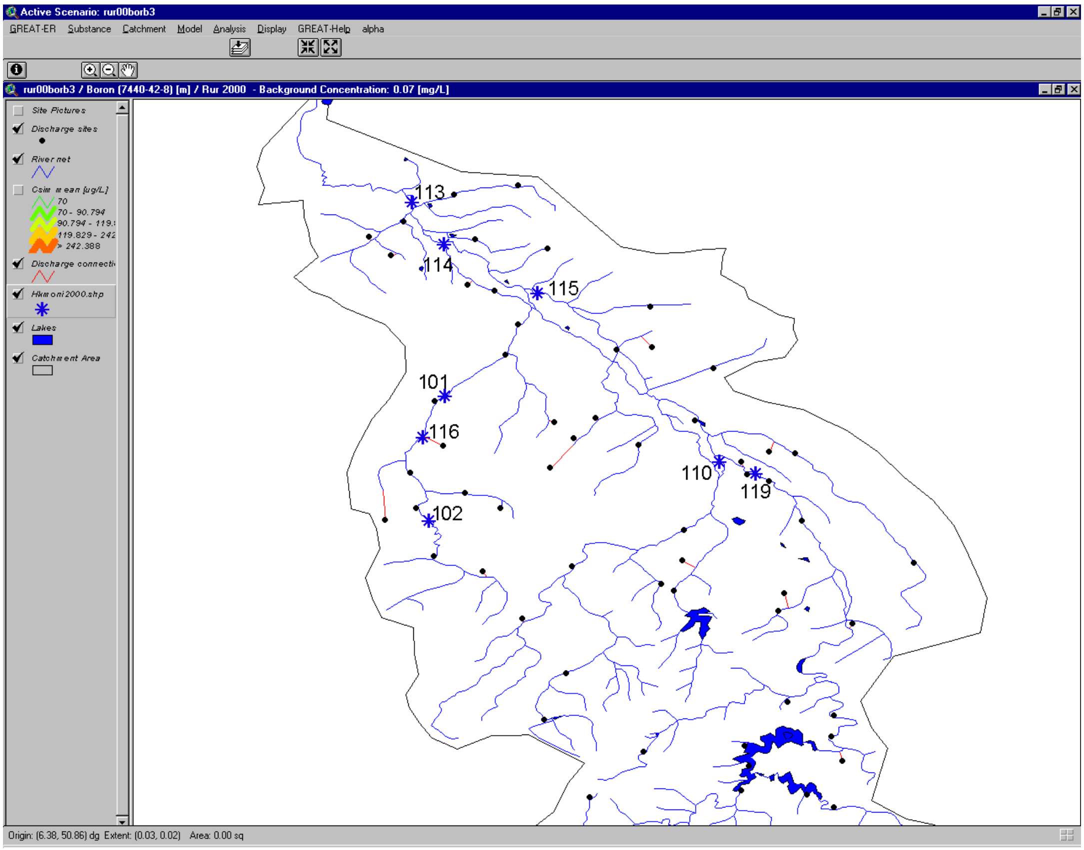

Figure 6.10.: **Sampling sites of the 2000 monitoring programme in the Rur catchment.** Sampling sites are given as asterisks, whereas the discharge sites are represented by dots. IDs refer to the sampling sites.

6.3. Results using the 2000 data

In order to provide a first insight into the data sets, this section is divided into a first part presenting the combined monitoring data and a second part comparing the monitoring data with simulation results of the GREAT-ER software.

6.3.1. Monitoring results

All monitoring results are given in Table 6.1. The water quality parameters show moderate pollution at the sites. For TOC and the nutrients, an evaluation according to a German chemical water quality classification provided by the Landesumweltamt Nordrhein-Westfalen (1997, LUA) can be performed. With respect to TOC, all measured river stretches would be ranked in stage II-III (critically loaded). According to ammonia, the stretches in the rivers Rur and Inde would be classified as class I (very slightly polluted), while the four sites in the Wurm river would each represent a different class, i.e. I, II, II-III and III (heavily polluted). The nitrite-based classification is almost identical to the ammonia-based one. Referring to nitrate, Krauthausen would be classified as class II, while all other sites would be classified as class II-III.

Table 6.1.: **Overview of the Rur catchment monitoring results (May 2000).** For each river the order of the sampling sites is from left to right downstream. The sites are located near Krauthausen (119), Hilfarth (115), Vloodrop (113), Kohlscheid (102), Rimburg (116), Hommersche (101), Kempen (114), and Kirchberg (110).

River name	Rur			Wurm				Inde
Site ID	119	115	113	102	116	101	114	110
DOC (mg/l)	4.8	4.9	5	7.6	6.8	8.8	7.3	5
TOC (mg/l)	5.1	5.6	5.9	8.8	8.1	9.2	7.8	5.5
Ortho-P (mg/l)	0.10	0.10	0.14	0.15	0.28	0.66	0.45	0.09
NO_2-N (mg/l)	0.03	0.03	0.04	0.04	0.15	0.23	0.15	0.03
NO_3-N (mg/l)	1.87	2.97	3.21	4.37	3.6	4.18	4.16	2.47
NH_4-N (mg/l)	0.03	0.03	0.05	0.03	0.84	0.41	0.15	0.03
MBAS (mg/l)	0	0.01	0.02	0.03	0.03	0.05	0.03	0
LAS (μg/l)	<1	<1	3	1	<1	3	3	<1
SAS (μg/l)	<1	<1	<1	<1	<1	<1	<1	< 1
AS (μg/l)	<1	2	<1	<1	1	4	1	<1
AES (μg/l)	<1	<1	<1	<1	<1	2	<1	<1
AE (μg/l)	6	3	8	11	6	8	13	2
Bor (mg/l)	0.11	0.16	0.22	0.34	0.39	0.44	0.42	0.17
NTA (μg/l)	21	8	9	2	5	2	35	3
EDTA (μg/l)	71	80	55	25	50	9	160	17
caffeine (μg/l)	<0.5	<0.5	5	<0.5	<0.5	<0.5	<0.5	<0.5

With respect to the measured ortho-phosphate concentrations, the sampling sites in the rivers Inde and Rur are assigned to classes II or II-III, while in the river Wurm the measured concentrations are classified to stages II-III, III, and III-IV (very heavily polluted). It can thus be seen that the Wurm is more heavily affected by ortho-phosphate than the other rivers in this catchment. However, because a more robust water quality classification requires further measurements and probably also water quality modelling, the classification given above can only be regarded as screening for the anthropogenic impact of the catchment.

Although anthropogenic influences can be presumed from this water quality monitoring programme, concentrations of detergent ingredients are rather low. This is especially true for the anionic surfactants. The taking of measurements of anionic surfactants in surface waters was undertaken using two methods: determination of the sum-parameter ‘Methylene Blue Active Substances’ (MBAS) and ‘High Performance Liquid Chromatography’

(HPLC). The latter enables the determination of the different single anionic surfactants and their homologues[2]. For the single substances more than half of the measurements are near or below the detection limit, while the MBAS concentrations are comparable to those determined by the LUA during the nineties. It can be seen that the sums of measured anionic surfactants are always smaller than the MBAS concentrations. These low values do not allow very distinct GREAT-ER verifications. Concentrations of the nonionic surfactant alcohol ethoxylathe (AE) are also moderate, but show a distinct profile usable for a comparison of monitoring and simulation results.

The measured boron concentrations in the Rur and Inde rivers are comparable to concentrations measured in 1993, while concentrations in the Wurm river seem to have decreased from 1993 to 2000. For NTA, at two sites (114, 119) high measured concentrations are remarkable, as they are also higher than average values measured by the LUA in 1993. The other sites show concentrations similar to the values from 1993. EDTA concentrations especially in the Rur river have significantly increased compared to data from 1993. This increase cannot be observed in the rivers Wurm and Inde. If the monitoring data reflect the real situation, this would suggest one or more additional industrial discharges into the river Rur. At sampling site Kempen (ID 114) both NTA and EDTA concentrations seem to be higher than usual. These values may be regarded as outlier.

The low concentrations of caffeine are not promising with respect to using the compound for GREAT-ER verification studies.

6.3.2. Boron

Since boron is neither adsorbed nor chemically or biologically converted (Schröder et al., 1999), consumption data and (geogenic) background concentration are the only input data necessary for GREAT-ER simulations (see also sections 2.3.3 and 6.1.2). The consumption figures are based on the consumption data from 1999 (0.0424 kg per capity and year, IKW, 2000), whereas the value of 0.07 mg/l determined in the 1993 calculations (see section 6.1.2) is used as the background concentration.

The 1993 study showed the existence of additional (industrial) input, which was assumed to occur at the Linnich and Herzogenrath WWTP, where in fact emissions from glass and paper industry occurred, see section 6.1.2. The loads determined in the 1993 study were 20 t/a at Herzogenrath WWTP (river Wurm at 20 km) and 70 t/a at Linnich WWTP (river Rur at 105 km). To check these industrial loadings, results from scenarios without these additional inputs as well as with the additional loads are given and shown in Figure 6.11.

It can be seen that the measured boron concentrations are underestimated in the lower courses of the Rur and Wurm rivers if only the detergent-based per-capita consumption is used as emission data, whereas in the scenario assuming additional discharges according

[2] A recent overview of different analytical techniques for determining surfactants in environmental matrices is given by Thiele et al. (1999).

to the 1993 scenarios boron concentrations are overestimated.

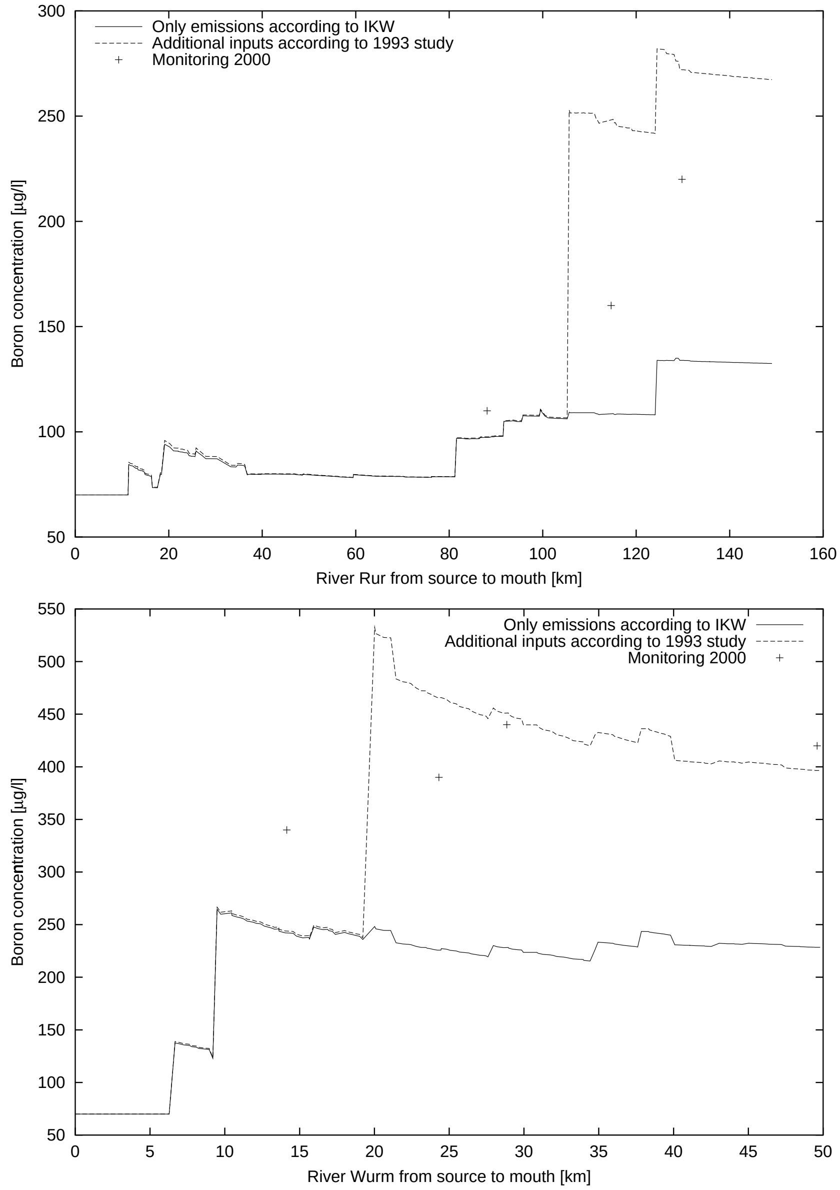

Figure 6.11.: **GREAT-ER results for boron vs. measurements (2000 data)**

At Kirchberg (near the mouth of the Inde river), mean concentrations of 174 and 177 μg/l are calculated in the two scenarios. These values are close to the measured concentration, i.e. 170 μg/l. Thus, the background concentration, which was determined on the basis of the 1993 data, provides good results when applying the 2000 data set. The difference of 3 μg/l calculated at Kirchberg in the two scenarios is due to the stochastic variabilities.

When looking at the second scenario, in which additional discharges are considered, it may be concluded that the additional loads entering at Herzogenrath and Linnich WWTPs have changed in quantity. However, this change may also partly be due to the uncertainty introduced by using the per-capita consumption from 1999.

By inverse-modelling, which aims for the optimal agreement between modelling and monitoring at one or more sites, likely quantities of additional discharges at different sites can be obtained. However, regarding the small amount of monitoring data, it seems questionable whether this would give any new insight. Nevertheless, to exemplify inverse modelling, the additional discharge at Linnich was changed to a load giving results close to the monitoring data at the next downstream sampling site Hilfarth. This load, 25.66 t/a, was derived by a mass balance. The resulting concentration profile of the river Rur is given in Figure 6.12.

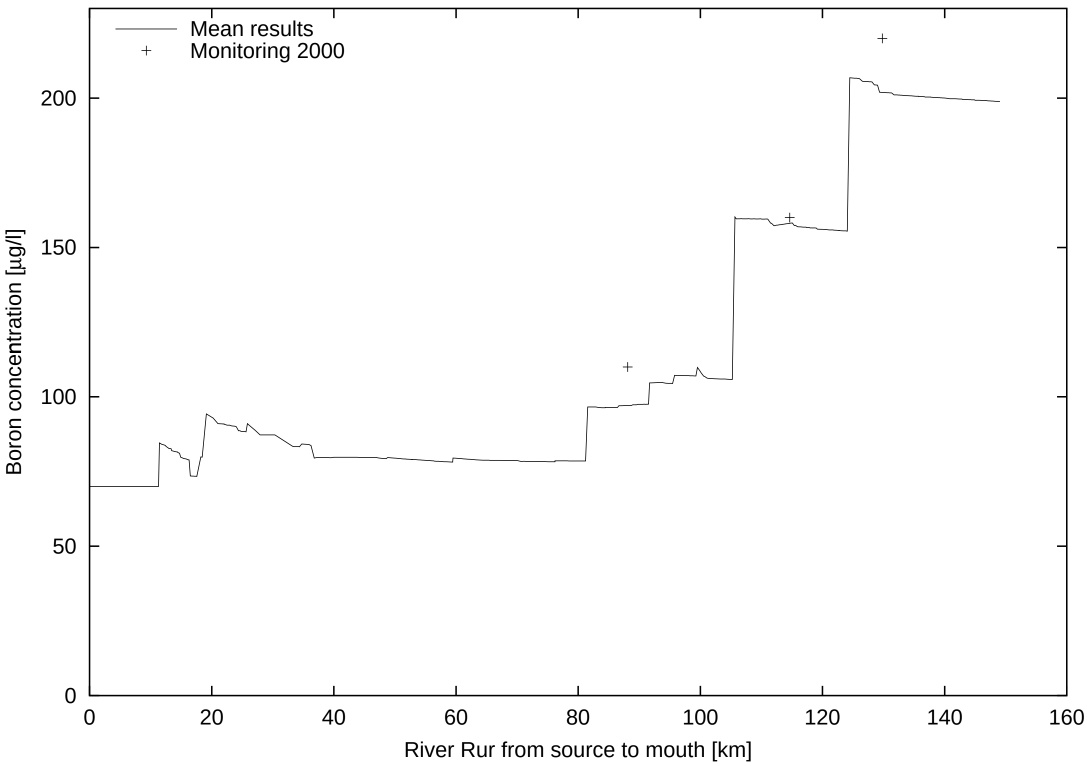

Figure 6.12.: **GREAT-ER results for boron vs. measurements (Rur river, 2000 data)**

With this adjustment, the simulation and monitoring results at Hilfarth (113 km) are very close. Their deviation is only caused by variations due to the stochastic part of GREAT-ER. Also, at Vloodrop (130 km) the deviation has considerably decreased. Thus, by collecting additional information about industrial discharges, further insight into spatial boron distributions may be derived. However, regarding the aim of this thesis, this is not considered necessary.

6.3.3. Anionic surfactants

In the Rur monitoring programme, MBAS as well as the anionic surfacants linear alkylbenzene sulphonate (LAS), alcohol (or alkyl) sulphate (AS), alcohol (or alkyl) ether sulphate (AES), and secondary alkane sulphonate (SAS) were measured. For all these substances emission data are available from TEGEWA (2000). Comparisons of measurements and simulation results have only been conducted for LAS and AS because monitoring results for SAS and AES in all cases but one are below the detection limit of 1 μg/l (see Table 6.1).

LAS

It is clearly visible that the measured LAS concentrations are very low, since 4 out of 8 values are below the detection limit of 1 μg/l. Due to this fact a comparison of measured and simulated concentrations is difficult. 1998 consumption figures revealed a per-capita consumption of 0.4777 kg per capita and year (TEGEWA, 2000). As in the 1993 simulations, two scenarios were defined using the ECETOC and Itter substance data sets. Regarding the very low measured concentrations, no background concentration is assumed. This differs from the 1993 study, where 3 μg/l was used as the background concentration. The simulation results at the different monitoring sites compared to the measured data are given in Table 6.2.

Table 6.2.: **GREAT-ER results for LAS vs. measurements (μg/l, 2000 data)**

Sampling Site	Measured concentration	Mean simulation results: Itter data set	Mean simulation results: ECETOC data set	River
Krauthausen	<1	2.7	3.4	Rur
Hilfarth	<1	1.2	2.7	Rur
Vloodrop	3	1.1	3.1	Rur
Kohlscheid	1	12.6	21.3	Wurm
Rimburg	<1	5.0	12.5	Wurm
Hommersche	3	5.1	11.5	Wurm
Kempen	3	2.2	6.3	Wurm
Kirchberg	<1	2.3	6.0	Inde

In both scenarios overpredictions of LAS concentrations occur at most sites. Especially in the Wurm river, except for at the sampling site Kempen, systematic deviations occur, which are caused by the calculated LAS load emitted by the largest municipal discharge of the catchment at Aachen-Soers. The dominance of this plant is not reflected by the measurements. This disaccordance was already observed in the 1993 study, see section 6.1.3.

Different studies show WWTP removal efficiencies higher than 98% (AISE/CESIO, 1996, Schröder et al., 1999). Applying these higher elimination efficiencies would lead to smaller GREAT-ER simulation results, and thus to smaller differences of measurements and predictions.

The in-stream removal assumed in the Itter data set leads to smaller deviations from the monitoring data. This differs from the 1993 study, in which the ECETOC data set was more accurate at modelling the measured concentrations.

However, with respect to the present low range of measured concentrations, variability in the measurements as well as uncertainties in the emission estimates may have large influence on the comparison of monitoring and simulation results. Therefore, a further calibration of LAS substance data based on only these monitoring data does not seem to be justified. Showing that a substance data set derived in a different study can be applied in this study with only limited variations between monitoring and simulation results is a more valuable result.

AS

The second anionic surfactant for which comparisons of monitoring and simulation results could be performed is alcohol sulfate (AS). Consumption data for 1998 are provided by TEGEWA (2000, 0.122 kg per capita and year), while information about the in-stream removal and wastewater treatment behaviour is given by Painter (1992), Schröder (1995a), AISE/CESIO (1996), and in a BUA report (BUA, 1997). In general, these parameters are similar to the figures of LAS. Therefore, the LAS Itter data set is also used for AS (data set A in Table 6.3). In data sets B and C, the WWTP removal efficiency is increased, because the literature cited above in general indicate slightly higher WWTP efficiencies for AS than for LAS.

Similar to LAS, at four sampling sites measured AS concentrations are below the detection limit of 1 μg/l, which in turn makes GREAT-ER verifications very difficult. Results for the different data sets are given in Table 6.4, while the input data sets are given in Table 6.3.

Table 6.3.: **Removal rates for AS.** The WWTP are of the activated sludge type.

Data set	Sewer %	WWTP %	In-stream h^{-1}
A	25	98	0.03-0.35
B	25	98.5	0.03-0.35
C	25	98.5-99.3	0.03-0.35

Unlike for LAS, no general trends of over- or underprediction can be observed for AS. Also, the discrepancy observed for LAS in the Wurm river is only visible at the sampling site near Kohlscheid, the first sampling site below the WWTP Aachen-Soers, while in the LAS modelling this could be observed in large parts of the Wurm river. From the three AS data sets, the first (A) seems to be the most appropriate, although such a statement is highly difficult considering variabilities and uncertainties in both modelling and monitoring.

Table 6.4.: **GREAT-ER results for AS vs. measurements (μg/l, 2000 data)**.

Sampling Site	Measured concentration	Mean simulation results Data set A	Data set B	Data set C	River
Krauthausen	<1	0.7	0.5	0.4	Rur
Hilfarth	2	0.3	0.2	0.2	Rur
Vloodrop	<1	0.3	0.2	0.2	Rur
Kohlscheid	<1	3.2	2.4	1.8	Wurm
Rimburg	1	1.3	0.9	0.7	Wurm
Hommersche	4	1.3	1.0	0.7	Wurm
Kempen	1	0.6	0.4	0.3	Wurm
Kirchberg	<1	0.6	0.4	0.3	Inde

6.3.4. Nonionic surfactants - Alcohol Ethoxylate

The most widely used nonionic surfactant in German detergents is AE. Surprisingly, the literature on the fate behaviour of AE is relatively sparse compared to the literature on LAS, for example. However, some studies concerning the fate of AE were conducted, the results of which could be used in this thesis.

As for LAS and AS, consumption data are based on information provided by TEGEWA (2000, 0.697 kg per capita and year), while measured WWTP and sewer elimination efficiencies are given by AISE/CESIO (1996), republished in Matthijs et al. (2000) and Feijtel et al. (2000). For sewer removal the mean value of 42% given there is used for the simulation. However, the average WWTP removal reported there seems very high (99.8%). Other studies (e.g. Holt et al., 1992) report values of only 98% and higher. Therefore, 98% and 99% are used as WWTP efficiencies in the standard scenarios. Data on the in-stream removal rates are among others given by Steber (1997, used in data sets A), and Marcomini et al. (2000, used in data sets B and B2). The substance data sets used for the three scenarios are given in Table 6.5. Simulation results of these scenarios are given in Figure 6.13 and in the text. The difference between data sets B and B2 lies in the consideration of removal in the sewerage system, which is not assumed in data set B2. The differences between the results of these two scenarios therefore depict the influence of this uncertain parameter. This uncertainty is caused by the fact that the removal efficiency in the sewerage system depends on the mean residence time within the sewers connected to a specific WWTP. This value is highly site-specific.

In the Rur and at the mouth of the river Wurm GREAT-ER underpredicts the measured concentrations, while this is not the case at the other sites. It is most likely that the wastewater treatment efficiency of WWTP Aachen-Soers is better than the average, since an overprediction in the Wurm river was also observable for the other surfactants in the 1993 and 2000 simulations. However, this can only be presumed. At the sampling site Kirchberg (Inde river), mean simulation results based on the different data sets are 2.5 μg/l (data set A), 5.5 μg/l (data set B) and 9 μg/l (data set C), while 2 μg/l were measured.

Table 6.5.: **Removal rates for AE.** WWTP removal assumes WWTPs of the type activated sludge, which is the case for all plants in the catchment.

Data set	Sewer %	WWTP %	In-stream h^{-1}
A	42	98	0.14
B	42	99	0.012-0.055
B2	0	99	0.012-0.055

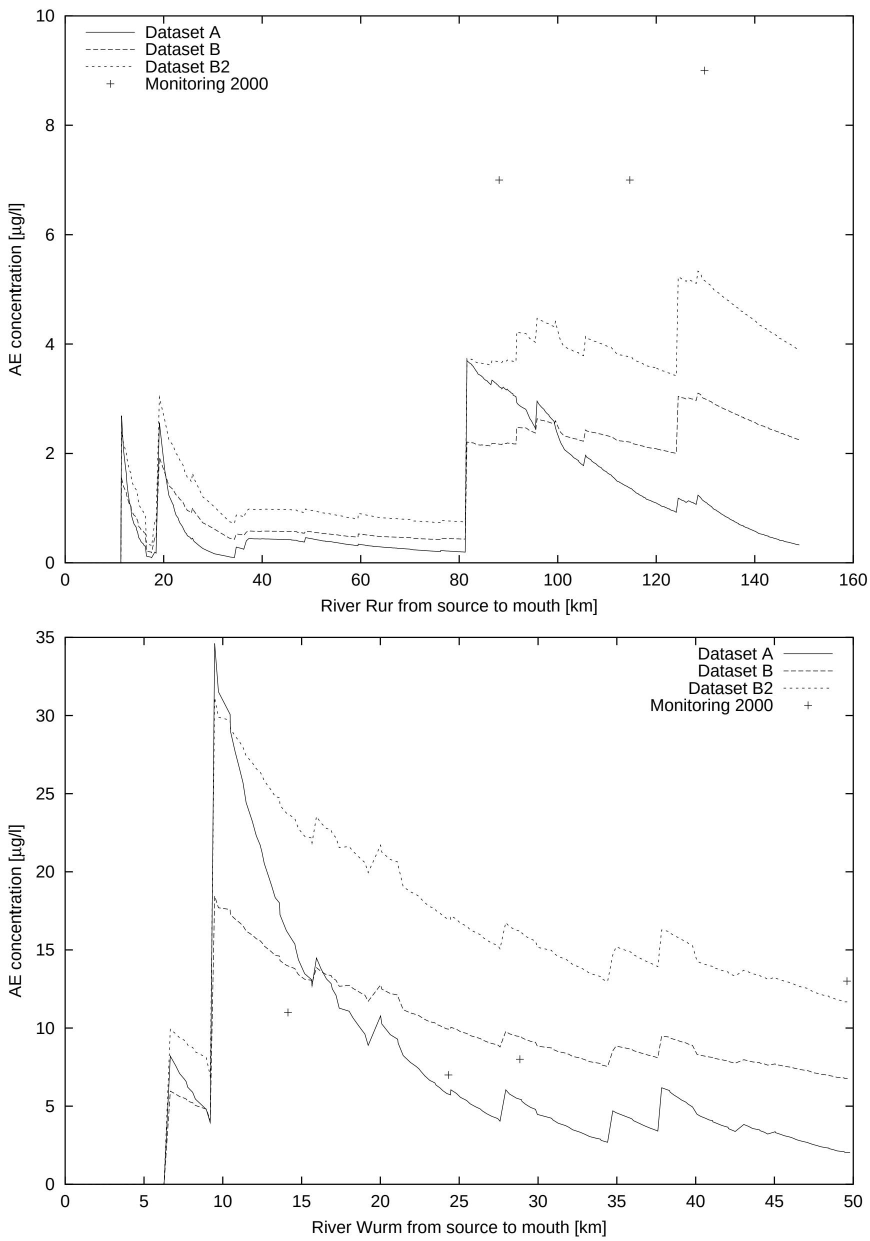

Figure 6.13.: **GREAT-ER results for AE vs. measurements (2000 data)**

However, especially in the Rur river, deviations are small, i.e. less than 5 μg/l. The deviations may therefore also be caused by variabilities in the monitoring data. Despite this, the factor of three criterion is met for most of the sites in all scenarios. Exceptions exist for data set A at the sampling sites Hilfarth and Vloodrop and for data set B2 at the sampling site Kirchberg. Data set B leads to results fulfilling the factor of three criterion at all sites (at Vloodrop the deviation reveals exactly a factor of three). If a choice has to be made between one of the three data sets, data set B seems most appropriate for GREAT-ER modelling of AE in the Rur catchment.

6.3.5. NTA

Consumption data for NTA used in detergents and industrial as well as household cleaning agents are regularly published by IKW (IKW, 2000). For 1999, 400 t/a are given for Germany, which is equivalent to 0.0049 kg per capita and year. Three scenarios are defined accounting for different WWTP efficiencies, which were determined in three monitoring studies. In the first scenario a uniform distributed elimination of between 95 and 98% (scenario A, Alder et al., 1997) is assumed as the WWTP efficiency. In the second a uniform distributed elimination of between 84 and 88% (scenario B, BUA, 1986), and in the third scenario a uniform distributed elimination of between 94.9 and 96.2% (scenario C, Schröder, 1998) are assumed. The in-stream removal rate measured for NTA in-situ in the Greifensee (Ulrich, 1991) is again used in all scenarios, keeping in mind the potential source of error arising from different elimination kinetics in rivers and lakes. The first two substance data sets were also applied in the 1993 study, whereas the third elimination efficiency (scenario C) has not yet been used. Simulation results of all scenarios together with the monitoring data are given in Figure 6.14 and Table 6.6.

Table 6.6.: **GREAT-ER results for NTA vs. measurements (Rur and Inde rivers, 2000 data).** Results are given in μg/l.

Sampling site	Measured	Simulated with WWTP removal of 84-88% (A)	95-98% (B)	94.9-96.2% (C)
Krauthausen (Rur)	21	0.4	0.1	0.1
Hilfarth (Rur)	8	0.6	0.2	0.2
Vlodroop (Rur)	9	1.0	0.3	0.3
Kirchberg (Inde)	3	1.6	0.4	0.5

When applying the consumption data according to IKW (2000), underestimations occur in the Rur river and at sampling site Kirchberg. This was also observed in the 1993 calculations. However, in the Wurm river such underpredictions are not clearly visible.

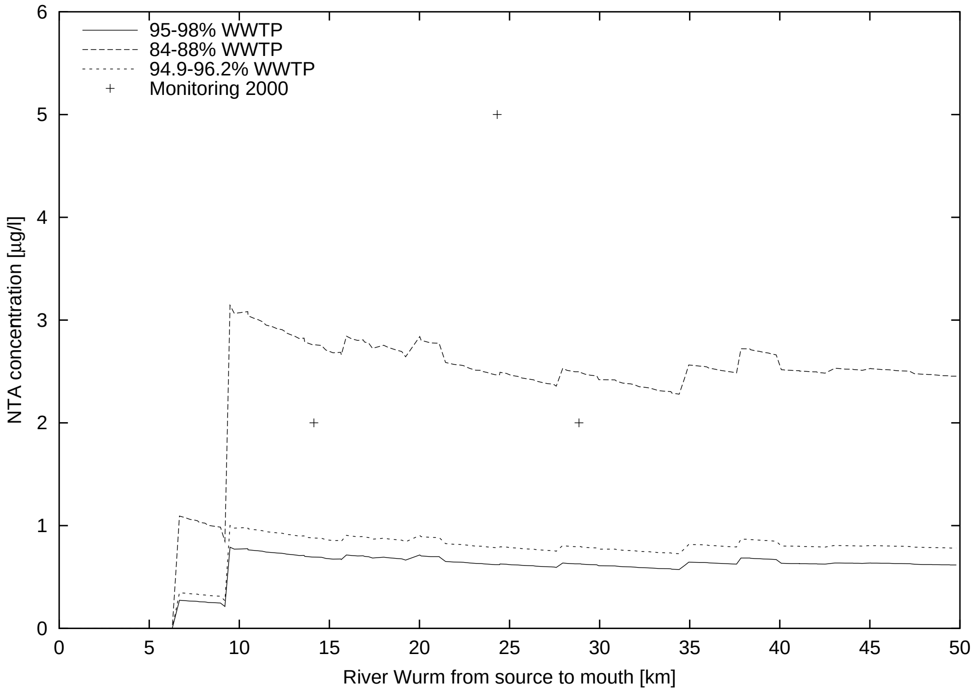

Figure 6.14.: **GREAT-ER results for NTA vs. measurements (Wurm river, 2000 data).** The probable outlier near the mouth (Site ID 114, Kempen) is not shown.

In a second set of scenarios, consumption data for 1999 published by CEFIC (2000, 0.031 kg per capita and year) are used that consider all applications. In this calculation, only the first two WWTP scenarios (A and B) are considered. Since the differences in the simulation results between the second (B) and the third (C) data set are minimal, the third scenario is no longer used.

The results for the Wurm and Rur rivers are given in Figure 6.15, while at Kirchberg (Inde river) the calculated mean concentrations are 10 (data set A) and 2.5 μg/l (data set B) respectively, compared to a measured concentration of 3 μg/l.

The factor of three criterion is not generally met. Since both over- and underpredictions occur, the deviations cannot be explained by erroneous substance removal rates. It is more likely that the assumption to uniformly assign the total amount of NTA that was used in Germany uniformly to the population is not valid. From these results one may conclude that the spatial distribution of NTA concentrations in surface waters is not predominantly determined by private households. Furthermore, general underpredictions in the Rur river are more likely due to above-average industrial input. Thus, in order to accurately assess the spatial distribution of NTA in the surface water of the Rur catchment, industrial sources would need to be identified and investigated.

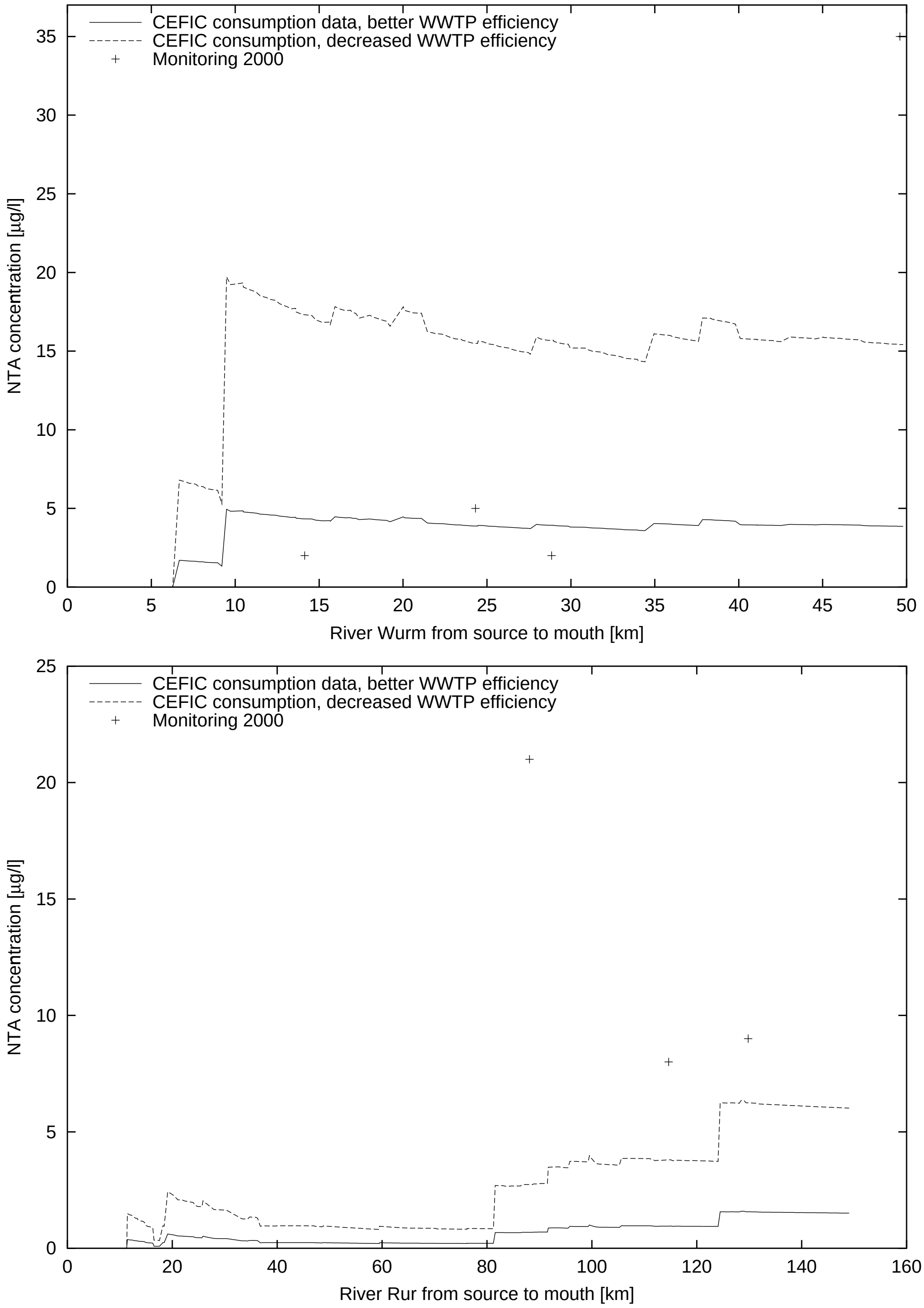

Figure 6.15.: **GREAT-ER results for NTA vs. measurements (2000 data).** Consumption data are based on CEFIC (2000). Here, the probable outlier at the mouth of the Wurm as well as a second in the Rur river are included in the plot.

6.3.6. EDTA

German consumption data published by CEFIC (2000) are divided into different applications. In the 1993 study, the best results were obtained by assigning the EDTA applied in household and industrial cleaning products as well as that in cosmetic products on a per-capita basis. In 1999, these applications accounted for 32% of the total EDTA consumption of 3,894 t/a in Germany (calculated as edetic acid), which is almost identical to the percentage in 1993 (31%), although the partitioning among the three applications has changed.

The different kinds of uncertainty present in a fate modelling of EDTA have already been discussed in the previous EDTA simulations using the 1993 data set. Due to these findings, 3 scenarios are defined which account for different in-stream removal rates. The emission data are based on use of EDTA in household and industrial cleaning products as well as cosmetic products. In the 1993 study, this assumption gave the best results. In the three scenarios, no in-stream removal (scenario A), an in-stream removal rate of 0.02888 h^{-1}, which corresponds to a half-life of one day (scenario B), and a uniform distributed in-stream removal of between 0.02888 and 0.006 h^{-1}, are assumed (scenario C). The latter value corresponds to a half-life of 48 days.

The results of three scenarios are shown in Figure 6.16. At sampling site Kirchberg (Inde), mean simulated concentrations were 17 μg/l (photolysis rate 0.03 h^{-1}), 28 μg/l (0.0006-0.03 h^{-1}) and 39 μg/l (no photolysis) respectively, while 17 μg/l were measured.

Two main observations can be made from the three EDTA scenarios. Firstly, the results clearly show that the influence of variable in-stream removal rates is limited, as the differences in the simulation results considering no in-stream removal (scenario A) versus considering a half-life of a day are only a factor of 2. Second, large deviations between measurements and simulated EDTA concentrations can be observed. In the Rur river underpredictions occur at all sampling sites, while in the Wurm river, except for the probable outlier near the mouth of the Wurm, overpredictions occur at the monitoring sites.

These findings are most probably due to the following two reasons: First, only 32% of the EDTA released in Germany has been applied in the three scenarios. Therefore, additional industrial emissions are possible and likely. Secondly, the general relation reflected by the GREAT-ER model, i.e. the correlation between population-density in a (sub-)catchment and concentration level in the environment, is not valid for this monitoring: In the Rur the measured concentrations are higher than those in the river Wurm despite a higher population density in the Wurm subcatchment.

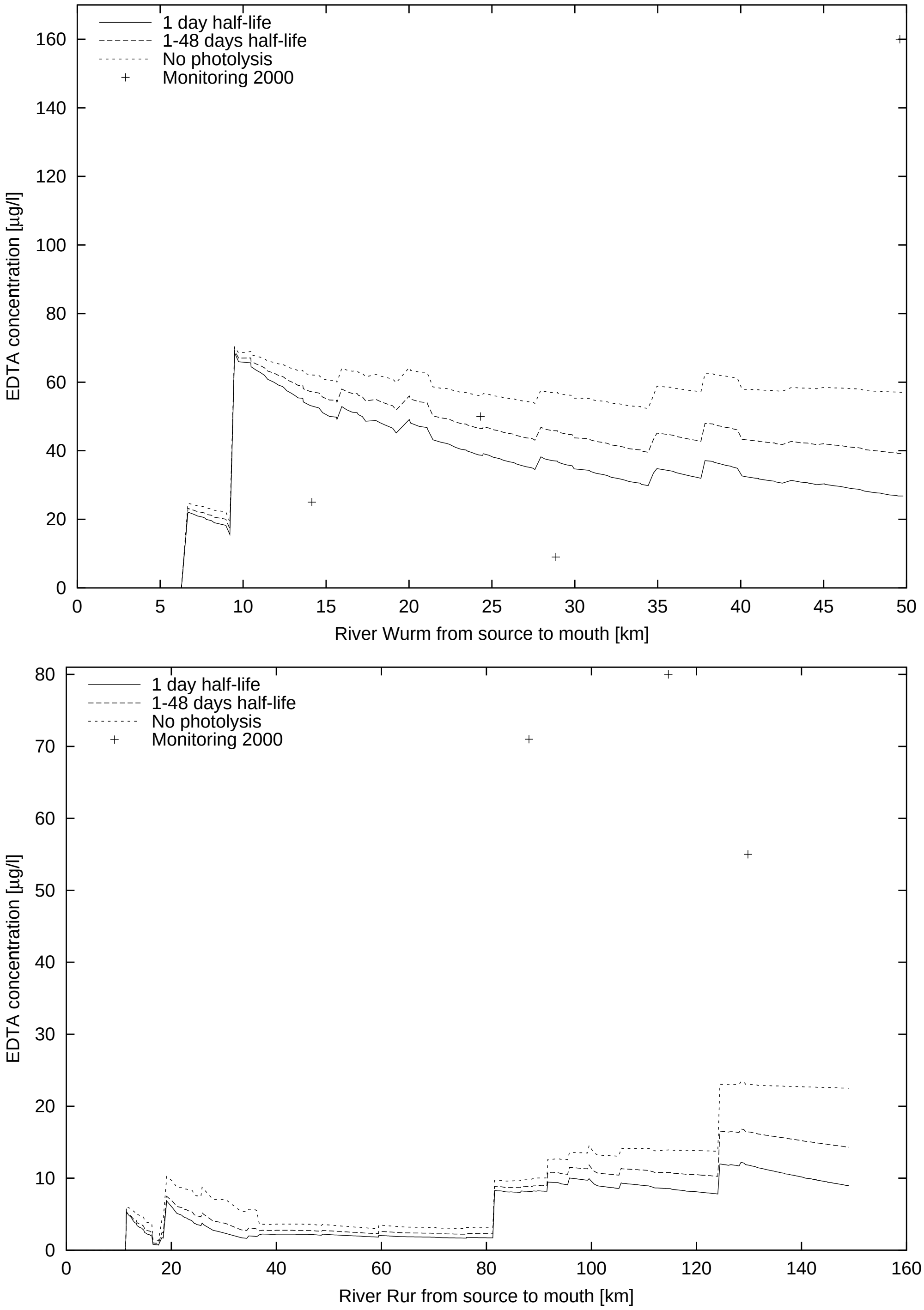

Figure 6.16.: **GREAT-ER results for EDTA considering different photolysis rates vs. measurements (2000 data).** Consumption data are from CEFIC (2000).

6.4. Discussion

6.4.1. Simulation using 1993 data

It was shown that for the three substances boron, LAS, and NTA the desired accuracy of a factor of three could directly be achieved for the main rivers of the Rur catchment by using average consumption data and physico-chemical properties from the literature. For LAS and boron, background concentrations had to be defined. A background concentration was assumed in the case of boron due to its natural occurrence. For LAS this is not obvious. However, in all GREAT-ER catchments, i.e. in the UK, Italy, and Germany, concentrations above zero were measured in the headwaters (ECETOC, 2000). This should be considered in the design of future LAS monitoring studies, which aim to determine the spatial distribution of LAS or other surfactants. For EDTA the selected emission data scenario strongly influenced the model output, which demonstrates how carefully these important data must be derived.

The calculated concentration profiles of all four substances in the Wurm river were dominated by the discharges of the largest WWTP Aachen-Soers. Although the monitoring data did not contradict these results, the measured concentrations did not show peaks in the respective part of the river. Reasons may be two-fold. Either the monitoring sites are too far away from the discharge site to identify an actually existing peak or, alternatively, Aachen-Soers WWTP has a better elimination efficiency. By measuring effluents of the WWTP, the first could be investigated.

For boron, the concentration profile in the Wurm was less pronounced, which is most likely due to industrial discharges. This was shown in the case of Herzogenrath WWTP, where a considerable additional input was identified which increased the accuracy significantly. Besides boron, the other substances NTA and EDTA might be discharged due to industrial use. For a more precise modelling of these substances further investigations concerning industrial use and discharge would be necessary. However, as this thesis focuses on household laundry detergents that neither contain NTA nor EDTA, this has not been done.

The influence of variable in-stream removal rates could be seen for EDTA. Since in GREAT-ER the fate of substances in surface waters depends on both dilution and in-stream removal, which is due to the open nature of this catchment-based system, the differences between considering slow and no in-stream removal were negligible. An increasing half-life therefore becomes less sensitive.

The comparisons were carried out on the basis that the mean measured concentrations really reflect the mean concentrations on an annual basis. However, measurements were not taken over the whole year, but only during the period from April to December. It has not been investigated whether in-stream removal or wastewater treatment efficiency is reduced in the Rur catchment during the cold season from January to March. However, GREAT-ER mode 1 does not consider such a temperature-dependency either. For this reason, the comparison of measurements and simulation may be slightly biased, although AISE/CESIO (1996, p. 38f.) cite studies from which they conclude that biodegradation rates of surfactants are not or only to a small extent temperature-dependent.

6.4.2. Simulation using 2000 data

Similar findings as in the analysis using the 1993 data were obtained when using the 2000 data. The envisaged 'factor of three' criterion has been met for the investigated substances except for NTA and EDTA. Regarding EDTA, the criterion was achieved only at some sites, but no agreement in the spatial distribution of measured versus simulated concentrations was observed. The main factor influencing environmental EDTA concentrations, and to a lesser extent also NTA concentrations, is therefore most likely industrial applications rather than private households. However, for the investigated surfactants and boron, which can typically be regarded as household-related 'down-the-drain' chemicals, an accordance between measurements and simulation results could be observed, although some over- and underpredictions occurred, depending on the choice of substance parameters applied in the different scenarios.

A further interesting aspect is the fact that substance data sets derived for other catchments and in the 1993 study could be transferred by only adjusting the per-capita consumption to actual values. This could convincingly be shown in the case of LAS, where the data sets derived from the Itter catchment (Itter data set) and in the English pilot study areas (ECETOC data set) could successfully be transferred to the Rur catchment. The fact that in the 1993 study the ECETOC data set resulted in lower deviations, while with respect to the 2000 data the Itter data set seems more appropriate, is only of minor importance. The only difference between these two data sets is the in-stream removal rate, the influence of which is limited, as was shown in the EDTA scenarios.

In the case of boron, the background concentration determined in the 1993 study could directly be used in this study. Regarding the results at the sampling site Kirchberg (Inde river), the chosen value seemed to be realistic, which in turn confirms the correctness of the assumed geogenic origin of the chosen background concentration.

Another general trend that could be observed in almost all scenarios of the 1993 and 2000 studies is the fact that GREAT-ER generally underpredicts concentrations near the outlet of the catchment. This may suggest the existence of unknown additional input(s), besides the considered per-capita ones. Near the catchment's outlet, discrepancies can best be seen, since at this location all additional inputs are added, as long as they have not yet been eliminated from the water column.

All these presumptions could further be investigated, especially by collecting additional information for relevant industries discharging via the WWTPs. However, this is not done here, since within the context of this thesis, this is not necessary. If in a different context a more thorough understanding of, for example, the NTA and EDTA loads in the Rur catchment is desired, these next steps could be performed. In such a more detailed study, the validity of the monitoring data should also be ensured, since the monitoring data are only based on a few measurements sampled on two days in May 2000. The aforementioned possibility of a biased comparison of measurements and predictions is even more likely under these conditions. In addition, besides the uncertainty related to the monitoring, model simplifications exist, among them the way the environmental fate of substances in lakes is modelled.

6.4.3. Environmental fate of substances in lakes

There are large water reservoirs in the upper parts of the Rur catchment. A model designed for lakes would be required for adequate fate modelling. However, in GREAT-ER only a very rough model is implemented for lakes at present. This model is based on the GREAT-ER model for river stretches, since it also assumes one-dimensional transport and uniform horizontal and vertical mixing. Elimination is modelled by first estimating the residence time within the stretch which represents a lake and then calculating a one-dimensional spatial concentration profile based on the lumped first-order in-stream removal rate. The residence time is calculated by dividing the volume of water present in the lake by the outflow, i.e. it is calculated separately in each Monte Carlo shot based on the random number of the actual shot.

This approach neglects processes typically occurring in lakes, such as vertical mixing and the formation of temperature zones with only very little exchange processes. Also, in the deeper parts of lakes anaerobic conditions may occur, under which the degradability of some substances may be reduced or even inhibited. Furthermore, sedimentation is usually higher. Thus, an in-stream removal rate for rivers, which shall represent a combined rate accounting for the different elimination pathways, is probably not valid for lakes. For some surfactants this is discussed by AISE/CESIO (1996).

A model which assumes vertical transport processes by subdividing a lake into different layers with different environmental conditions was proposed by Ulrich (1991). He assumes a lake with constant volume, i.e. inflow equals outflow, and stratified layers at different depths. The number of layers and their heights can be altered. Elimination processes may be defined differently for the different layers. Also, the model handles different outflow rates for the different layers. Simulation results for NTA, EDTA, the solvent tetrachloroethylene (PER), and the herbicide Atrazin were compared to measurements taken from the Greifensee (Switzerland) in order to calibrate the model.

Such a model could in principle be incorporated into the GREAT-ER system. However, this requires large software modifications and extensions of data-structure. In addition, calibration of such a model requires monitoring data preferably from different water depths and from different lakes. Given the aim of this thesis, the integration of an appropriate lake model is not feasible here.

In order to apply the GREAT-ER lake model, the temporal distribution of the quantity of water present in a lake is needed. For some of the water reservoirs in the Rur catchment these data are available, i.e. for the Olef, Urft, Rur, Wehebach, and Obermaubach water reservoirs (WVER, 1996), while for the Perlenbach and Dreilägerbach water reservoirs this information is not available. However, as there are no known discharges above these two water reservoirs, this would not pose a problem. Therefore, in principle, the GREAT-ER approach of modelling lakes could be followed. However, in the Rur catchment the water reservoirs are modelled as rivers due to the following reasons.

Firstly, compared to the current GREAT-ER model this is a conservative approach, since in GREAT-ER the only difference in modelling the fate of chemicals in rivers and lakes is the calculation of the residence time. As mentioned above, the residence time in a stretch considered as lake is calculated by dividing volume by flow, whereas the residence time in a river stretch is derived by dividing length by velocity. The latter gives significantly shorter residence times, which is realistic, since the residence time in a lake is usually longer than in a river stretch. Also, sedimentation is higher in lakes. Thus, it is most likely that elimination is higher in lakes than in rivers. Of course, this only occurs for substances which are eliminated to some extent, i.e. for persistent substances such as boron the problem discussed here is not apparent.

Secondly, regarding the modelling of concentrations of detergent ingredients in the Rur catchment, the potential overprediction due to this conservative approach is not important. Looking at the results of GREAT-ER simulations performed in the Rur catchment shows that in those stretches representing lakes the concentrations are generally very low, i.e. near the background concentration if one is assumed or near zero if no background concentration is assumed. This is shown in Table 6.7 for all water reservoirs receiving discharges from upstream locations by comparing the minimal value, i.e. zero or the background concentration, and the predicted mean concentration near the outlet of the reservoir.

The table shows that the error introduced for the substances LAS, NTA, and AE due to the consideration of the water reservoirs as rivers instead of as lakes is always smaller than 1.6 μg/l. Therefore, as long as the GREAT-ER lake model is applied, neglecting that such a stretch is actually a lake does not lead to relevant changes in the results. For this reason, it was decided not to model lakes explicitly, since applying the GREAT-ER model would neither significantly influence the results nor improve the understanding of environmental processes.

Table 6.7.: **Mean GREAT-ER results in stretches representing water reservoirs.** Mean calculated and smallest possible concentrations (in μg/l) are given for one stretch of each reservoir.

Water reservoir	LAS		NTA		AE	
	Sim	Min	Sim	Min	Sim	Min
Rur	3.81	3	0.23	0	0.57	0
Urft	4.61	3	0.41	0	1.23	0
Obermaubach	3.78	3	0.22	0	0.48	0

6.5. Conclusions

The sufficient accordance between estimated and measured concentrations of detergent ingredients shown for the Rur catchment allows the application of the GREAT-ER model for an environmental evaluation of detergents using the GREAT-ER product mode. The discrepancies between predictions and monitoring data of NTA and EDTA show that it is more difficult to assess substances that are not primarily used in a wide-dispersive way.

Sensitivity of GREAT-ER results mainly depends on the emission data and the wastewater treatment, which determine the loads entering the surface water. The influence of in-stream removal is bound due to the open nature of each catchment and the dilution, which occurs for all substances regardless of their physico-chemical properties. This was shown in the case of EDTA. Since in the GREAT-ER product mode the per-capita consumptions are calculated, the wastewater treatment efficiency is the most important input parameter. Concerning an application of GREAT-ER within the context of ERA of substances, a sound emission estimate, i.e. concerning consumption data and wastewater treatment parameters, is most relevant. Thus, further research concerning emission scenarios should be conducted.

A further interesting aspect is the fact that substance data sets derived for other catchments can be transferred if only the per-capita consumption is adjusted, which was shown in the case of LAS. Data sets derived in the Itter catchment and in the other pilot study areas (ECETOC data set) could successfully be transferred to the Rur catchment. The fact that in the 1993 study application of the ECETOC data set leads to lower deviations, while in the 2000 study the Itter data set seems more appropriate, is only of minor importance since the only difference between these two data sets is the in-stream removal rate, the influence of which is limited due to the open nature of the GREAT-ER model. In addition, substance data sets appropriate for the Rur catchment could be identified for boron, LAS, AE, and AS. These data sets are used in the GREAT-ER product mode assesments.

When applying GREAT-ER as a valuation tool to compare chemicals, the open nature of the system must be kept in mind. A large fraction of the emitted load may leave the system. Especially for persistent substances, the fate and exposure in marine systems would therefore have to be considered. However, since expected environmental impacts of detergent ingredients more likely occur in freshwater systems near discharge sites rather than in oceans, neglecting impacts occurring outside of the system is not considered as a large problem. A more relevant aspect currently not adequatly assessed within GREAT-ER is sedimentation and the consideration of a sediment compartment.

7. Results of the product mode assessment

It was shown that GREAT-ER is able to predict observable environmental concentrations of detergent ingredients when using realistic consumption figures. For this reason, the GREAT-ER product mode is seen as an appropriate method for performing an aquatic fate assessment of detergents. In this chapter, results of the assessment of aquatic impacts of household laundry by using the GREAT-ER product mode are given.

First, results of the main Rur scenarios, are given, in which variabilities due to different use habits and products are analysed. Potential combined toxic effects of the detergent ingredients are also analysed. Then, the PRR_x evaluation is being done differently in order to reduce its sensitivity to single substances, which has become visible in the reference scenarios. Afterwards, in section 7.3, the influence of different catchments and catchment-specific parameters is analysed. Finally, the environmental relevance of the inorganic ingredients is analysed by comparing results from GREAT-ER product mode assessments with measurements of inorganic compounds.

In all scenarios, except for those related to the catchment comparison, the Rur catchment data set from 1993 is used. 2000 Monte Carlo shots are always performed, unless stated otherwise. Since the results are very numerous, a first discussion of the results is already performed in this chapter. In addition, at the end of each analysis of section 7.1, the central results are repeated for easier understanding.

7.1. Main Rur scenarios

In this first series of calculations, the PLA scenarios are assessed by initially analysing the reference scenarios, which are based on the model households as defined in the PLA (see Table 4.2), and subsequently performing simulations of all permutations of use habits and products, both assuming dosages according to products and use habits. It should be noted that in the Rur catchment there are 3174 stretches, 1561 of which are downstreams from WWTP effluents. The average stretch length is 313 m.

7.1.1. PLA reference scenarios

These scenarios are influenced most by consumer choices, since the dosage, amount of laundry, laundry per wash, and detergent are chosen by the consumer. With these scenarios, the contributions of both product formulations and use habits to the total critical length can be determined. In addition, the most important substances can be identified. In Table 7.1, the number of stretches in which PRR_{90}s exceed the given values by at least one substance are summarised.

Table 7.1.: **PRR_{90} evaluation of the reference scenarios** The number of stretches in which the PRR_{90} are exceeding the given values are listed.

Use habit	PRR_{90}				Detergent
	>1	>0.1	>0.01	>0.001	
Smart	0	15	676	1,542	3-component system
Wishy-Washy	77	1,249	1,559	1,561	Compact heavy-duty
Scrubbed	441	1,528	1,560	1,561	Heavy-duty

PRR_{90} evaluation

The three scenario results show significant differences. Assuming the Smart use habit PRR_{90}s do not exceed 1 in any stretches. Furthermore, only in 15 stretches, i.e. less than 1% of all loaded stretches, they exceed 0.1. On the contrary, the Scrubbed use habit leads to PRR_{90}s that are larger than 1 in 441 stretches. In addition, in 1528 stretches, i.e. 98% of all affected stretches, the PRR_{90}s are larger than 0.1. The Wishy-Washy use habit produces results that are between the other two use habits.

Further analysing the results reveals a strong dependence on the bleaching agent, since in the cases of the Wishy-Washy and Scrubbed use habits the boron content entirely determines the number of stretches exceeding the different chosen thresholds for all stretches. Besides boron, the surfactants LAS, AE, and AS have the highest PRR_{90}s. Since the 3-component system neither uses boron nor LAS, in the Smart calculation AE is the most relevant substance, followed by AS, and sodium carbonate.

The results demonstrate a high sensitivity of the approach. The PRR_{90} results may be dominated by a single substance, as here the case with boron. If an analysis only intends to compare product alternatives as they are, this sensitivity is acceptable. However, if the analysis aims to identify options for product improvements rather than to perform a simple ranking of alternatives, this sensitivity is disturbing. For this reason, in section 7.2 the product risk ratio approach will be slightly altered to receive further insights from this threshold evaluation.

CL evaluation and comparison with the PLA

The critical lengths (CLs) are based on the ‘less-is-better’ paradigm. Table 7.2 shows the CLs of the different scenarios based on the mean concentration increases together with the contributions of the different ingredients and detergent components. In addition, the main results of the PLA are given. Finally, the result variabilities, defined as ratio of the largest and smallest values, are also given. These ratios are important figures, since they explain the variability of the total CLs. The table is subdivided for easier understanding.

Table 7.2.: **CLs of the reference scenarios**. Some Max/Min ratios can not be calculated due to division by zero. Electricity consumption does not consider drying. The PLA results are per year.

Use habit	Smart	Wishy-Washy	Scrubbed	Max/Min
Product	3-component system	Compact heavy-duty	Heavy-duty	-
Dosage (g)	72.3	103	175.1	2.4
Annual detergent cons. (kg/cap)	3	8.3	22.1	7.4
CL (m)	7,836	112,826	279,267	35.6
CL/ann. det. cons. (m·cap/kg)	2,613	13,610	12,637	4.8
PLA results (per capita and year)				
Electricity (kWh)	16.6	53.9	101.2	6.1
Water (m^3)	2.5	4.0	5.7	2.3
CO_2 (kg)	17.3	70.8	198.7	11.5
Acid. equiv. (g)	61.9	190.3	504.4	8.2
VOCs (g)	70.8	230.1	619.5	8.8
CL per substance (m)				
LAS	-	5,992	18,880	-
AS	930	1,203	3,545	3.8
Soap	58	26	81	3.2
AE	4,457	4,724	10,556	2.4
Zeolite A	488	714	1,806	3.7
Polycarboxylates	-	116	302	-
Sodium silicates	97	209	531	5
Sodium carbonate	1,771	4,143	8,174	4.6
Sodium sulphate	2	150	3,178	1,387.6
Sodium citrate	1	6	-	-
Boron	-	94,685	230,447	-
DAS-1	<0.5	778	1,665	-
CMC	33	73	99	3.0
DAED	<0.5	76	4	24.7
PVP	-	-	-	-
CL per detergent component (m)				
Anionic surfactants	988	7,220	22,506	22.8
Bleaching	138	94,693	230,451	1,671.3
Builder	586	1,046	2,640	4.5

The CLs for the three scenarios vary by a factor of 35.6. This is a larger variation than the variation of the PLA results, which is always below a factor of 11.5. The different variabilities of the PLA results is due to the fact that electricity consumption is given without considering the drying step (Grießhammer et al., 1997, p. 103), while the CO_2 emissions and acidification equivalents as well as the VOC score also consider variabilities in drying.

Variabilities of the annual detergent consumption and of the CLs show the influence of use habit versus choice of detergent. The first variability reflects the influence of use habits, as they determine the annual mass of detergent used. This value has a linear influence on the CL variability. Thus, the ratio of CL and annual detergent consumption is a combined descriptor for the detergent formulation, the catchment characteristics, the simulation model and the implicite weighting performed in the CL aggregation. The variability of these ratios is 4.8 and thus smaller than the variability due to varying use habits. It should be mentioned that the definitions of the use habits largely determine this result, which have not been derived from purely scientific knowledge.

There is one conceptual difference in PLA results and the CL that is worth mentioning. In Table 7.2, all data are based on a per-capita evaluation, which implies that transfer to a household-based evaluation increases the PLA results by the average household size, which is 2.26 (Grießhammer et al., 1997, p. 153). However, the CL results are invariant to this transformation. Therefore, comparing the PLA and CL results should only be based on a comparison of the results variabilities, since these are invariant to the transformation from household to capita. Still, the main advantage of the CL evaluation is the possibility to analyse the results with respect to the contributions of the different ingredients.

Dominance of boron

The most important substance is boron, which was already pointed out in the PRR_x evaluation. This outcome suggests separating coloured and white laundry, which is a possibility for the consumer to reduce emissions, while the choice of bleaching agent is controlled by the producers. Please note that the row 'Bleaching' combines the bleaching agent and DAED. The large variability of the bleaching agents' results reflects the fact that in the Scrubbed and Wishy-Washy scenarios a bleaching agent is included in each wash, while in the Smart scenario the bleaching agent sodium percarbonate is only used in 15% of the cycles.

Influence of surfactants

Apart from boron, the surfactants are the most relevant substances. For example, the percentual contribution of LAS and boron in the Wishy-Washy and Scrubbed scenarios is larger than 89%. The CLs of the anionic surfactants vary by a factor of 23, which is caused by both emitted mass and substances used. Dividing the CL variability of the anionic surfactants by the variability of the annual detergent consumptions, which exclusively reflects the use habits, gives a value of 2.5. Thus, the use habits have a larger influence on the variability of the anionic surfactants than the product formulations.

Variability of the nonionic surfactant AE is very small. However, AE is relevant with regard to the total CL. Furthermore, the importance of AE becomes apparent in section 7.3.2.

Analysis of additional ingredients

The highest max/min ratio of a single substance occurs for sodium sulphate, which is, however, not of prime importance due to its limited contributions observable in the three scenarios. On the other hand, the builders do not vary significantly. This emphasises that large room for improvement cannot be expected, when only taking into account those builders that are considered.

For some substances, the span between the scenarios cannot be calculated, since they are not present in all formulations. However, when an optical brightener is used it contributes only marginally to the total CL, since the contribution of the optical brightener DAS-1 is either 0.7 or 0.6%. This small share has not been expected, especially since a worst-case estimate was performed using DAS-1 as the only optical brightener. Finally, sodium carbonate contributes considerably to the total CL. However, since the application of an ecotoxicity criterion for this substance seems questionable, carbonate is further analysed in section 7.4.

Summary of main results

Summarising, the main results of this first analysis are the dominance of boron, the importance of the surfactants LAS and AE, the fact that the use habits influence the total CLs stronger than the product formulations, and the observation that the PRR_x evaluation can be dominated by a single substance. It should further be noted that the variabilities of the PLA results is much lower than the variability of the total CLs.

7.1.2. Comparison of products - Dosage according to product

This analysis examines the differences in the results due to the use of four different product alternatives. In this first part, dosage according to the product information is assumed, while afterwards the influence of inappropriately dosing is investigated. Dosage according to the product information entirely assesses the differences in the outcomes due to product formulations. The results are therefore primarily relevant for the producer, who is responsible for the formulations.

In Table 7.3, the PRR_{90} evaluations assuming the dosage according to the product are given.

PRR_{90} evaluation

The number of stretches in which the PRR_{90} of at least one substance exceeds 1 varies significantly. A clear distinction can be seen between the 3-component system and tandem system on the one hand, and the two remaining alternatives on the other. In addition, a further distinction between the heavy-duty and compact heavy-duty detergents is apparent. This is a similar result to that stated in the PLA (Grießhammer et al., 1997, p. 14).

The sensitivity of the PRR_x approach mentioned previously is clearly visible when comparing the results of the tandem system and of the compact heavy-duty detergent. The main difference between these alternatives is the fact that in the colour compact detergent, that is used 85% of the times in the tandem system, no bleaching agent is contained. When only using the compact heavy-duty detergent instead, boron is used in each wash, which then dominates the PRR_x results.

In addition, it can be seen that a PRR_x between 1 and 0.1 gives the strongest differentiation.

Table 7.3.: **PRR_{90} evaluation of the product comparison (dosage according to product)**

Product	PRR_{90}				Use Habit
	>1	>0.1	>0.01	>0.001	
3-component system	0	15	668	1,542	Smart
Tandem system	1	34	1,080	1,559	Smart
Compact heavy-duty	11	794	1,556	1,561	Smart
Heavy-duty	28	1,093	1,558	1,561	Smart
3-component system	1	56	1,115	1,559	Wishy-Washy
Tandem system	1	172	1,312	1,560	Wishy-Washy
Compact heavy-duty	42	1,141	1,559	1,561	Wishy-Washy
Heavy-duty	163	1,309	1,560	1,561	Wishy-Washy
3-component system	1	166	1,273	1,560	Scrubbed
Tandem system	2	412	1,430	1,560	Scrubbed
Compact heavy-duty	173	1,312	1,560	1,561	Scrubbed
Heavy-duty	402	1,423	1,560	1,561	Scrubbed

CL evaluation and comparison to PLA results

CL only allows for a relative comparison. When using the dosage according to the products, the use habits are only varying with respect to the number of washes, being the ratio of total amount of laundry and laundry per wash. This implies that the different use habits are only a linear factor, which can be cancelled out. Therefore, only results for one use habit are given in Table 7.4; in this case Smart was arbitrarily chosen.

Smaller variations can be found compared to the reference scenarios: the CLs only vary by a factor of 9.9. This decrease of variability has been expected, since the variation of this compound is entirely caused by the product formulations, while in the reference scenarios the use habits further increase the variability. The order of the product alternatives is the same as in the PLA, i.e. the heavy-duty detergent has the largest CL, followed by the compact heavy-duty detergent, the tandem system, and finally the 3-component system. However, when looking at the absolute CLs of the single substances, it can be seen that the ranking of the compact heavy-duty detergent and the tandem system is only due to the fact that the latter uses bleaching agent in only 15% of the cycles. For most of the substances the tandem system has a higher CL than the compact heavy-duty detergent.

Table 7.4.: **CLs of the product comparison (dosage according to product)**

Product	Heavy-duty	Compact heavy-duty	Tandem system	3-component system	Max/Min
Dosage (g/wash)	146	89	86.5	73.7	1.98
CL (m)	78,133	51,642	16,483	7,922	9.86
EU-Points	39	63	66	72	-
PLA results (g/wash)					
CO_2	241	161	150	137	1.8
Acid. equiv.	1.6	1.1	1.2	1.1	1.5
VOCs	1.3	0.9	1.0	1.0	1.4
CL per substance (m)					
LAS	5,074	2,643	3,458	-	-
AS	962	523	704	967	1.9
Soap	23	11	24	58	5.25
AE	2,893	2,101	3,366	4,462	2.1
Zeolite A	491	298	431	488	1.7
Polycarboxylates	84	53	61	-	-
Sodium silicates	143	92	69	104	2.1
Sodium carbonate	2,249	1,850	1,659	1,806	1.4
Sodium sulphate	896	68	107	2	386.3
Sodium citrate	-	3	8	1	-
Boron	64,830	43,613	6,444	-	-
DAS-1	459	351	4,693	-	-
CMC	27	33	24	35	1.4
DAED	1	3	1	<0.5	11.0
PVP	-	-	81	-	-
CL per detergent component (m)					
Anionic surf.	6,060	3,178	4,187	1,025	5.9
Bleaching	64,832	43,616	6,445	141	461.1
Builder	717	446	570	593	1.6

Compared to the CL variability, the PLA results vary only very little. They only refer to the production of the detergent. Therefore, they mainly depend on differences in the dosage. However, these results do not reflect potential impacts on the aquatic ecosystems. In the PLA, these are assessed using the EU points scheme. According to this scheme, at least 63 points are necessary to aquire the ecolabel[1], which is fulfilled by all alternatives except the heavy-duty detergent. Taking into account the large influence of boron, the nearly identical scores of the tandem system and the compact heavy-duty detergent seem questionable.

Influence of bleaching agent

The CLs of the bleaching components vary by a factor of 461. As previously mentioned, this is determined by the choice of having a bleaching agent either in any wash (heavy-duty and compact heavy-duty) or only in those washes where it is necessary (tandem system and 3-component system). In addition, by comparing the CLs of the different bleaching components of the tandem system and the 3-component system it can be seen that also the type of bleaching agent plays a role. This is not observable in the reference scenarios. It should be noted that in the 3-component system, the bleaching agent is a part of the sodium carbonate fraction.

The bleaching activator TAED, from which a small fraction enters the surface waters in the form of DAED, turns out not to be relevant. Therefore, the decision to choose a bleaching agent should not depend on the question whether one or the other alternative needs TAED in the formulation.

Significance of surfactants

Besides the bleaching agents, surfactants are most relevant in determining the CLs. The anionic surfactants vary by a factor of 6, which is determined by the CLs of the alternatives heavy-duty (maximum) and 3-component system (minimum). Comparing the heavy-duty detergent and the 3-component system shows that they give similar results for AS. However, the main anionic surfactant used in the heavy-duty detergent is LAS, which accounts for 83.7% of the anionic surfactants of this alternative. On the contrary, LAS is not contained in the 3-component system. The results suggest that the variability of the anionic surfactants is partly compensated by the one of AE, whose CL is larger in the 3-component system scenario than in the heavy-duty detergent scenario. The results also show that AS has in general a lower CL than LAS. With respect to the substance data used, this was expected.

Further ingredients

Similar to AE, the CLs of the builders show only moderate variation of a factor of 1.6. Sodium carbonate is relevant for all product alternatives. In the 3-component system the bleaching agent sodium percarbonate also contributes to the CL of sodium carbonate. Considering this, the CLs of sodium carbonate present in the detergent are almost the same for the 3-component and tandem systems, whereas for the other two alternatives it is higher.

[1]It should be mentioned that the criteria applied therein refer to the first implementation of the scheme (European Union, 1995). This was updated three years later which led to the same criteria but with different threshold values (European Union, 1999a).

The optical brightener DAS-1 has only limited influence on the CL. It is much more relevant than, for example, TAED, but only of minor importance compared to more relevant ingredients. Variance between coloured and white laundry is also visible in the DAS-1 results, since it is not used in detergents for coloured laundry.

Summary of main results

Main results of this comparison are the limited variability of the product alternatives, the importance of the decision to distinguish between white and coloured laundry, the importance of the substances used for bleaching and as anionic surfactants, and the fact that AS is environmentally superior to LAS.

7.1.3. Comparison of products - Dosage according to use habit

In this section, a comparison of the product alternatives is made assuming that the detergent is dosed according to the use habits, i.e. not as recommended on the product. It focuses therefore on the uncertainty introduced by the consumer, who may not apply the recommended dosage but who may dose ‘as always’. This puts into perspective the results of the dosage according to product scenarios, since it cannot be expected that all consumers behave according to informations provided on the products.

Again, the comparison of the PRR_{90}s has to include all use habits due to the absolute nature of this value, whereas the comparison of the CLs can be done by looking at only one use habit. Again, the Smart use habit is chosen for comparing the CLs. In Table 7.5 the number of stretches in which PRR_{90}s of at least one substance exceed the different thresholds are given, whereas in Table 7.6 the CLs are listed.

PRR_{90} evaluation

Variabilities between the different product alternatives decrease compared to the previous analyses, which is due to the fact that the recommended dosages, which are product attributes, are replaced by use habit dosages, which are not product attributes. Regarding the number of stretches with a PRR_{90} exceeding 1 or 0.1, one can again clearly distinguish between the 3-component system and tandem system on the one hand and the other two alternatives on the other. Regarding stretches with PRR_{90}s exceeding 0.01, this differentiation is only visible for the Smart use habit.

Change in ranking

The second major observation is the fact that the heavy-duty detergent generally turns out to be slightly better than the compact heavy-duty detergent, which is due to wrong dosage. The compact heavy-duty detergent is designed to give the same washing performance as the heavy-duty detergent using a smaller amount of detergent. As the ingredients of both alternatives are nearly the same, this can only be achieved by 1) reducing those ingredients that are not responsible for the main washing functions, e.g. sodium sulphate, and 2) by optimising the relationships between the ingredients. In fact, those substances that are most important for the washing process are also most relevant in terms of potential aquatic ecotoxicity, i.e. boron and the surfactants. Thus, applying the same dosage when considering the two detergents leads to higher emissions of those substances which are environmentally most relevant in the compact heavy-duty scenario. This demonstrates the sensitivity of emission estimates in a comparison of products. It also emphasises the need for a sensitivity analysis of varying consumer behaviour in a comparison of detergents, as being done in this section.

Table 7.5.: **PRR_{90} evaluation of the product comparison (dosage according to use habits)**

Product	PRR_{90}				Use Habit
	>1	>0.1	>0.01	>0.001	
3-component system	0	15	676	1,542	Smart
Tandem system	0	26	884	1,558	Smart
Compact heavy-duty	4	630	1,538	1,560	Smart
Heavy-duty	3	576	1,535	1,560	Smart
3-component system	1	139	1,252	1,560	Wishy-Washy
Tandem system	1	259	1,321	1,560	Wishy-Washy
Compact heavy-duty	77	1,249	1,559	1,561	Wishy-Washy
Heavy-duty	47	1,199	1,559	1,561	Wishy-Washy
3-component system	10	578	1,532	1,561	Scrubbed
Tandem system	11	769	1,547	1,561	Scrubbed
Compact heavy-duty	480	1,535	1,560	1,561	Scrubbed
Heavy-duty	441	1,528	1,560	1,561	Scrubbed

CL evaluation

As was already observable in the PRR_x table, the differences between the product alternatives have decreased. The CLs vary by only a factor of 5.4, which is rather small compared to the factor of 9.9 by assuming recommended dosage or to the factor of 35.6 in the reference scenarios, respectively. In addition, as in the PRR_x evaluation, the CL of the compact heavy-duty detergent is larger than of the heavy-duty detergent, caused by the fact that, due to the equal dosage applied in these scenarios, larger amounts of surfactants and bleaching agent are used in the compact heavy-duty scenario than in the heavy-duty one.

Despite the fact that also the 3-component and tandem systems are overdosed, their total CLs are smaller than those of the heavy-duty and compact heavy-duty detergents. This shows that the formulations also significantly influence the results. The PLA results have been derived on the basis of the results given in the PLA. Again, they only refer to the production of the detergent. Assuming equal dosage leads to very similar results for the different alternatives. The ranking of the alternatives has even changed, which only shows that the production of the different ingredients causes different emissions. This shows, that the LCA performed in the PLA mainly considered the production of the ingredients. It also shows that an assessment as conducted in the PLA is not sufficient for the evaluation of detergents.

Table 7.6.: **CLs of the product comparison (dosage according to use habits)**

Product	Heavy-duty	Compact heavy-duty	Tandem system	3-component system	Max/Min
Dosage (g/wash)	72.3	72.3	72.3	72.3	1.0
CL (m)	38,057	42,376	13,898	7,838	5.4
PLA results (g/wash)					
CO_2	119.3	130.8	125.4	134.4	1.1
Acid. equiv.	0.8	0.9	1.0	1.0	1.3
VOCs	0.7	0.8	0.8	1.0	1.4
CL per substance (m)					
LAS	2,531	2,188	2,864	-	-
AS	470	426	585	930	2.2
Soap	11	8	21	58	6.9
AE	1,381	1,706	2,861	4,457	3.2
Zeolite A	243	248	373	488	2.0
Polycarboxylates	39	43	50	-	-
Sodium silicates	72	77	58	97	1.7
Sodium carbonate	1,105	1,504	1,373	1,771	1.6
Sodium sulphate	444	54	87	2	193.8
Sodium citrate	-	2	7	1	-
Boron	31,519	35,810	5,488	-	-
DAS-1	229	281	38	-	-
CMC	13	27	20	33	2.6
DAED	1	3	<0.5	<0.5	8.7
PVP	-	-	70	-	-
CL per component (m)					
Anionic surf.	3,011	2,622	3,471	988	3.5
Bleaching	31,519	35,812	5,489	138	259.7
Builder	354	370	489	586	1.7

With respect to the single substances, it can be seen that the variabilities have decreased. This decreased variability is entirely caused by the different formulations, not by the combination of formulation and dosage, since a constant dosage is assumed in this assessment. However, those substances having large variabilities in the previous analyses again have the largest variabilities.

Summary of main results

The main result of this analysis is the observation, that a ranking of detergents may change if these are not used as recommended. In addition, the results of the 3-component system show that also the formulation is important in determining the results, since this alternative always has the best results.

7.1.4. Mixture toxicity

In section 3.3, it is described that by assuming additive toxicity the sums of the product risk ratios of the different ingredients of a product describe the combined product risk of this scenario. This is applied in this subsection by deriving mixture product risk ratios from the results of the three reference scenarios and a fourth scenario assuming the Wishy-Washy use habit in combination with the Tandem system. Table 7.7 shows the number of stretches (from those 1561 loaded) in which the mixture product risk ratios exceed 1.

Table 7.7.: **Mixture toxicity assessment of reference scenarios** Number of stretches in which the mixture product risk ratios are larger than 1.

Scenario	All substances	Excluding boron	Only surfactants
Smart	1	1	1
Wishy-Washy + Tandem	11	7	3
Wishy-Washy	126	3	2
Scrubbed	539	25	14

By comparing the first two columns the large influence of boron becomes apparent. Not considering boron gives that the sum of the product risk ratios are larger than 1 in only 1.6% of the stretches even in the Scrubbed scenario, while when considering boron, this is the case in 34.5% of the stretches. The assessment of mixture toxicity is therefore also dominated by the use of boron. The relevance of the surfactants on the other hand is limited which is visible in the last column of Table 7.7.

7.2. Differentiating the number of substances in the PRR$_x$ evaluation

It has been shown that the PRR$_x$ may be dominated by the most significantly contributing substance. Therefore, if this substance were replaced by a less relevant one, the results may change dramatically. To account for this sensitivity, the number of substances exceeding the different PRR$_x$s in the different stretches are investigated in this section. This can directly be obtained by counting the stretches differently. This analysis also aims to determine the number of substances relevant in this assessment.

In the following three tables the number of stretches are given, for which the PRR$_{90}$s of different numbers of substances exceed 1 (Table 7.8), 0.1 (Table 7.9), and 0.01 (Table 7.10). This is done for the three reference scenarios and for a fourth scenario, in which the Wishy-Washy use habit is applied in junction with the tandem system. The calculations were performed for the Rur catchment.

With respect to the number of stretches in which PRR_{90}s exceed 1, the results of all scenarios are dominated by just one substance. The numbers of stretches exceeding a PRR_{90} of 1 for more than 1 substance are negligible. Even in the Scrubbed scenario the PRR_{90}s exceed 1 for a second substance in only 8 stretches, i.e. 0.5% of all loaded stretches. This finding corresponds well with the analysis of the CLs showing a major relevance for only very few substances (Table 7.2). In fact, boron dominates the results.

Table 7.8.: **Number of stretches with PRR_{90}s exceeding 1**

Scenario	Number of substances					
	1	2	3	4	5	6
Smart	0	0	0	0	0	0
Wishy-Washy + Tandem system	1	1	1	0	0	0
Wishy-Washy	77	1	0	0	0	0
Scrubbed	441	8	1	1	0	0

Regarding the number of stretches in which PRR_{90}s of 0.1 are exceeded (Table 7.9), still a limited number of substances is significant. However, this number is larger than 1. For example, using the Scrubbed scenario the PRR_{90}s are at least 0.1 for 3 substances in 108 stretches. When using the tandem system, this is the case in 36 stretches. It can be observed that more substances appear to be relevant in the tandem system scenario than in the compact heavy-duty detergent scenario (Wishy-Washy). This is due to the fact that in the compact colour detergent used in 85% of the washes more surfactants are present than in the compact heavy-duty detergent, whereas the results of the latter are entirely dominated by boron. The most relevant substance of the 3-component system (Smart use habit) is AE.

Table 7.9.: **Number of stretches with PRR_{90}s exceeding 0.1**

Scenario	Number of substances					
	1	2	3	4	5	6
Smart	15	2	1	0	0	0
Wishy-Washy + Tandem system	259	83	36	8	4	1
Wishy-Washy	1,249	53	21	9	3	1
Scrubbed	1,528	271	108	42	20	3

An increasing number of substances becomes relevant, when evaluating the results on the basis of the number of stretches in which the PRR_{90}s exceed 0.01. Assuming the Scrubbed use habit, in about a third of the loaded stretches the PRR_{90}s of at least 6 substances exceed

0.01. If the tandem system is applied according to the Wishy-Washy use habit, this is the case in 63 stretches, i.e. in 4% of the loaded stretches.

Table 7.10.: **Number of stretches with PRR_{90}s exceeding 0.01**

Scenario	Number of substances						
	1	2	3	4	5	6	10
Smart	676	397	103	20	2	1	0
Wishy-Washy + Tandem system	1,321	1,099	880	616	243	63	1
Wishy-Washy	1,559	925	688	608	162	42	1
Scrubbed	1,560	1,305	1,219	1,107	625	523	3

The number of substances regarded as relevant depends on the chosen PRR_x percentile, i.e. 90 is chosen in this thesis, the chosen threshold, in this case 1, 0.1 or 0.01, and on the percentage of stretches in which the PRR_{90}s are exceeding the chosen threshold. In Table 7.11, the substances are given that are relevant when arbitrarily choosing that thresholds may be exceeded in 5% of the stretches, which is equivalent to 78 stretches. The substances are given differentiated for the PRR_{90} thresholds 1, 0.1, and 0.01.

Table 7.11.: **Substances regarded as relevant in the Rur catchment.** The relevance is defined by the three thresholds 1, 0.1 and 0.01, a results percentile of 90 and the stretch percentile of 5.

Scenario	Relevant substances based on PRR_{90}s larger than		
	1	0.1	0.01
Scrubbed	Boron	AE, LAS, sodium carbonate	AS, DAS-1, zeolite A, sodium sulphate
Wishy-Washy +Tandem system	-	Boron, LAS	AE, sodium carbonate, AS
Wishy-Washy	-	Boron	AE, LAS, sodium carbonate, AS
Smart	-	-	AE, sodium carbonate, AS

The table clearly shows the most relevant substances. When taking as reference the number of stretches in which the PRR_{90}s exceed 0.001, the results of which are not shown here, only DAED and sodium citrate turn out not to be relevant.

7.3. Comparison of catchments

Results analysed so far have all been derived from calculations performed in the Rur catchment. However, some factors that influence the results vary from region to region. For example, one important factor that varies between different countries is the way in which wastewater is treated. Also, the formulations and fractions of cycles performed at different temperatures vary between different countries. Further variable factors are the sizes of the washing machines and the dosage per wash as well as average detergent consumption.

A country-based assessment of energy consumptions and requirements as well as water consumption of washing machines has been performed by the Group for Efficient Appliances (1995), where distinctions between the types and sizes of washing machines and use habits, such as temperature and number of washing cycles, were made. Internal LCA studies conducted by Henkel KGaA investigated variabilities of washing machines, use habits, dosage, and national energy scenarios (Gutzschebauch and Klüppel, 1998). However, known LCA and ERA studies do not explicitly analyse the influence of different types of wastewater treatment facilities.

In this section, the influence of parameters that vary between different catchments are analysed. In order to identify the contributions of the different parameters, this analysis is sub-divided into three parts, each investigating a specific aspect. In the first part, three methods of wastewater treatment are compared by keeping all other parameters constant. This analysis is conducted in just one catchment. Then, a product comparison is conducted for the different catchments currently available in the GREAT-ER database. In this analysis, besides the differing wastewater treatment facilities the mean number of washes are country-specific, while the dosage relates to the product. Finally, the dosage is derived from mean detergent consumption in the different European catchments and the influence of varying dosage is investigated.

Catchments currently included in the GREAT-ER database are located in England, Italy, Belgium, and Germany. Concerning the way in which wastewater is treated, three options are relevant: i) primary settler only which is relevant for Belgium, ii) trickling filter plants, which are mainly used in England, and iii) activated sludge type plants, which are used in the Italian and German catchments.

7.3.1. Comparison of different wastewater treatment options

In order to assess the influence of the types of WWTPs, three product scenarios have been defined in the Rur catchment, in which the WWTP types of all discharge sites have been altered. Thus, in the first scenarios all WWTPs are of type primary settler (PS), in the second of type PS and activated sludge (AS+PS), and in the third scenario of type PS and trickling filter (TF+PS). In all scenarios, the Wishy-Washy use habit and the tandem system are used by assuming the recommended dosage, i.e. 86.5 g per wash. The AS+PS scenario is identical to the scenario in the product comparison (section 7.1.2), which assumes the tandem system and the Wishy-Washy use habit.

The results are analysed by comparing the different critical lengths (CL) and product risk ratios (PRR_x), the former being based on mean concentration increases, while the latter is based on the 90 percentiles. In Table 7.12, the number of stretches are given in which the PRR_{90}s are larger than 1 for a different number of substances. Therefore, the previously analysed sensitivity in the PRR_x evaluation is accounted for. Table 7.13 shows the results of the critical lengths calculations, differentiated for the different substances and components.

Table 7.12.: **Number of stretches with PRR_{90}s exceeding 1 by assuming different WWTP types**

WW treatment	Number of substances 1	2	3	4	5
AS + PS	1	1	1	0	0
TF + PS	51	35	2	1	0
PS only	679	375	53	1	1

Table 7.13.: **CLs in the Rur catchment assuming different WWTP types**

	Wastewater treatment type AS+PS	TF+PS	PS only	Max/Min
CL (m)	38,000	160,352	824,122	21.7
Per substance (m)				
LAS	7,906	50,517	260,680	33.0
AS	1,646	10,506	58,585	35.6
Soap	54	341	2,331	43.0
AE	7,799	80,211	48,0342	61.6
Zeolite A	1,021	2,010	3,392	3.3
Polycarboxylates	142	297	1,597	11.2
Sodium silicates	158	135	134	1.2
Sodium carbonate	3,764	3,174	3,273	1.2
Sodium sulphate	242	209	204	1.2
Sodium citrate	20	17	666	40.0
Boron	14,898	12,631	12,395	1.2
DAS-1	105	86	232	2.7
CMC	56	51	62	1.2
DAED	1	1	41	39.1
PVP	187	164	188	1.1
Components (m)				
Anionic surf	9,606	61,364	321,596	33.5
Bleaching	14,899	12,632	12,436	1.2
Builders	1,341	2,459	5,789	4.3

The influence of the wastewater treatment facilities is significant. When assuming WWTPs with only a primary settler technique, the number of stretches in which the PRR_{90}s are larger than 1 is considerable, i.e. 43.5% in the first column. On the contrary, in AS+PS scenario, only in one stretch a PRR_x exceeds 1. The results of the trickling filter scenario lie between those of the other two scenarios.

The CL evaluation of the WWTP options shows a variation of a factor of 21.7. This is a smaller variation than in the reference scenarios (factor of 35.6), but a larger variation than that due to either products or use habits. Variability is mainly caused by the increasing influence of surfactants due to decreasing WWTP efficiency.

7.3.2. Product comparison in different catchments

It was shown, that the way in which wastewater is treated plays a significant role. Therefore, it is interesting to see whether relative rankings of the detergents vary in different regions that have specific wastewater treatment facilities. For this reason, a product comparison of the four model detergents is repeated for different catchments by assuming recommended dosage. The reason behind is to 1) investigate whether product rankings differ from region to region and 2) analyse the influence of other geographical parameters besides wastewater treatment. This is achieved by performing product comparisons in the catchments Itter, Rur (both Germany), Rupel (Belgium), Lambro (Italy), and Aire (United Kingdom). In this assessment, different numbers of washes are assumed for the different catchments, which are based on a statistical analysis of the washing habits in different European countries (Gutzschebauch, 1999). In this survey, the average numbers of washes per year and person were compiled for the member states of the European Union. The average number of washes per capita are 88 in Belgium, 80.6 in Germany, 74 in Italy, and 108.5 in the United Kingdom. Assuming recommended dosage allows for a product comparison for different catchments based on the average number of washes.

Since the product ranking is analysed, CL evaluations are sufficient. Except for the Rur and Rupel catchments, the data sets are all given on the GREAT-ER 1.0 CD (ECETOC, 2000). The Rupel data set was integrated as first Belgian GREAT-ER case study (Verdonck et al., 1999). Since the catchments differ with respect to size and population density, the calculated critical lengths are normalised by the population living and discharging into the catchment, thus giving the critical length per capita.

In Table 7.14, normalised critical lengths of the four product alternatives for the different catchments are given. Column WWTP indicates the way in which wastewater is treated. In principle, different techniques may exist within a catchment. However, in the considered catchments, this has not been the case. The CLs are based on mean values of all input parameters. This assures the exclusion of variabilities caused by variable or uncertain parameters.

The variabilities of the results are very large. For example, with respect to the 3-component system it is 3 orders of magnitude. In addition, the ranking has changed in the Rupel catchment. In this catchment, the compact heavy-duty detergent receives the lowest CL, whereas in all other catchments the heavy-duty detergent receives the lowest score. The reason for this is discussed below Table 7.15. A further core result is the fact that the CLs of the different products are much less variable in the Rupel catchment than in those with activated sludge WWTPs. Furthermore, the three catchments in which wastewater is treated in activated sludge type plants show very similar results.

Table 7.14.: **Normalised CLs of model detergents in different catchments assuming average country-specific numbers of cycles**

Catchment	WWTP	Heavy-duty	Compact heavy-duty	Tandem system	3-component system	Max/Min
Rupel	PS	1.552	0.975	1.280	1.145	1.59
Rur	AS+PS	0.111	0.074	0.024	0.012	9.29
Itter	AS+PS	0.097	0.064	0.025	0.012	8.11
Lambro	AS+PS	0.013	0.009	0.003	0.001	8.99
Aire	TF+PS	0.072	0.046	0.039	0.030	2.40

A comparison of the Itter and Rur catchments shows that the influence of geographical parameters apart from wastewater treatment, i.e. population density or the residence time in the catchment, are of minor importance. Although the Itter catchment is a small and very densely populated catchment, while the Rur catchment is less influenced by anthropogenic activities, the normalised critical lengths are almost the same. This is an interesting result with respect to the question as to whether it is sufficient to use a reference catchment for each country in such an assessment.

A comparison between the three catchments that have activated sludge plants shows larger differences: The CLs in the Lambro catchment are significantly lower than in the two German catchments. Two reasons seem plausible, which most likely both contribute to this result. First, the country-specific number of washes is smallest in Italy. Second, all WWTPs are connected to the main river, the Lambro. For this reason, the dilution ratios below the discharges are higher than in both Rur and Itter catchments, due to which the predicted concentration increases are in general lower in the Lambro river. The variabilities in the use habits will be further investigated in the following section. In the Aire catchment the ranking is the same as in the German and Italian catchments, but variability has decreased and the per-capita CLs are significantly higher. The reason for the different ranking of the products observed in the Rupel catchment can be investigated with the help of Table 7.15, in which the percentual contributions of the relevant ingredients, i.e. the surfactants and boron, are given.

Influence of AE

It can clearly be seen that the different ranking in the Rupel catchment shown in the previous table is mainly caused by the nonionic surfactant AE. The contributions of AE to the normalised CLs is much larger in the Rupel catchment than in the other catchments, which is true for all detergent formulations.

AE undergoes only limited elimination in the primary settler, while it is efficiently removed from the water column in biological wastewater treatment plants (Matthijs et al., 2000, see also section 4.5). As the AE precentage in the compact heavy-duty detergent is significantly lower than in the other product alternatives, in the Rupel catchment this alternative has a smaller CL than both the tandem and the 3-component system.

Table 7.15.: **Contributions of relevant ingredients to the normalised CLs (%)**

Catchment	Heavy-duty	Compact heavy-duty	Tandem system	3-component system
Rupel				
Anionic surf.	47.42	39.20	38.87	13.32
AE	40.01	47.19	58.27	85.10
Boron	10.67	11.58	1.32	0.00
Rur				
Anionic surf.	7.90	6.12	24.41	11.77
AE	3.93	4.34	21.65	57.19
Boron	82.39	83.94	38.48	0.00
Itter				
Anionic surf.	13.34	10.45	35.40	17.40
AE	4.51	5.05	21.36	57.34
Boron	76.73	79.16	30.80	0.00
Lambro				
Anionic surf.	8.93	6.92	26.68	12.83
AE	4.08	4.52	21.78	57.52
Boron	81.28	83.00	36.75	0.00
Aire				
Anionic surf.	31.30	25.25	39.17	12.76
AE	21.81	25.15	48.70	82.23
Boron	43.45	46.13	8.22	0.00

Influence of anionic surfactants and boron

Besides AE, also the contributions of the anionic surfactants vary considerably, which is caused by two phenomena. Firstly, in both 3-component system and tandem system, relatively more surfactants are used than in the other two alternatives. Secondly, the ratios between LAS, AS, and soap in the different formulations vary. Due to this, the different wastewater treatment efficiencies of the anionic surfactants influence the different results. The already known dependency of the boron contribution on the differentiation between white and coloured laundry is again visible, to some extent even in the Rupel catchment.

7.3.3. Comparison of different catchments

Finally, a general comparison of different catchments with respect to aquatic impacts is performed. In this section, the influence of variable detergent consumptions and all catchment characteristics is analysed. The tandem system has again been chosen as the model detergent. The only additional information required is the average use of laundry detergents for the different countries, which was provided by Gutzschebauch (1999).

The analysis is carried out for both the PRR_{90}s and CLs, the latter based on mean concentration increases. The statistical per-capita consumptions for 1997 are 9.67 kg for Belgium, 7.73 kg for Germany, 10.77 kg for Italy, and 9.96 kg for the United Kingdom (Gutzschebauch, 1999). Table 7.16 shows the percentages of stretches in which PRR_{90}s exceed 1 and 0.1 for different numbers of substances, whereas Table 7.17 shows the results of the CL calculations.

These scenarios are investigating the aquatic ecotoxicological impacts of houseshold laundry in different catchments by assuming actual detergent consumptions from 1997. The only hypothetical aspect is the choice of the product, i.e. the tandem system. A small uncertainty may be introduced by the fact that it is unknown whether the discharge site data of the different regions reflect realistic conditions from 1997.

Table 7.16.: **Percentage of stretches with PRR_{90}s exceeding 1 and 0.1 for the different catchments** (Wishy-Washy, Tandem system)

Catchment	Number of substances						Number of substances				
	1	2	3	4	5		1	2	3	4	5
$PRR_{90}s > 1$:						$PRR_{90}s > 0.1$:					
Rupel	67	40	15	2	1		95	92	92	20	20
Itter	0	0	0	0	0		91	55	55	0	0
Rur	0	0	0	0	0		14	5	5	0	0
Lambro	0	0	0	0	0		27	15	15	0	0
Aire	4	4	0	0	0		66	57	57	13	13

The table shows the significant influence of wastewater treatment. In catchments with activated sludge plants there are no stretches in which PRR_{90}s exceed 1. In the Aire catchment, which has trickling filter type plants, this occurs in 4% of the stretches, which originates from LAS and AE. However, simulating a catchment with only primary settler plants gives that the PRR_{90}s exceed 1 in the majority of stretches.

In the Rupel catchment the threshold of 0.1 is exceeded by 3 substances in more than 90% of the stretches. This second part of the table also shows the influence of the catchment structure. Higher percentages are estimated for the Itter than for the Aire catchment, although in the Itter a more efficient wastewater treatment technology is used. But because the Itter catchment is much more anthropogenically influenced than the Aire catchment, the percentage of considerably affected stretches is higher in the German catchment.

Furthermore, the table shows that the number of relevant substances has increased in the different catchments. Most relevant are the surfactants LAS and AE, followed by boron, AS, and sodium carbonate. The most significant change by shifting from the threshold 1 to 0.1 occurs in the Itter catchment. The percentages change from 0 to 91 and 55%. It demonstrates that looking at both values 1 and 0.1 gives additional insight. It is also apparent that in those catchments having activated sludge type plants, the number of relevant substances is restricted to 3, i.e. LAS, AE and boron.

Table 7.17.: **Normalised CLs in different catchments (Wishy-Washy, Tandem system)**

	Rupel	Rur	Itter	Lambro	Aire	Max/Min
CL (m)	2.5741	0.0379	0.0327	0.0073	0.0563	353.7
Per substance (%)						
LAS	31.15	20.47	26.50	21.34	32.77	-
AS	8.34	4.14	5.39	4.23	6.84	-
AE	57.21	21.08	21.61	20.94	47.09	-
Boron	1.32	38.75	33.07	38.17	8.87	-
Zeolite A	0.87	3.14	2.76	3.22	1.27	-
Sodium carbonate	0.35	9.88	8.39	9.61	2.30	-

The CL results differ strongly between the catchments. The ratio of maximum and minimum of the normalised CLs is about ten times larger than the ratio of the CLs of the reference scenarios, which so far showed the largest result variability (Table 7.2). This is due to the type of wastewater treatment, catchment characteristics, and detergent consumption, whereas variability in the reference scenarios was due to varying consumption figures and product formulations. The large variation is above all caused by variations of the surfactants that are used in large quantities, and for which elimination efficiencies vary significantly between the catchments.

The consumption figures have a linear influence on the result, as they linearly determine the emitted loads. It is observable that in this analysis the consumption even lowers the total variability of the normalised CLs: The highest per-capita consumption of detergents occurs in Italy (10.77 kg, Gutzschebauch, 1999). Despite this fact, the smallest normalised CL is calculated in the Lambro catchment. This result summarises the influence of the wastewater treatment technique on the one hand and of catchment characteristics such as variable dilution ratios on the other.

7.4. Assessment of inorganic compounds

It seems debatable whether all ingredients should be considered in the ecotoxicological evaluation. For example, a combined evaluation of organic substances such as surfactants or optical brighteners on the one hand and inorganic ingredients on the other is only partly meaningful. However, unwanted impacts may also occur from inorganic detergent ingredients, for example eutrophication resulting from the use of phosphate. Also, the inorganic salts present in detergents contribute to the total salt content, the sodium ions increase the amount of kations dissolved in surface waters, and silicium and zeolite A emissions presumably contribute to the silicon balance in surface waters. For this reason, the environmental relevance of these emissions is investigated in this section.

Firstly, new product formulations are derived from the four model formulations by only considering the sodium, sulphate, carbonate, and silicon contents. Product calculations are then performed for the three reference scenarios and the fourth scenario assuming the Wishy-Washy use habit and the tandem system using these new detergent formulations. The results are based on 2000 Monte Carlo shots. The calculated concentration increases are then compared to monitoring data and, in the case of sulphate, to existing water quality objectives. The derivation of the new detergent formulations is based on the molecular weights and is explained in detail in appendix C. The new product formulations are given in Table 7.18.

The investigated elements and compounds are regularly surveyed by regional authorities from the LUA. In addition, the predicted concentration increases of sulphate ions can be compared to water quality objectives (Landesumweltamt Nordrhein-Westfalen, 1997). For sodium, drinking water limits are defined in German legislation (*'Trinkwasserverordnung'*, Deutscher Bundestag, 1990). No water quality objectives are available for carbonate and silicon. Therefore, in these cases only a comparison to measured concentrations is performed.

Table 7.18.: **Altered detergent formulations only considering inorganics (%).** The difference between silicon A and B is explained in appenix C.

Substance	Heavy-duty	Compact heavy-duty	Tandem system	3-component system	Comment
Sodium	12.65	15.48	14.50	14.88	
Silicon A	3.12	3.18	4.57	6.18	From zeolite A
Silicon B	1.15	1.23	0.93	1.60	From silicates
Carbonate	5.16	7.20	6.51	8.57	
Sulphate	12.85	1.62	2.57	0.07	

Aluminum and citrate are not included in this study, since neither monitoring data nor water quality objectives are available. However, it was shown in the previous calculations that citrate can be classified as environmentally irrelevant, which is supported by different authors (Hoyt and Gewanter, 1992, Schöberl and Huber, 1988). Thus, not considering citrate does not lead to false results concerning the assessment of water quality. Concerning aluminum, Kurzendörfer et al. (1997, p.161) demonstrated that the quantification of zeolite-based aluminum to the aluminum balance in freshwaters *"lacks a scientifically sensible background"*. The reasoning considers the huge variety of to a large extent inconsistent measured concentrations, which depend on the pH condition, the presence of particulate matter, temperature, ionic strengths, and further factors. Besides the discussion outlined there, the non-existence of monitoring data makes interpretations impossible. Thus, aluminum is also omitted from this analysis.

7.4.1. Sodium

The threshold value for sodium in drinking water is 150 mg/l (Deutscher Bundestag, 1990). Within the Rur catchment, annual mean measured concentrations in the upper courses are typically about 10 mg/l, in the middle parts of the catchment they are around 50 mg/l, and between 150 and 230 mg/l in the lower courses. Interestingly, the spatial concentration distribution corresponds to the population density. For example, higher concentrations are measured in the Wurm river than in the Rur river. This may suggest that riverine sodium concentrations may identify anthropogenic emissions. This would not be surprising with respect to the percentage of sodium in detergents and most probably also in other cleaning products.

Since all sodium ions are released during the washing process and are not eliminated during wastewater treatment, the total emitted amount is discharged into the surface waters and finally reaches the sea.

GREAT-ER calculations in the Rur catchment (1993 data set) are performed considering no elimination. In Table 7.19, the mean concentration increases in the Rur and Wurm rivers of the four scenarios are given together with measured values. However, monitoring data were only available for 1991, while the discharge site data represent the Rur catchment in the year 1993.

Depending on the use habit, the calculated fraction of detergent-based sodium of total measured sodium concentrations varies significantly. Assuming the Smart use habit, a contribution of between 0.4 and 3% is calculated, while assumption of the Scrubbed use habit gives percentages as high as 20% (Einruhr sampling site). The observation mentioned in the introduction of this section, i.e. measured sodium concentrations are generally higher in river stretches that discharge wastewaters of more densely populated areas than in less influenced streams and rivers, can be seen by comparing the measured concentrations at the sampling sites at Einruhr and above the Inde confluence, where the population density is smaller, with the concentrations at the other three sites.

As the Wishy-Washy use habit was defined to represent average German washing habits, this scenario is most probably the most realistic. With respect to the mean simulated and measured concentrations, the detergent-based sodium is between 1.2 and 8.1% of the total sodium content. Interestingly, the fraction is higher in less anthropogenically influenced sites (Einruhr, 8.1%) than below large discharges (below Soers WWTP, 4.8%). This suggests that the observed increase of sodium concentrations cannot fully be explained from the use of detergents alone. Other sources also exist, whose emitted quantities are most likely larger than the ones related to detergents.

Table 7.19.: **Sodium concentration increases from its use in detergents** All concentrations are given in mg/l.

Sampling site	River	Simulated Mean	Simulated 90%ile	Measured Mean	Measured Min-Max	Sim/Meas of means (%)
Scrubbed						
Einruhr	Rur	1.84	4.19	9.3	6.6-12	19.78
above Inde	Rur	1.79	2.79	31.5	24-39	5.68
Steinkirchen	Rur	4.11	6.05	152.5	97-208	2.7
below Soers WWTP	Wurm	13.12	19.83	122	83-162	10.75
near mouth	Wurm	10.16	14.67	233	185-281	4.36
Wishy-Washy						
Einruhr	Rur	0.75	1.70	9.3	6.6-12	8.06
above Inde	Rur	0.81	1.23	31.5	24-39	2.57
Steinkirchen	Rur	1.87	2.69	152.5	97-208	1.23
below Soers WWTP	Wurm	5.91	8.69	122	83-162	4.85
near mouth	Wurm	4.61	6.53	233	185-281	1.98
Wishy-Washy + Tandem system						
Einruhr	Rur	0.73	1.66	9.3	6.6-12	7.85
above Inde	Rur	0.75	1.15	31.5	24-39	2.38
Steinkirchen	Rur	1.74	2.50	152.5	97-208	1.14
below Soers WWTP	Wurm	5.53	8.20	122	83-162	4.53
near mouth	Wurm	4.29	6.09	233	185-281	1.84
Smart						
Einruhr	Rur	0.27	0.61	9.3	6.6-12	2.9
above Inde	Rur	0.28	0.43	31.5	24-39	0.89
Steinkirchen	Rur	0.64	0.93	152.5	97-20	0.42
below Soers WWTP	Wurm	2.02	3.01	122	83-162	1.66
near mouth	Wurm	1.60	2.26	233	185-281	0.69

7.4.2. Silicon

Modelling silicon can not directly be done since, resulting from the use of detergents, it enters surface waters in two different forms, i.e. as silicate and bound in zeolite A. Silicate is a degradation product of the latter. Especially the fate of silicate and zeolite A in WWTPs varies significantly, which is described in appendix C. For this reason, in the GREAT-ER calculations silicon is treated as two different substances. By assuming an instantaneous and complete hydrolysis of zeolite A in surface water, silicon concentration increases based on use in detergents can be calculated by adding the two calculated concentrations.

Due to this assumption, this is a worst-case scenario for silicon. Kurzendörfer et al. (1997) also used this approach in order to perform worst-case estimates of concentration increases of silicon in surface waters due to the use of zeolite A in detergents.

Table 7.20 shows a comparison of measured and simulated silicon concentrations in the largest rivers Rur and Wurm for the four scenarios. Mean and 90th percentiles are given for both monitoring and simulation results. As described above, the simulated concentration increases are the sums of the simulation results of the two considered silicon compounds.

Table 7.20.: **Silicon concentrations from its use in detergents.** Concentrations are given in mg/l.

Sampling site	River	Simulated		Measured		Sim/Meas
		Mean	90%ile	Mean	Min-Max	of means
Scrubbed						
Einruhr	Rur	0.18	0.40	1.98	2.30	9.47
above Inde	Rur	0.19	0.28	2.23	3.66	8.52
Steinkirchen	Rur	0.43	0.63	3.27	3.74	13.15
below Soers WWTP	Wurm	1.39	2.05	5.50	6.22	25.27
near mouth	Wurm	1.08	1.54	5.24	5.84	20.61
Wishy-Washy						
Einruhr	Rur	0.08	0.17	1.98	2.30	4.04
above Inde	Rur	0.08	0.12	2.23	3.66	3.59
Steinkirchen	Rur	0.18	0.26	3.27	3.74	5.50
below Soers WWTP	Wurm	0.56	0.83	5.50	6.22	10.18
near mouth	Wurm	0.43	0.62	5.24	5.84	8.21
Wishy-Washy + Tandem system						
Einruhr	Rur	0.07	0.15	1.98	2.30	3.54
above Inde	Rur	0.07	0.1	2.23	3.66	3.14
Steinkirchen	Rur	0.15	0.23	3.27	3.74	4.59
below Soers WWTP	Wurm	0.49	0.71	5.50	6.22	8.91
near mouth	Wurm	0.39	0.55	5.24	5.84	7.44
Smart						
Einruhr	Rur	0.04	0.09	1.98	2.30	2.02
above Inde	Rur	0.04	0.06	2.23	3.66	1.79
Steinkirchen	Rur	0.09	0.13	3.27	3.74	2.75
below Soers WWTP	Wurm	0.29	0.43	5.50	6.22	5.27
near mouth	Wurm	0.22	0.32	5.24	5.84	4.20

In the Wurm river and the lower parts of the Rur river, i.e. at Steinfelden, which is below the confluence of the Wurm to the Rur, the silicon contribution resulting from the use of detergents is considerable. Applying the Wishy-Washy use habit scenario, which best represents realistic conditions, approximately 8-10% of the silicon present in the Wurm river can be explained by emissions from the use of laundry detergents. The fact that measured concentrations increase along the rivers suggests that observable silicon concentrations have to some extent anthropogenic origins. However, due to the highly variable natural content of silicon in different soil types, which may be partly washed out, and due to the conservative assumption of immediate and complete hydrolysis, the results have to be interpreted with caution.

Schöberl and Huber (1988) report measured hydrolysis half-lives for zeolite A of between 1 and 2 months. Regarding the much shorter mean residence time in the catchment, only a small fraction of the silicon emitted in the form of zeolite A may contribute to the concentration of silicon in surface waters. Thus, the zeolite-based contribution is most likely overestimated.

Only 25 to 30% of the predicted silicon effluent concentrations originate from the use in zeolite A, while the larger fraction is due to the use of silicates. This is directly derived from the GREAT-ER results of the two silicon compounds. Thus, silicate largely determines the silicon concentration increase resulting from the use of detergents.

7.4.3. Carbonate

Since no water quality objectives exist for carbonate, the interpretation is only based on the comparison of monitoring data and simulation results. In Table 7.21, the percentual contribution of the predicted 90^{th} percentile concentration increases of the worst-case scenario Scrubbed to mean measured values in the Rur and Wurm rivers are given. Results of all other scenarios are much lower than those of the Scrubbed scenario. In addition, the ratio 90^{th} percentile divided by mean values is also a conservative approach. The realistic contribuion is therefore much smaller. Therefore, other sources, both natural and anthropogenic, are dominating measurable carbonate concentrations rather then emissions due to the use of laundry detergents.

Table 7.21.: **90^{th} percentile carbonate concentration increases of the Scrubbed scenario vs. measurements**

	Rur sampling sites				Wurm sampling sites		
	1	2	3	4	5	6	7
$C_{\mathrm{meas,mean}}$ (mg/l)	29.7	64.2	96.4	163.3	170.4	247.9	248.8
$C_{\mathrm{sim,90}}$ (mg/l)	1.6	1.1	1.4	2.4	7.7	6.5	5.8
Percentage	5.4	1.7	1.5	1.5	4.5	2.6	2.3

It is worth mentioning that in the Smart use habit percarbonate is used as a bleaching agent, which enters the surface waters as carbonate. This bleaching agent therefore is not a cause of environmental concern regarding its fate in aquatic systems.

7.4.4. Sulphate

A classification according to the German water quality scheme exists for sulphate, which is given in Table 7.22 (Landesumweltamt Nordrhein-Westfalen, 1997). For deriving the water quality classification, this scheme shall be applied to monitoring data, from which the 90th percentile values are to be used. Therefore, in this analysis the 90th percentiles of the simulated concentrations are compared to the monitoring data, given by the mean, minimum and maximum values. The use of measured maximum concentrations does most likely not influence the interpretation, because at sites at which 90th percentiles have been determined the deviations between these values and the maximum concentrations have always been less than 3 mg/l. In addition, the procedure for applying the water quality classes instructs the use of the maximum value, if less than 3 samples are available at a site (Landesumweltamt Nordrhein-Westfalen, 1997, p. 55). Both measurements and simulations are based on data from 1993.

Table 7.22.: **Water quality classes for sulphate (mg/l)**

Class	I	I-II	II	II-III	III	III-IV	IV
Upper limit	25	50	100	200	400	800	>800

Figure 7.1 shows comparisons of measured and simulated concentrations for the Rur and Wurm rivers, the latter being based on the 90th percentiles. Firstly, in combination with Table 7.22, it can be seen that with respect to measured sulphate concentrations the water quality in the Wurm ranges from stages II to III, while in the Rur river sulphate concentrations are generally lower, leading to a stage I classification in the upper courses. In the lower courses the highest measured concentrations of slightly above 100 mg/l lead to stage II-III. Secondly, it becomes clear that the contribution of detergent-based sulphate does not determine the actual concentrations. The concentration increases from use in detergents are much lower than measured concentrations. Contributions above 1%, i.e. 5 to 8%, are only calculated, when applying the worst-case use habit Scrubbed, in which the heavy-duty detergent is used. Due to this worst case estimate, the realistic contribution is most likely to be much smaller than predicted in this scenario.

Natural sulphate concentrations can be determined by measurements near the sources of the different streams. In the Rur, Urft, and Olef rivers, mean concentrations range between 7 and 13 mg/l, while near the sources of the Wurm samples containing up to 50 mg/l were repeatedly taken. The natural variation is therefore larger than estimated contributions from detergents. This suggests that the share of detergents in actual sulphate concentrations is limited.

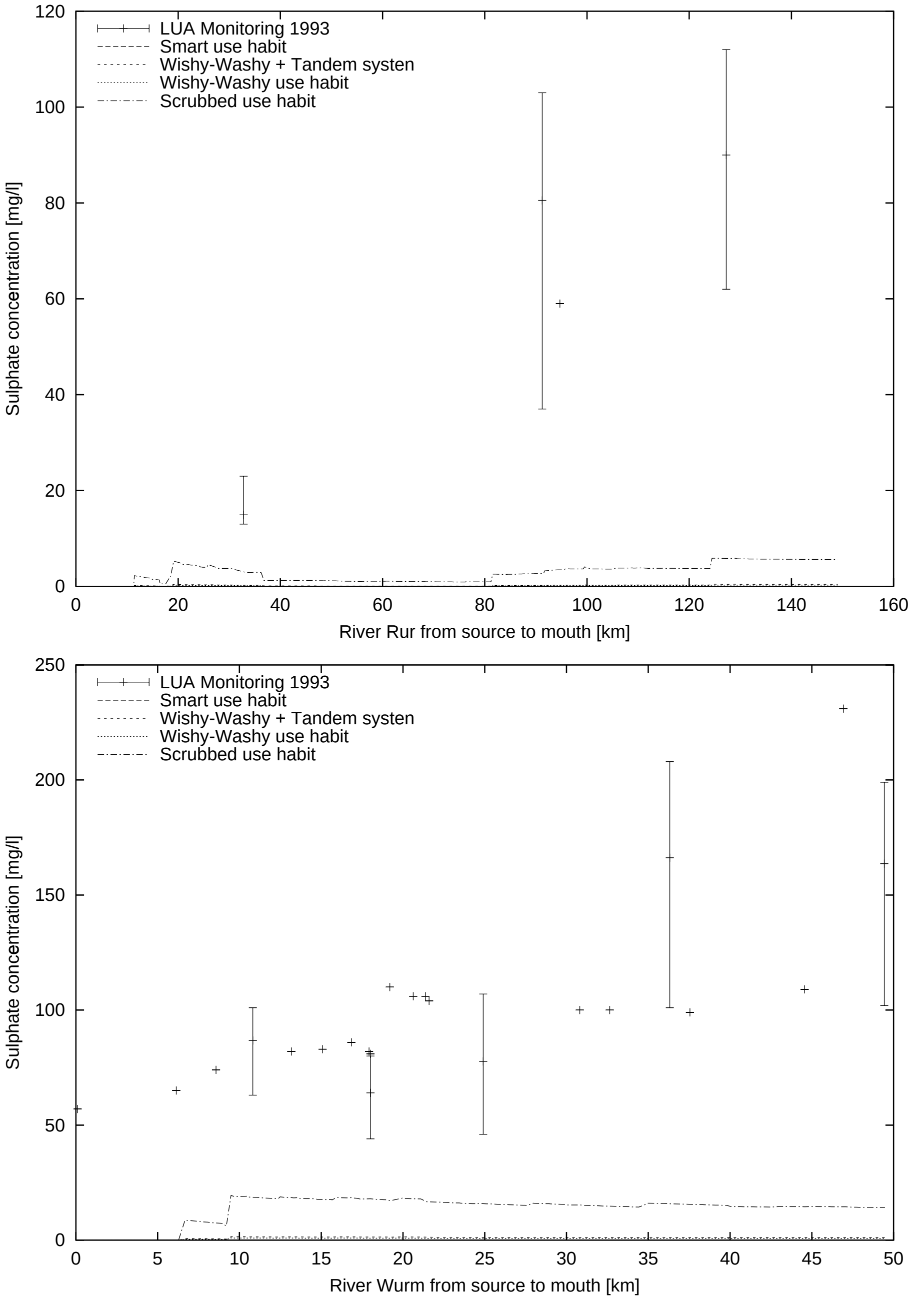

Figure 7.1.: **90th percentile sulphate concentration increases from its use in detergents vs. measurements**

8. Discussion

The following discussion focuses on the methodology of the GREAT-ER product mode and on the results derived in the case study. Finally, further potential relevant aspects that were not explicitly considered in this thesis are discussed.

8.1. Methodology of the product mode

The methodological aspects discussed in this section include the relationship of the GREAT-ER product mode to LCA and ERA, the kind of information that can be derived from this method, the number of substances considered in the PRR$_x$ calculation, the sensitivity of the model, the kind of weighting implicitly performed in the CL assessment, and finally a discussion about the differences and similarities of the 'less-is-better' and 'only-above-threshold' approaches.

8.1.1. Relation to ERA and LCA

The GREAT-ER product mode combines elements from ERA and LCA. It is not a method of ERA, since the product scenarios and therefore the results are partly based on unrealistic assumptions. The results do not even allow an evaluation of all expected impacts given that the assumptions concerning the entire use of a product according to a specific use habit would be true, because emissions and environmental concentrations of the considered substances from other anthropogenic sources or from natural origins are not considered. For this reason, the GREAT-ER product mode is primarily to be seen in the context of LCA. However, the assessment and evaluation method extends typical LCA methods. The interpretation possibilities outlined in section 3.2 have a much larger environmental relevance than typical category indicator results, for example those applied in section 2.2. This is only possible due to two restrictions. First, only the use phase instead of the entire life cycle is assessed, and second, only the impact category aquatic ecotoxicity is analysed. Due to these restrictions, the GREAT-ER product mode should not be used as a sole instrument, but it should be combined with other LCIA methods that both adress other impact categories as well as other stages of the life cycle of detergents. Still, the first restriction is often being done in LCAs, since many LCAs are based on a 'cradle-to-gate' rather than a 'cradle-to-grave' approach (e.g. Bretz and Frankhauser, 1996).

The development of the GREAT-ER product mode was not intended to be in compliance with the ISO schemes on LCA (DIN, 1998). However, the GREAT-ER product mode corresponds well with the definitions of LCA and LCIA as given in ISO (see also section 2.1.2). Especially regarding the LCIA definition, it is not clear how the significance of emissions can be evaluated on the basis of results as calculated by the LCIA methods discussed in section 2.2. The GREAT-ER product mode is more useful for this. Due to these limitations regarding LCA, some authors (e.g. Thiel et al., 1999, Udo de Haes, 1996a) propose the application of different methodologies and instruments on the basis of an LCA.

8.1.2. CL and PRR_x evaluation

In this section, the information derived by evaluating the CL and PRR_x results is discussed.

Comparison of PLA and GREAT-ER product mode results

The product comparison scenarios assuming recommended dosage and the reference scenarios give the same rankings as the PLA. This is true for both CL and PRR_x evaluation. However, the GREAT-ER product mode provides additional information not directly provided by the PLA. The CL evaluation allows the explicit assessment of the contributions of the different detergent ingredients, whereas the PRR_x evaluation analyses whether thresholds are exceeded by the scenarios.

For example, the major relevance of boron and the surfactants proven in the case study was not stated in the PLA. Furthermore, the ecotoxicological evaluation in the PLA gives very similar results for the tandem system and compact heavy-duty detergent (Grießhammer et al., 1997, p. 108, see also Table A.2 in appendix A.2), whereas in this analysis a major difference between the two alternatives can clearly be observed: The tandem system distinguishes between coloured and white laundry, while the compact heavy-duty detergent does not.

Comparison of use habits

In the PLA, an evaluation of aquatic ecotoxicological impacts in the comparison of households, or use habits, as depicted in this thesis, has not been conducted. There, only acid formation potentials, emissions of CO_2 and VOC, as well as energy, detergent, and water consumptions are calculated for the different use habits (Grießhammer et al., 1997). The ecotoxicological evaluation system used in the PLA only allows an assessment of products, but not of different washing habits. In this thesis, the influence of variable use habits is visible in the results of the reference scenarios and by investigating the differences induced by the assumptions to either dose according to the product recommendations or according to the use habits. From the latter it can be seen that the variability of the CLs assuming the same product is linear to the dosage, except for small deviations due to the stochastic simulation procedure. Thus, for this comparison the CL approach does not give any new information, since the dosage alone provides the same information. In fact, the linear nature of the GREAT-ER model is responsible for this. On the contrary, evaluating the PRR_{90}s gives additional information. Increasing the dosage leads to an increased number of stretches in which an threshold is exceeded. The magnitude of this increase can only be determined when performing the PRR_x analysis, but not from the detergent consumption alone.

Combination of intrinsic properties and mass emitted

The heavy-duty and compact heavy-duty detergents almost have the same ingredients. Thus, the largely varying results observed in the product comparison are mainly due to the emitted quantity per wash, which depends on the recommended dosage. This shows that evaluation systems based on purely intrinsic properties of the substances are not sufficient for evaluating the aquatic fate of laundry detergents.

Comparison of catchment characteristics

The influence of catchment characteristics has not been analysed in the PLA. Furthermore, the methodology of the PLA does not allow the analysis of these parameters, since no fate analysis was performed there. However, wastewater treatment is the most important factor in the comparison of different catchments. In addition, other spatially varying factors also have some influence. Both was omitted in the PLA but considered in this thesis.

Comparison of the Rur and Itter results derived in sections 7.3.2 and 7.3.3 demonstrates different perspectives of the CL and PRR_x evaluations. The normalised CL is higher in the Rur catchment than in the Itter catchment, while the PRR_{90} evaluation gives the opposite outcome. This can be explained in the following way. The PRR_{90} evaluation describes the catchment's state concerning concentration increases of detergent ingredients in the surface waters resulting from the underlying assumptions concerning washing habits and product choice. Due to the high population density and the small river discharging the population's wastewater, concentrations are fairly high compared to simulation results in most rivers of the less densely populated Rur catchment. However, the normalisation procedure performed in the CL calculation cancels out the influence of population density. As a larger percentage of detergent ingredients is flushed out of the Itter catchment compared to the Rur catchment, the CL is higher in the Rur than in the Itter catchment.

A limited contribution may also be due to the slight differences in weighting performed by both approaches, since the CL weighs by the lengths of the river courses, while the PRR_x approach apportions equal share to each stretch.

8.1.3. Number of substances considered in the PRR$_x$ calculation

A weakness of the basic PRR$_x$ definition is the fact that it can be dominated by one single substance. For this reason, the PRR$_x$ evaluation has been enhanced in order to reflect the number of substances for which thresholds are exceeded in different numbers of stretches. This procedure leads to a relative ranking of the ingredients, which is very similar to the results of the CL analysis. This is not surprising, since both calculations are based on the same simulation results.

However, it was shown that the PRR$_x$ evaluation may change after the substitution of just one substance. This can be seen when comparing the results of the compact heavy-duty detergent and the tandem system. Considering only one substance leads to a different ranking than considering more than one substance. Thus, by replacing the most relevant substance of the compact heavy-duty detergent, the ranking may change. Thus, PRR$_x$ evaluations investigating options for improvements concerning product formulations should be conducted by considering different numbers of substances that exceed the threshold in the calculated number of stretches in order to identify room for improvements.

8.1.4. Model sensitivity

The sensitivity of the model can be divided into sensitivities of the GREAT-ER model and of the new product mode.

Sensitivity of the GREAT-ER 1.0 model

A sensitivity analysis of the GREAT-ER model has been performed in the EDTA simulations described in sections 6.1.5 and 6.3.6. The influence of both consumption data as well as in-stream removal rates has been analysed. It was observed that concentrations predicted by GREAT-ER linearly depend on the per-capita consumption, while the influence of variable in-stream removal rates is limited. This is due to the open nature of the model, due to which advective ouflow out of the catchment exists, which limits the influence of the in-stream removal rate.

Careful attention should be given to WWTP efficiencies. For many detergent ingredients the elimination efficiencies in activated sludge type plants are very high, e.g. usually 98% or higher. However, increasing the efficiency by 1% to 99% halves the emitted load and therefore the predicted concentrations. Thus, a careful choice of the WWTP efficiency data is important. Unfortunately, a true removal efficiency cannot be determined. Since the actual efficiency in a plant depends on plant-specific characteristics, it is even critical to assign the same efficiency for all plants of the catchment. Therefore, the choice of WWTP efficiency is always partly subjective. One way to reduce the influence of this choice is to use a stochastic distribution function for the efficiency rather than a single value. However, this does not completely eradicate the problem.

A similar problem is the elimination in the sewerage system. The mean sewer length from the household to a WWTP is unknown. Thus, the residence time within the sewerage system, which also depends on the slope, cannot be calculated. The sewer efficiency is therefore a highly uncertain parameter. However, its sensitivity is limited for substances with high WWTP elimination efficiencies. This can be deduced from the following GREAT-ER model equation.

$$\mathrm{L_{effl}} = \mathrm{Cons} \cdot \mathrm{Pop} \cdot (1 - \mathrm{eff_{sewer}}) \cdot (1 - \mathrm{eff_{WWTP}})$$

where $\mathrm{L_{effl}}$ is the effluent load of the WWTP, Cons is per-capita consumption, Pop the population connected to a WWTP, and $\mathrm{eff_{xxx}}$ describes the elimination efficiencies in the sewerage systems and the WWTPs respectively[1]. Due to this equation a very large WWTP efficiency is limiting the influence of the sewer efficiency.

Sensitivity of the product mode

All equations in the product mode are linear. Thus, the predicted per-capita consumptions and also the CL calculations depend linearly on the following parameters: dosage, total amount of laundry, and number of washes. A change of percentage of an ingredient influences linearly the predicted concentration increases of the respective ingredient. Its influence on the total CL result depends on its percentage in the detergent formulation. This influence is less than linear.

The situation is more difficult in the PRR_x calculation. First, as previously discussed, the PRR_x calculation may be dominated by a single substance. Second, as the stretches in which a threshold is exceeded are counted, small changes in the input parameters may have very different influence. If due to this variation in many further stretches thresholds are exceeded, the influence is large. If, on the other hand, the changed input data do not lead to a change in the number of stretches in which thresholds are exceeded, this variation has no influence at all.

However, if the catchment is sufficiently large, there are usually heavily, moderately and only slightly influenced stretches. In such a case, the influence of the parameters that linearly influence the emission data on the PRR_x results may become nearly linear. This could partly be observed in the different product mode scenarios performed in the Rur catchment, and is further discussed in section 8.1.6 below.

The sensitivity of the toxicological data on the PRR_x results is comparable to that of the ingredients' percentages. If in a considerable number of stretches the predicted concentration increases are near the threshold, small changes may significantly alter the result. On the contrary, changes of the effect data of less relevant substances may have no influence at all on the PRR_x outcome. In the CL evaluation, the effect data linearly determine the CL of the specific substance, i.e. the contribution to the total CL is less than linear.

Concluding, general statements regarding the sensitivity of both the GREAT-ER model

[1] Typically, the WWTP efficiency is further divided into efficiencies for the different sections of a plant, e.g. primary settler and activated sludge tank.

as well as the product mode are difficult to derive. In addition, due to the large numbers of stretches and discharges in most catchments in combination with the stochastic simulation, a systematic sensitivity analysis is not feasible. In fact, a methodology for this has not yet been developed. For the moment, different scenarios are conducted in order to reduce uncertainty, which provides some insight into the model's behaviour.

8.1.5. Length- versus volume-based aggregation

Instead of calculating critical lengths (CL), critical volumes (CV) could have been calculated. This approach would correspond with other LCA methodologies (e.g. Consoli et al., 1993), environmental valuation schemes such as the ecolabel for laundry detergents (European Union, 1999a) or current GREAT-ER 1.0 aggregation procedures, which calculate a mean concentration in a catchment based on weighting by either length, volume or flow increment (Boeije et al., 2000). However, the volume-based weighting, i.e. the calculation of critical volumes instead of critical lengths, has not been followed for two reasons: i) technical restrictions, and ii) consideration of a value-choice.

The value-based reason arises from the question of equivalency of potential impacts. A volume-weighted approach would consider river segments with the same volume of water, e.g. at mean flow, as equally important, whereas a length-based approach would assign equal weight to segments with the same length.

The difference is illustrated with an example. The calculation of both CL and CV only considers loaded stretches. In the case of the Itter catchment three discharges exist, from which river courses with a total length of 18.8 km and a total volume of 23,659 m^3 at mean flow are influenced. The Itter flows into the Rhine river in a section in a southern district of Düsseldorf. Weighting by length would consider the streams of the Itter catchment to be as important as the Rhine river 18.8 km downstream from the confluence of the Itter, which is near Düsseldorf harbour. Weighting by volume, based on the mean flow, would consider the streams of the Itter to be as important as a Rhine river segment having a length of only 18.3 m (near the confluence of the Itter), which has been calculated from a Rhine river data set (Koormann et al., 1998). The difference in this realistic example is three orders of magnitude.

Concerning potential aquatic ecotoxicological impacts resulting from the use of laundry detergents, it was shown in several monitoring programmes that especially smaller streams form a major point of concern, since the highest concentrations can often be found there. This is most probably due to smaller dilution ratios mainly occurring in small streams. For example, in the Itter catchment the stream dilution factors, defined as mean flow below the discharge divided by mean effluent flow of the discharges, are as low as 1.74 at Solingen-Gräfrath WWTP, 2.06 at Solingen-Ohligs WWTP, and 4.74 at Hilden WWTP (see also the data on the GREAT-ER CD, ECETOC, 2000). Consequently, higher concentrations of detergent ingredients can be found in the Itter than in rivers with higher dilution ratios. This is also predicted by the GREAT-ER model, which can be see by comparing GREAT-ER results derived in the Itter catchment with results from main rivers of the Rur catchment. Also, the highest concentrations in the Rur catchment can be found in locations with small dilution ratios, i.e. in the brook Gereonsweiler Fließ below Setterich WWTP and in the upper parts of the Wurm below Aachen-Soers WWTP. On the other hand, observable and predicted concentrations below Düren WWTP, which is the second-largest WWTP in the catchment but which discharges into the main river of the catchment, are generally lower. For this reason, focussing on the smaller streams by using a length-based aggregation seems more appropriate for an assessment of laundry detergents.

Besides this value-based reason there is a technical reason which even forbids a volume-based approach. The flow is one of the most important input parameters in calculating the concentrations. However, it also determines the volume of water in a stretch, which leads to an inherent correlation between concentration and volume. CL calculations performed so far are based on the mean concentration increases. These depend on the release estimation, the distributed flow, flow velocities, and the substance-specific input parameters, which may also be distributed. There is no general relation regarding which flow and thus which volume corresponds to the mean concentration nor to any other concentration percentile. In fact, this relationship will in most cases be different for each stretch. The relationship is only known, when performing a deterministic simulation, which is possible within GREAT-ER. In this case the calculation is based on mean values for all input data. However, in such a simulation the stochastic aspect of GREAT-ER is eradicated.

Concluding, weighting of concentrations by volume of water in a stretch can only be done if the relationship of flow and predicted concentration increase is available. Within GREAT-ER, this is typically not the case. Implementing a volume-based weighting would require immense effort, because central parts of the GREAT-ER model and data structure would have to be changed. In addition, since it is reasonable in the case of household laundry to focus on smaller streams, a weighting by length is performed in the CL evaluation.

8.1.6. ‘Less-is-better’ versus ‘Only-above-threshold’

An on-going discussion in the LCA community is the distinction between ‘less-is-better’ and ‘only-above-threshold’ methods. Most LCA methods are based on the ‘less-is-better’ paradigm (Potting et al., 1999). With respect to toxicological impact categories, in which, based on the ‘less-is-better’ approach, impact scores of completely different toxic mechanisms are added, this is seen as a serious problem of LC(I)A (Potting, 2000, p. 6). ‘Only-above-threshold’ methods, on the other hand, are based on the paradigm that with respect to toxicological effects threshold concentrations often exist, below which no environmental harm is likely to occur. This paradigm is typically applied in ERA. It is usually not applied in LCA, since a threshold evaluation is generally infeasible within an LCA.

However, the GREAT-ER product simulations performed here do not lead to the conclusions that the approaches are incompatible. In most calculations there are at least some stretches in which a threshold, expressed in the PRR$_x$ evaluation, is exceeded. Therefore the alternative giving the least number of stretches in which a given threshold is exceeded should be preferred, which gives the same findings as a 'less-is-better' evaluation.

Concluding from this thesis, the 'less-is-better' approach is not fundamentally different to the 'only-above-threshold' perspective. This result is especially important for LCAs, since it justifies the 'less-is-better' approach.

8.2. Case study

8.2.1. Reference scenarios and product comparison

The reference scenarios give results that are consistent with those obtained in the PLA. However, both CL and PRR$_x$ evaluations give further insights. The CL assessment differentiates more strongly than the LCA-based methodology applied in the PLA, which can be seen in the different variabilities of the results. This variability is due to variabilities of both use habits, which is identical to the variability of detergent consumptions, and product formulations. It was shown that the influence of varying use habits' is larger than the influence of variable product formulations. However, this result is largely dependent on the definitions of the use habits, which are partly based on subjective choices.

The CL evaluation allows the explicit assessment of the contributions of the different detergent ingredients. This analysis shows that the variability caused by varying product formulations is mainly due to the fact that the two most important substances of the detergents used in the Scrubbed and Wishy-Washy scenarios, i.e. boron and LAS, are not contained in the detergent used in the Smart washing habit.

The PRR$_x$ evaluation emphasises the significant differences in the results of the three reference scenarios, because the number of stretches in which the different thresholds are exceeded varies significantly. An important result of the two product comparisons is the fact that the ranking of the products may change if the detergents are not dosed as recommended. This occurred for the heavy-duty and compact heavy-duty detergents.

8.2.2. Relevance of detergent ingredients

The most important substances in the CL and PRR$_x$ analyses were boron and both an- and nonionic surfactants. Only minor relevance was assigned to zeolite A, DAS-1 and sodium carbonate. Substances of no importance were TAED/DAED, CMC, PVP, sodium sulphate, sodium citrate, sodium silicate and the polycarboxylates. Among these irrelevant substances are all those substances for which a conservative modelling approach was followed due to lack of appropriate substance data. This conservative approach did therefore not lead to biased results.

The minor significance of the optical brightener is surprising, especially since a worst-case estimate was performed by using DAS-1 as the only optical brightener. This small share of DAS-1 shows a weakness of the current GREAT-ER model, since DAS-1 may above all be relevant to the sediment compartment or concerning its fate in sewage sludge. This is further discussed in section 8.3.2.

The case of AE shows a different aspect of importance. Predicted AE concentrations do not vary largely in the product comparison. On the basis of the model detergents, no considerable room for improvements is seen, thus it is not an important substance with respect to the variability of the product comparison results. However, due to its large absolute share, AE is indeed one of the most relevant substances, especially when less effective wastewater treatment occurs. In fact, AE is responsible for the change of ranking occurring in the Rupel catchment.

Zeolite A, and sodium carbonate are the only inorganic substances besides perborate that have some relevance with respect to the CL evaluation. However, the analysis of the inorganic compounds, performed in section 7.4, has shown that these emissions contribute only to a minor extent to observed concentrations of the respective substances. For this reason, their environmental relevance is considered limited. These examples raise the question whether all ingredients should be considered in the ecotoxicological evaluation. For example, Guhl (2000) proposed to use only the organic ingredients present in the formulations. Inorganic salts would then be ignored. This is reasonable for compounds such as sodium sulphate, carbonate or citrate. On the other hand, relevant ingredients such as the bleaching agent sodium perborate would be omitted too. A different approach is the exclusion of some ingredients classified as irrelevant based on toxicological data. Such classifications have been applied by Schöberl and Huber (1988) and Walz et al. (1996). However, this would imply a valuation based only on toxicological information prior to a fate analysis, which is not desirable. Instead, it has been chosen to include all substances in the assessment and to investigate their relevance. It turned out that the number of relevant substances is limited.

8.2.3. Dominance of boron

The boron content in the detergents dominates the results in those alternatives that do not differentiate between coloured and laundry detergent. However, actual measured boron concentrations in German surface waters as well as perborate consumption data show that overestimations of boron consumptions and thus emissions do indeed occur in those scenarios in which boron is used in each wash, i.e. in those considering the heavy-duty or the compact heavy-duty detergent[2].

In 1993, the highest concentrations observed in the entire Rur were approximately 900 μg/l (see section 6.1.2), which is lower than the value given in the DID-list transformed

[2]The actual consumption data required for this conclusion are, for example, given in the GREAT-ER simulations performed in the Rur and Itter catchments in section 2.3 and chapter 6.

to boron, i.e. 985 μg/l. In addition, Metzner et al. (1999) conclude from a large survey of boron concentrations in Germany that *"the vast majority of values from ground water, surface water, and drinking water lie well below the maximum acceptable concentration of 1 mg/l (...)"*. Haberer (1996) reports boron measurements in Germany, in which 3 out of 100 measurements are above 1 mg/l and 10 are between 0.5 and 1.0 mg/l. Thus, boron is an environmentally relevant substance in freshwater systems, but it is not likely to cause environmental harm in the majority of river courses in Germany. Due to this outcome, efforts should aim at decreasing boron emissions from the use of detergents, either by the use of colour detergents or by its replacement by percarbonate.

8.2.4. Influence of catchment characteristics

Different wastewater treatment techniques

Assuming less efficient wastewater techniques, the increasing importance of the surfactants becomes apparent. Consequently, the relative influence of boron decreases, although its absolute CLs remain constant. The variation of the different wastewater techniques is considered more relevant than the variability of the reference scenarios, which was about a factor 35, because the results variability of the reference scenarios is determined by both choice of product and by use habit, whereas the variability due to varying wastewater treatment techniques, a factor of 21, is entirely due to the variability of one parameter. In addition, this variability is caused by the considerable increase of the contribution of the most toxic substances (according to the DID list), i.e. the surfactants, whereas the variability of the reference scenarios is mainly caused by the different bleaching options.

According to the PRR_{90} evaluation, the influence of different methods of wastewater treatment is highly important, since the number of stretches in which the PRR_{90} exceeds 1 significantly increases if less efficient wastewater treatment is assumed.

Combined influence of regional characteristics

The ranking of detergents is different in the Rupel catchment, which is mainly caused by the different wastewater treatment techniques, which is shown in section 7.3.2. Compared to this, all other geographic factors such as geographical characteristics or variable consumption patterns, only have a limited influence. The influence of variable consumption data was analysed by comparing Rur and Lambro results. Assuming equal dosage, as was the case in section 7.3.2, gives higher normalised CLs in the Rur than in the Lambro catchment, which is due to catchment parameters. Also considering actual detergent consumptions shows that the Lambro catchment is most likely to be more heavily influenced by detergents than the Rur catchment. This is caused by higher detergent consumption in Italy.

8.2.5. Contribution of inorganic compounds to measured concentrations

The assessment of the inorganic compounds, performed in section 7.4, estimated potential contributions of these substances to measured concentrations, based on the assumptions of the different product mode scenarios. Concerning sodium, it can be concluded that the sodium concentration is the sum of a natural background concentration and anthropogenic sources, to which detergents only contribute to a limited extent. With respect to the existing sodium limit for German drinking water of 150 mg/l, the environmental relevance of detergent-based sodium emissions is limited. Similar conclusions can be drawn for sulphate and carbonate. This limited relevance of carbonate is a further argument to use percarbonate as a bleaching agent, since it is emitted into surface water in the form of dissolved sodium carbonate.

It was shown that with one exception the contribution of detergent-based silicon to measured silicon concentrations is higher than the contributions of the other investigated inorganic ingredients. The largest fraction of silicon originates from the use of silicon in silicate, not from zeolite. This is in line with estimations performed by Kurzendörfer et al. (1997), who estimated that the contribution of zeolite A to the silicon balance in the freshwater balance is below 1%. Since natural variations are much larger, they considered this contribution to be irrelevant. Schöberl and Huber (1988) state that no ecologically problematic properties of silicate are known. Falcone and Blumberg (1992) state that anthropogenic silicate emissions may be relevant concerning eutrophication, if natural concentrations are very low, i.e. smaller than 0.1 mg/l, which corresponds to 0.047 mg/l silicon. Measured silicon concentrations in the headwaters of the Rur catchment are much higher, since mean values ranging between 2 and 5.5 mg/l were repeatedly measured. Following the arguments put forward by Falcone and Blumberg (1992), this implies that in the Rur catchment additional silicate emissions are not relevant for euthrophication. However, since this may be different in other catchments, the silicate emissions into surface waters due to applications in detergents should not be ignored.

8.2.6. Mixture toxicity

The analysis of mixture toxicity by assuming additivity does not give any further insight. The substance that was already identified as being most relevant. i.e. boron, also dominates the results of the combined toxicity assessment. The PRR_{90}s of the different ingredients only lead to a small increase in the number of stretches with an exceeded threshold. This result confirms that only few substances are relevant in the ecotoxicological evaluation of the aquatic fate of detergents.

8.3. Further aspects

Some potentially important aspects have not been considered in the assessments. The reasons are either due to the fact that the GREAT-ER model does not model them or due to fact that they have not been considered in the case study.

8.3.1. Case study

The PLA did not consider the use of fabric softener. The reason given for this was time limitations (Grießhammer et al., 1997, p. 53). In addition, liquid detergents were not included in the PLA, although the PLA gives a formulation for a liquid detergent. However, many uncertainties related to different existing formulations as well as the limited market share in Germany have led to the decision not to consider liquid detergents in the PLA (Grießhammer et al., 1997, p. 50). Apart from liquid detergents, the model detergents do not span the full range of available detergents. A reason for that was the lack of adequate formulations. A second reason is the emphasis on detergent systems rather than on specific detergents that was followed in both the PLA and this thesis.

A further aspect raised in the PLA but neither assessed there nor in this thesis are improvements that may be achieved by the installation of laundrettes in residential areas. If these were efficiently organised, overdosing may be avoided, which would then eventually lead to a decrease in waterborne emissions of laundry detergents. Laundrettes would most probably have further economic, social, and environmental implications.

Rainwater may also be used for the domestic washing of clothes. Since rainwater is in general softer than tap water, reductions in the use of detergent may be expected. Bronchi et al. (1999) have analysed this by using scenarios defined in the PLA and conducting an LCA applying the CST method (Jolliet and Crettaz, 1997). Reductions in detergent consumptions were indeed calculated. However, other potential impacts increased, e.g. heavy metal concentrations in agricultural soils (Bronchi et al., 1999).

Finally, the model detergents as defined in the PLA do not reflect the current state of knowledge regarding potential ingredients. Other substances have been proposed that were not considered in the PLA. Examples are the nonionic surfactant alkyl polyglucoside (APG) (Steber et al., 1995, Hirsinger and Schick, 1995) as an alternative for AE, the crystalline layered disilicate SKS-6^{TM} as an alternative for zeolite A (Bauer et al., 1999) or polyasparagine acid as an alternative for polycarboxylates (Puls et al., 1999).

8.3.2. Model restrictions

Some aspects that are considered important in an environmental assessment of detergents could not be analysed due to GREAT-ER model constraints.

Sedimentation

A major current limitation is the absence of a sediment compartment within the GREAT-ER model. Sedimentation may be modelled explicitly in modes 2 and 3 of the current GREAT-ER model if the necessary environmental data are available. However, even then sedimentation is only considered as an elimination process. A calculation of detergent ingredient concentrations in the sediment compartment would be a large model improvement, because the environmental relevance of some waterborne emissions is not within the water column, but within the sediment. Examples are cationic surfactants, and fluorescent whitening agents.

Sewage sludge

The mode 2 and 3 WWTP models in GREAT-ER are based on the SIMPLETREAT 3.0 model (Struijs et al., 1991) which calculates the elimination efficiencies and the concentrations in sewage sludge. However, this model requires a large amount of plant-specific parameters, which strongly restricts its use within the GREAT-ER scope. The required data are very difficult to obtain for the large number of existing WWTPs. Therefore, the concentration of detergent ingredients in sewage sludge has not been calculated. However, given the tendency of some detergent ingredients to partition to sludges, for example, zeolite A, polycarboxylates, DAS-1, and LAS, this aspect should be considered in an environmental assessment of detergents that does not only consider the aquatic environment.

The relevance of this environmental pathway depends largely on how the sludge is further processed, i.e. whether it is used as a fertilizer or not. According to the WVER (1996, p. 31), in 1996, 26% of the sewage sludge was used as fertilizer, while 73% was burned and 1% was deposited (from a total of 17,000 t). Using assumptions on the fate of the detergent ingredients in primary and secondary sludge, a very rough estimate of the mean concentration in sludge could be derived. By incorporating informations about the further processing of the sludge and about the area of agricultural soils treated with sludge, concentrations in the soils may be derived.

However, this has not been done here, because the uncertainties involved are considered to be too large. In addition, the aim of this thesis is to develop a method for assessing aquatic impacts, not those occurring in the terrestrial environment, although this is a highly relevant environmental compartment.

Degradation products

Degradation kinetics given in the literature usually only describe primary degradation. However, it may occur that not the parent compound but its transformation products are of environmental concern. One example is the nonionic surfactant alkylphenol ethoxylate, which degrades to the persistent, more toxic, estrogenic active, and more bioaccumulative metabolite alkylphenol (Destaillats et al., 2000). In addition, some of the detergent ingredients considered in this thesis have also been investigated concerning the formation of metabolites. In some cases, transformation occurs already in the WWTP. If the WWTP efficiencies as used in the GREAT-ER product mode assessment only reflect primary degradation, the degradation products would be falsely omitted in the assessment. An example for this is AE, which may degrade to free fatty alcohol (FFA) and polyethylene glycol (PEG, Szymanski et al., 2000). A second example is LAS. Di Corcia et al. (1999) analysed the environmental fate of its metabolites and also that of LAS coproducts.

There are two reasons why degradation products have not been considered. Firstly, the consideration of degradation products is not yet implemented in the GREAT-ER 1.0 model. Secondly, and more important, not enough literature is available in which these degradation processes are investigated with respect to detergent ingredients. In addition, no studies were found at all from which the kinetics of such degradation processes could have been quantified, which is a prerequisite for modelling these processes. The inclusion in GREAT-ER may, therefore, only be envisaged if sufficient research has been conducted, from which quantifications of these processes can be derived. Currently, metabolites are omitted, since not enough knowledge of the environmental fate of metabolites of the different detergent ingredients is available.

9. Sustainable Development Indicators

Since 1992, sustainable development has become a main political and ethical principle on which environmental and developmental policy is based. This principle challenged scientists to develop methods that analyse the degree of sustainability of human activities. This task has not yet been fulfilled, since tools and methods enabling such an evaluation are still lacking.

In this chapter, it is investigated how the GREAT-ER product mode can be used to define sustainable development indicators (SDIs) describing certain environmental aspects of household laundry. Since the GREAT-ER product mode has proven to be a useful method to assess and evaluate aquatic impacts of household laundry, it may be used to describe the sustainability of this activity. This chapter may be regarded as an outlook with respect to further applications of the GREAT-ER product mode.

9.1. Sustainable Development

Sustainable development as a guiding principle and paradigm for global development was first mentioned in a report provided by the World Commission on Environment and Development (WCED, Brundtland commission), who defined sustainable development as *"development that meets the needs of the present without compromising the ability of future generations to meet their own needs"* (WCED, 1987). A core element of this is the interdependency of social, economic, and ecological constraints, since it was recognised that, especially on a global scale, environmental issues cannot be seen distinct from economic development.

At the United Nations Earth Conference in Rio de Janeiro in 1992, sustainable development became an accepted goal of both industrialised and developing countries. The conference ended with the resolution of the global action programme for the 21st century, *'Agenda 21'*, which was signed by more than 170 countries (UNCED, 1993). The governments that signed the Agenda 21 started to develop national action plans. Furthermore, similar programmes were initiated also on regional and local levels.

On an international level, the *'Commission for Sustainable Development'* (CSD) of the

United Nations was founded to pursue ongoing activities following the Rio conference (CSD, 2000). They started work on the development of SDIs. It soon became apparent that such indicators, and thus sustainable development, may mean something different for different cultures and generations.

In Germany, the Federal Environmental Agency (UBA) published a report entitled *'Sustainable Germany'* (UBA, 1997), in which different development pathways for selected human activities were shown with respect to how they could be classified as being sustainable. In the authors' point of view sustainable development implies *"firstly, the interdependency of ecological, economic, social and cultural development; secondly, the prioritisation of the precautionary principle, and the larger-scale environmental objectives and strategies that must now be specified at national, regional and local level"* (UBA, 1997, p. 5).

Focussing on material and substance flows, as early as 1994 the commission of enquiry *('Enquete-Kommission') 'Protecting Humans and the Environment'* of the 12th German Parliament published their final report entitled *'Die Industriegesellschaft gestalten'*, in which they used sustainable development as a general framework and paradigm[1] (Enquete-Kommission, 1994). They defined four basic rules that may not be disobeyed. The first two rules demand that the use of resources shall be below the renewable and compensation rates, whereas rules 3 and 4 define requirements for emissions.

Grießhammer et al. (1997, p. 19f.) formulated a set of requirements for sustainable development. They correspond to the four rules mentioned above, but further substantiate them. Requirements mentioned are inter- and intragenerational equity, limitation of population growth, human rights, replacement of non-sustainable production and consumption structures, solving substance-specific environmental problems, and the prevention of risks. However, as already admitted by the authors, some of these requirements need clarification and consensus-building. For example, which risks shall be avoided and what are (non-) sustainable production and consumption structures?

It is likely that due to the interdependency of economic, social, and ecological aspects the decision on the sustainability of a certain activity may turn out to be different in different regions. Accordingly, the sustainability of a product may be different between regions if some important aspects vary between the regions. Also, for reasons of economic equity it may be sustainable that one region produces larger emissions than another which has already received economic benefits in the past. A prominent example is the use of pesticides such as DDT. While DDT has been banned in industrialised countries, it is still used in developing countries due to its important role in combatting malaria (UNEP, 1998).

[1] To further pursue these efforts, the 13th German Parliament also set up an commission of enquiry (*'Konzept Nachhaltigkeit'*, Enquete-Kommission, 1998).

9.2. Existing SDI approaches

An indicator can be defined as a figure describing the state of a system (Walz, 1999). Different aspects and information may be combined in one indicator.

In order to derive SDIs, international as well as national bodies have published approaches for indicator sets. Since many of them are having a general character, specifications for different applications are required. Sandhövel (1999) gives an overview of existing indicator sets. Of these, those developed by the CSD (CSD, 1999) and the Organisation for Economic Co-Operation and Development (OECD, 1999) can be seen as foundation stones.

Both are based on the pressure-state-response approach (Walz, 1999). With respect to environmental aspects of sustainable development, **pressure indicators** describe emissions into the environment, for example, given as measured consumption data (e.g. per-capita water consumption in a region CSD, 1999) or as carbon dioxide equivalents. In the CSD approach, the term 'pressure' is replaced by the term 'driving force'. **State indicators** describe the state of an environmental system in a region. Finally, **response indicators** describe human activities aiming at sustainable development. Using freshwater systems as an example, pressure indicators may therefore be phosphate emissions or eutrophication equivalents emitted in a region. A state indicator may, for example, be the percentage of rivers with a defined water quality, and a response indicator may be the percentage of wastewater treatment plants in a region that carry out tertiary treatment[2]. Therefore, for each environmental impact category or problem area, three or more indicators may exist. In fact, the CSD approach contains for each chapter of the Agenda 21 three sets of indicators which represent driving force, state, and response aspects. Due to this, numerous indicators may be defined which may lead to a rejection of such an indicator set due to impracticability. For example, during efforts to develop a national indicator system for Germany, based on the 'pressure-state-response' approach, 400 indicators were proposed, of which 140 were selected for further investigation[3] (Walz, 1999). For this reason, the number of SDIs required for describing a human activity should be as small as possible.

Many of the proposed indicators are measurable indicators describing the pressure, state, and response in a region. However, if the focus is drawn to a specific human activity or a product family, it may become difficult or impossible to derive directly measurable indicators, because the contribution of a specific activity to a measurable indicator often cannot be derived from measurements. For example, water quality is also classified according to measured concentrations of total organic carbon (TOC, Landesumweltamt Nordrhein-Westfalen, 1997, p. 56). However, whether these observable concentrations result from surfactants used in detergents or from other sources cannot be measured. Models need to be applied to derive this information. If the results obtained by such models support

[2] Please note that these indicators are all spatially aggregated figures describing a region.

[3] In different regional programmes, further choices for the implementation of indicators at a regional to local level have been carried out (Schepelmann, 1999, Franke, 1999, Lühmann, 1999).

observations, the environmental relevance and thus the value of the information for the decision-making process is at its greatest.

A further important differentiation of SDIs is whether they are sectoral, i.e. they describe only sustainability aspects of a specific sector, or general. The indicator proposed by the the CSD are all general, whereas, concerning sectoral indicators, the OECD interim report on the development of sustainable development indicators concludes that *“there is considerable interest in developing indicators that consider how sectoral policies may impact on the environment (...)”* (OECD, 1999, p. 80).

9.3. Indicators describing the environmental sustainability of household laundry

Ratte (1999) gives a list of criteria for the choice of SDIs to be used in Germany. In an initial phase, Ratte proposes a prioritisation. Important criteria defined in this prioritisation are compatibility to the Agenda 21, comprehensibility, screening character, sensitivity concerning temporal trends, and a maintainable effort to derive the indicator. Further criteria considered important for household laundry are a limited number of indicators, the consideration of fate and toxicological information, and the ability to quantify the respective influence of the different actors.

It should be noted that in the Agenda 21 environmental, economic, social, and institutional dimensions of sustainability are mentioned. For this reason, indicators for all these aspects are required in a complete indicator set. However, in this chapter only indicators describing the environmental aspects of household laundry are defined.

9.3.1. Pressure indicators

In the case of household laundry the most obvious pressure indicator is per-capita detergent consumption. However, such an indicator only partially considers regional variabilities. Since regional variabilities such as wastewater treatment significantly influence the environmental evaluation of detergents, which was shown in section 7.3, indicator that do not take regional variabilities into account are not suited for describing the sustainability of household laundry. A better pressure indicator is the critical length normalised by the population, which describes the quantity of emissions in a region on a per-capita basis, but additionally includes fate and toxicological information regarding the ingredients of the detergent. It is proposed to calculate the CL assuming average washing habits and an average detergent formulation in a reference region. Since information on average washing habits and product formulations are in general available, such an indicator can be calculated without further data requirements. For example, in Germany the definition of average product formulations and washing habits may be performed by the Federal Environmental Agency, which already has the required information.

The normalisation based on the population includes a further requirement of sustainability, i.e. intra-generational equity, since it allows a comparison between regions. In addition, temporal trends may be analysed by calculating the CL for different years. One further advantage of the CL indicator is its independence from specific detergent ingredients, since it can be calculated for any detergent.

A measurable pressure indicator which is derived from the product mode analysis is the regional per-capita boron consumption from use in detergents. The predicted importance of the boron content in the detergent formulation makes the per-capita boron consumption suitable for describing environmental aspects of household laundry. However, it is possible that such an indicator may be outdated soon, for example, if boron was substituted by percarbonate. This may occur for any indicator that is based on a specific detergent ingredient. For this reason, an indicator such as the CL that does not depend on specific substances is to be preferred.

9.3.2. State indicators

The most common indicator for describing the environmental state of surface waters is the percentages of river stretches that have a defined water quality (Ratte, 1999). With respect to household laundry, a substance exclusively used in laundry detergents may be chosen as the basis for an indicator, which is similar to an indicator describing water quality. The percentage of stretches in which measurable concentrations are near or above a threshold chosen for this substance would then be a state indicator. Currently, LAS and AE may be candidates for this, since both substances are environmentally relevant, and they are almost exclusively used in detergents. However, as previously discussed, the use of substance-specific indicators does have some disadvantages.

Therefore, an indicator that does not depend on a specific compound is preferable. The product risk ratio (PRR_x) calculated from the same scenario as the pressure indicator CL is suited as state indicator, since it provides information about aquatic impacts in a region due to household laundry. The indicator should be given as a percentage per catchment in order to be able to compare different regions. A further advantage is the fact that this indicator, like the CL, can be estimated, whereas most proposed state indicators are measurable indicators. However, environmental monitoring is time-consuming and expensive. For this reason, the modelled indicator PRR_x should be used in a first screening. In order to gain further insight, other indicators may be used in a second step.

9.3.3. Response indicators

Response indicators measure the reactions of humans to environmental, economic or social threats. As was shown in the case study, the choice of detergents, their formulation, the amount of laundry, and wastewater treatment are the main factors influencing the likelihood and quantity of aquatic ecotoxicological impacts. Based on the case study, the market share of the tandem and 3-component systems in a region may be a response indicator for household laundry. However, in this indicator the most relevant factors are omitted, e.g. the consideration of the product formulation, washing habits, and wastewater treatment. Therefore, the previously proposed pressure and state indicators are sufficient for describing aquatic aspects of household laundry, since the product choice in a region is implicitly considered in these indicators.

A further response indicator that is relevant for the sustainability of household laundry is the percentage of WWTPs that perform activated sludge or even tertiary treatment. This indicator is already included in existing indicator sets (e.g. as proposed for the region Lower Saxony, Germany, by Schilling, 1999).

9.4. Discussion of proposed indicators

It is shown that pressure, state, and response indicators may be defined for household laundry. The CL is mainly a measure for emissions of laundry detergents, adjusted by fate and toxicological information without describing the state of the environment, whereas the PRR_x-based indicator describes aspects of the aquatic environment's expected state with respect to detergent ingredients. Both indicators are sectoral, since they only rely on household laundry. This is an advantage, since the need for sectoral indicators has been expressed at the beginning of this section. A further advantage is the fact that both indicators do not depend on specific detergents ingredients. A minor disadvantage of both indicators is their dependency on all actors, since use habits, product formulations, and wastewater treatment influence the indicators. This disadvantage can be eliminated by calculating different scenarios, as performed in chapter 7 of this thesis.

Both CL and PRR_x fulfill the criteria proposed by Ratte (1999). Both are comprehensible, since they are calculated using a transparent GIS-based model that is based on realistic input data. Due to the fact that they can be modelled, they have a screening character and can be calculated at a limited expenditure. They also allow to track temporal trends, since the indicators can be calculated for different years. Finally, they are compatible with the Agenda 21. since the indicators allow the comparison of regions, which is required to analyse the intra-generational equity mentioned in the Agenda 21.

A problem inherent to all indicators distinguishing sustainable from unsustainable conditions is to define the thresholds. Such a decision cannot be made by scientists alone, but also has to consider different human perceptions and values. One way in which to overcome this problem is to identify and track temporal developments of chosen indicators in order to analyse whether a society is moving towards a sustainable state. This strategy is also mentioned by Ratte (1999) and may be conducted using the proposed indicators.

10. Conclusions

The aim of this thesis was to develop a methodology for assessing and evaluating aquatic ecotoxicological impacts of household laundry. The methodology was tested using the case study defined in the comprehensive product assessment ‘Washing and washing agents’ (PLA, Grießhammer et al., 1997). As a further application, pressure and state indicators describing the aquatic ecotoxicological aspects of the sustainability of household laundry have been proposed on the basis of the GREAT-ER product mode.

10.1. Combination of LCA and ERA

An environmental risk assessment of chemicals (ERA) typically calculates environmental concentrations of substances based on emission scenarios, which may vary in their degree of complexity and realism. These concentrations are compared to effect concentrations in order to derive a risk characterisation. This procedure permits an evaluation based on observable impacts, as long as the modelling of both emission and environmental fate is done in a realistic way. Due to the pretense of Life Cycle Assessment (LCA) to consider all emissions and resource consumptions occurring during the entire life cycle of an investigated product system, such a high level of predictive power is in general not achievable within an LCA. Advantages of LCA compared to ERA are the focus on a product rather than on a single substance and the concept of a functional unit, which allows comparisons of different alternatives fulfilling the same service. LCA only performs comparative analyses, while ERA analyses and evaluates absolute impacts related to the use of a chemical compound in a defined manner.

In this thesis, the concept of a functional unit has been applied in order to compare alternatives fulfilling the same service, which is the annual household laundry in a region. From ERA, the GREAT-ER model and its capability to predict realistic concentrations in freshwater systems was chosen. Due to this combination, it is only possible to calculate concentration increases rather than concentrations, because the background concentrations of the detergent ingredients are unknown. These background concentrations may be of both geogenic and anthropogenic origin. In addition, due to the product scenario’s assumption that a single product is exclusively used in a defined manner, the predicted concentration increases are not expected to be realistic. Nevertheless, it has been shown that an evaluation of threshold exceedance provides useful information even under these restrictions. For this reason, the central purpose of the GREAT-ER product mode is to estimate concentration increases that are expected to occur in the surface waters of the selected catchment assuming the entire population were to use the chosen product in the defined manner.

The evaluation of the results of these scenarios is performed in two ways using concepts from both LCA and ERA. The critical length (CL) evaluation is similar to typical LCA methods, since it follows the 'less-is-better' paradigm, while the product risk ratio (PRR_x) evaluation is an 'only-above-threshold' method typically applied in ERA. It could be shown that, due to the geographical complexity of the river network, both approaches give similar conclusions. The advantage of the PRR_x approach is the fact that it gives results that are more closely related to measurable quantities. The advantage of the CL evaluation is the fact that it gives a relative measure independent of further choices, whereas in the PRR_x evaluation the acceptable ratio, e.g. 1 or 0.1, on which the evaluation is based, has to be chosen. In addition, if the exceedance of this chosen PRR_x is considered acceptable in some stretches, this percentage of stretches also has to be defined.

Concluding, the GREAT-ER product mode is related more closely to the general framework of LCA than to the basic concepts of ERA. Obviously, basic elements of LCA are not considered in the method, such as the consideration of all relevant impact categories and the assessment of all emissions and resource consumptions occurring in all life stages. However, it has been shown that LCA studies can be used as a basis for the definition of GREAT-ER product mode scenarios. Weighting and the interpretation phase can then jointly be based on the results from the LCIA method and on those from the GREAT-ER product mode. How the weighting can be done depends also on the chosen LCA methodology.

10.2. Case study

The product mode was tested using the scenarios defined in the PLA. The main result is the clear differentiation of the heavy-duty and compact heavy-duty detergents on the one hand, and the 3-component and tandem systems on the other. The reason is the significance of boron in the first two product alternatives. Concluding, from an environmental point of view consumers should use separate detergents for coloured and white laundry.

Furthermore, it has been shown that the surfactants are highly relevant. Based on the results of the scenarios calculated in this thesis, AS proved to be environmentally superior to LAS, which could be expected with respect to the substance data used. Compared to the surfactants and boron, all other ingredients are environmentally less relevant. This conclusion was also supported in the analysis of the mixture toxicity when assuming additive toxicity.

A further result derived from the reference scenarios is the fact that the variabilities due to dosage variations have a larger influence on the results than differences in the formulations of the detergents. This is largely dependent on the definitions of the use habits (the realism of which may be debatable). Nevertheless, the influence of washing habits proved to be highly relevant.

The largest results variability was observed when different wastewater treatment techniques were compared. It was shown that even the ranking of the different products was changing. Wastewater treatment is neither controlled by producers of detergents nor by consumers, but by regional authorities. For this reason, these three societal groups have the ability to influence environmental impacts of household laundry.

The results of the case study were partly expected. In fact, the ingredients that have turned out to be most relevant, i.e. the surfactants and boron, are those that are most often investigated by scientists. However, the predicted dominance of boron in some products was surprising. In addition, the minor relevance of almost all substances apart from boron and the surfactants was not expected. The fact that in the case study model detergents were analysed that have already been in existence for several years, suggests that their most relevant environmental impacts were already known. Having therewith confirmed the applicability of the GREAT-ER product mode, it would be interesting to analyse case studies with less investigated parameters concerning the region, the detergent ingredients, and washing habits. Furthermore, the analysis of new product groups promises to be highly interesting.

10.3. Required effort

Performing a product mode assessment necessitates considerable effort. This effort can be divided into three different parts: i) the development of the GREAT-ER product mode, ii) the incorporation of the Rur catchment data, and iii) the case study calculations.

The first aspect was performed with limited expenditure, since it is based on the GREAT-ER 1.0 model, which did not have to be developed within this thesis. The largest effort was required for the incorporation of the Rur catchment. One may argue that this has to be done only once, but this is only partly true, since data need to be updated. Finally, some efforts is required for the case study. First, substance data have to be derived from the literature. Second, the calculations have to be performed and evaluated.

Concluding, collecting all the required geographical data is the most time-consuming task. Regarding the new technologies available, this seems surprising. The question arises whether this substantial effort is due to the fact that data do not exist or that they are not publically available. For the data necessary in the GREAT-ER product mode, the latter is mainly the case. The discussion should therefore be raised, how this problem could be solved.

An alternative might be to work with a limited number of reference regions. This would ameliorate though not solve the previously mentioned problem. The first data collection phase might be achieved with limited expenditure, but keeping the data up-to-date requires a constant amount of work, unless means could be established to perform this updating automatically. Again, this raises the need for discussion with the owners of the data.

Judging the effort necessary to develop a method implies the analysis of the value of information and its potential use in other applications. For this reason, the application of the GREAT-ER model within different contexts should be thoroughly evaluated, if the general usefulness of the GREAT-ER system would be agreed upon. An application of the GREAT-ER model apart from ERA has been proposed with the development of the product mode. Thinking beyond this thesis, it seems easily possible to assess new detergents and washing habits, but also other product groups with the GREAT-ER product mode, as long as the use pattern is in accordance with the emission pathways modelled by GREAT-ER. For example, cleaning agents and cosmetic products such as hair shampoo or shaving creams may be modelled. In addition, with respect to GREAT-ER model developments and extensions, other product groups may be assessed and evaluated in the future. New products can be entered by directly specifying their formulations, while the incorporation of new use habits is facilitated by a brief manual given in appendix D.

10.4. Value of information

The value of the additional information depends on the question for which the information has been derived. The question depends on the person asking the question. Thus, the value of information of the GREAT-ER product mode is different for the different stakeholders involved. Consumers principally have the choice between different products. For them, the information about the contribution of a single ingredient to the total impact is not of prime importance, since they do not have the possibility to replace a single ingredient by another. To act environmentally consciously, consumers need information about the ranking of the different alternatives based on the same service. In addition, they need easy guidance regarding the dosage and the choice which product to use for which laundry.

Producers, on the other hand, may be interested in product optimisation. They have the possibility to alter detergent formulations. As such a decision may have large economic as well as ecological consequences, the decision should be based on arguments beyond those typically provided by an LCA. For them, the value of information of the GREAT-ER product mode is very high compared to other approaches, since most LCA methods do not evaluate the contribution of single ingredients to aquatic emissions occurring after the use phase. Regional authorities typically decide upon the wastewater treatment technique, the relevance of which was demonstrated within this thesis. Potential improvements possible due to different wastewater treatment techniques compared to the influence of both consumer and producer is an important information.

The value of information also depends on the paradigm preferred by the user, i.e. either ‘less-is-better’ or ‘only-above-threshold’. Although the results have turned out to be similar, the users should decide themselves whether to follow one or the other approach. This choice depends on the suitability for the actual decision-making process in which the study is used as well as on different cultural perspectives. An example of how to include different cultural perspectives within LCA has been proposed as part of the Eco-Indicator 99 methodology (Hofstetter, 1998, Goedkoop and Spriensma, 1999).

10.5. Sustainable Development indicators

It is a political aim of all countries that signed the Agenda 21 to aim towards sustainable development. As has been discussed, indicators describing the sustainability of human activites are required to achieve this aim. Besides the purpose of comparing product alternatives as previously explored, the CL and PRR_x figures can be used as sustainable development indicators. The normalised CL is proposed as pressure indicator and the percentual PRR_x is proposed as state indicator for describing relevant aspects of the sustainability of household laundry.

Such an application is beyond the scope of a simple product comparison, since it judges the environmental soundness of household laundry in a region based on average washing habits and a typical detergent. Repeating this analysis in constant intervals allows the analysis of temporal trends of detergent-related emissions into and impacts occurring in freshwater systems. The success of regional activities performed by the different actors - consumers, producers, and regional authorities - may be analysed with these indicators, which is important especially in regions and countries with less sophisticated wastewater treatment facilities. From this analysis, optimal solutions may be derived for different regions.

10.6. Concluding remarks

Finally, which detergent should be bought at the supermarket? Since this thesis focused on detergent systems rather than on single products, no specific product can and is intended to be named. Still, compared to conventional heavy duty detergents, compact detergents cause less emissions and therefore less impact in regions where impacts may occur. In addition, separate detergents should be used for the different clothes, i.e. white and coloured laundry. The appropriate choice between a tandem system or a 3-component system is difficult for customers, since, which was also stated in the PLA, the formulations of the specific alternatives determine their environmental competitiveness. In this case study, the 3-component system in general gave better results. However, this was due to the fact that in the tandem system perborate is used as bleaching agent and LAS is the main anionic surfactant, while the 3-component system contains percarbonate and AS for these purposes. In other 3-component or tandem systems it may be the other way round, which would then most probably alter the results.

ERA is capable of and useful for controlling and preventing environmental and human risks resulting from the use of chemicals. For this regulatory purpose, an evaluation of thresholds by assuming actual emission data seems reasonable. However, there are many uncertainties related to environmental fate modelling, realistic emission scenarios, the consideration of degradation products, toxicity of chemical mixtures, the spatially variable dilution ratios in rivers, and differences in wastewater treatment efficiencies. The subsequent application of a ‘less-is-better’ principle seems therefore appropriate for responsible and sustainable product development. Such an approach should not be applied within regulatory purposes. Instead, producers may consider it within an appreciation of environmental, economic, and social values, which is demanded by sustainable development. For such an evaluation, methods are necessary which characterise the added value of a decision. Concerning detergents and related product groups, the GREAT-ER product mode may serve as a method to evaluate the aquatic aspects of such a combined evaluation. The fact that the CLs and PRR_xs are also suited as SDIs further supports the usefulness of the GREAT-ER product mode in decision-making processes aimed at sustainable development.

Even though it seems that the largest and most visible aquatic environmental problems related to household laundry have been solved in Germany by using efficient wastewater treatment techniques in combination with degradable substances, encumbrances still may occur in other regions. Regarding the global scope of sustainable development, there are many countries and continents in which wastewater treatment is insufficient or even lacking. Similarly, detergent formulations and washing habits may differ significantly. In these countries there is a more urgent need for controlling environmental impacts potentially occurring in surface waters. Apart from the mentioned current model restrictions, an appropriate assessment and evaluation method for household laundry is now available. The integration of a case study area for such a region, however, remains to be carried out.

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A. Data appendix

A.1. Substance data

In Table A.1, all substance data used in the product mode assessments are given. Unlike the GREAT-ER 1.0 calculations, per-capita consumption data are not input parameters but are estimated within the model. It should be noted that the actual efficiency of a plant is calculated from the values of the three techniques activated sludge, trickling filter, and primary settler.

Table A.1.: **Substance data used in the product assessments**. AS, TF and PS describe the three currently considered WWTP techniques activated sludge (AS), trickling filter (TF), and primary settler (PS). The LTE concentration is taken from the DID list (European Union, 1999a).

Substance	In-stream removal rate h^{-1}	WWTP efficiency AS %	TF %	PS %	Sewer efficiency %	LTE conc. mg/l
LAS	0.03 - 0.35	97.5	81.25	20	25	0.3
AS	0.03 - 0.35	97.7	81.5	35	25	0.55
Soap	0.006 - 1.71	98	85	45	0	1.6
AE	0.012 - 0.055	98.67	84	25	42	0.24
Zeolite A	0	70	42	67	0	120
Polycarboxylates	0	89-96.3	81.7	18	0	124
Sodium silicates	0	0	0	0	0	1000
Sodium carbonate	0	0	0	0	0	250
Sodium sulfate	0	0	0	0	0	1000
Sodium citrate	0.198	96 - 99	96 - 99	0	25	85
Boron	0	0	0	0	0	0.985[1]
DAS-1	0.011	62	62	50	0	1
CMC	0	27	20	0	0	250
DAED	0.002	96 - 99	96 - 99	0	0	500
PVP	0	14.3	14.3	12.5	0	100

[1] In the DID list the value 6 mg/l is given (European Union, 1999a), which refers to metaborate (European Union, 1999c). A molecular weight based transformation gives the listed value of 0.985 mg/l.

A.2. PLA main results table

In Table A.2, the central results of the LCA conducted within the PLA (Grießhammer et al., 1997, p. 108) are given. Unlike the PLA, the emissions of the use habits are given per capita, not per household. The transformation factor, i.e. the average German household size, is 2.26 (Grießhammer et al., 1997, p. 153). In the PLA, an LCA of the total German washing activities has also been conducted, which is not shown here.

Table A.2.: **PLA main results**

	CO_2	Acid. equiv.	VOCs	EU-points
Model detergent (g per wash)				
Heavy-duty	241	1.64	1.32	39
Compact heavy-duty	161	1.09	0.93	63
Tandem system	150	1.21	1.01	66
3-component system	137	1.07	0.97	72
Model use habits (kg per year and capita)				
Smart	17.26	0.06	0.07	-
Wishy-Washy	70.80	0.19	0.23	-
Scrubbed	198.67	0.50	0.62	-

It should be mentioned that the use habits also consider differences in the washing temperature. In addition, in the Smart use habit no electrical drying is assumed, which differs from the other use habits.

A.3. Further data and source code

Both final GREAT-ER data sets as well as all raw data including hydrological data, discharge sites and attributes, substance data, and background data are stored in the file tree `/home/greatdev` of the file system at the Institute of Environmental Systems Research, University of Osnabrück. Next to the data, source files of all developed scripts and binaries are kept there.

B. Additive mixture toxicity

In this appendix, the proof is given that the sum of the product risk ratios for the different detergent ingredients is equal to a mixture product risk ratio of the detergent, if additive toxicity is assumed.

If additive toxicity is assumed, mixture ecotoxicity of a product can be described according to the model given by Loewe (1953) in the following way (Guhl, 1997).

$$EC_{prod} = 1/(\sum_{ingredients\ i} (c_i/EC_i))$$

or, equivalently,

$$1/EC_{prod} = \sum_{ingredients\ i} (c_i/EC_i)$$

where c_i is the percentage of ingredient i in the product, EC_i is the effect concentration of ingredient *i* and EC_{prod} is the corresponding effect concentration of the product. However, until having reached the surface waters, the composition of the product has changed due to the different environmental fate behaviour of the ingredients in the sewerage system, the WWTP, and finally the surface waters. Thus, c_i has to be replaced. The predicted in-stream percentage of ingredient i in the product can be described as follows:

$$c_i = C_{x,i}/\sum_{ingredients\ j} C_{x,j}$$

where $C_{x,i}$ is the predicted *x*-percentile concentration of ingredient i in the surface water. Combining both equations gives

$$1/EC_{prod} = \sum_{ingredients\ i} \frac{C_{x,i}/\sum_{ingredients\ j} C_{x,j}}{EC_i}$$

which is the same as

$$1/EC_{prod} = \sum_{ingredients\ i} (\frac{1}{\sum_{ingredients\ j} C_{x,j}} \cdot \frac{C_{x,i}}{EC_i})$$

The second quotient in the previous equation is simply the product risk ratio for substance *i* and percentile *x*. Therefore, the equation can be rewritten as

$$1/EC_{prod} = \sum_{ingredients\ i} \frac{PRR_{x,i}}{\sum_{ingredients\ j} C_{x,j}}$$

which can be transformed to

$$\sum_{ingredients\ i} PRR_{x,i} = \frac{\sum_{ingredients\ i} C_{x,i}}{EC_{prod}} = \frac{C_{x,prod}}{EC_{prod}}$$

Using the LTE concentration from the DID-list (European Union, 1999a) as effect concentration, EC_i is replaced by LTE_i, which gives

$$\sum_{ingredients\ i} PRR_{x,i} = \frac{\sum_{ingredients\ i} C_{x,i}}{LTE_{prod}} = \frac{C_{x,prod}}{LTE_{prod}}$$

Thus, the sum of the PRR_xs for the different ingredients equals a risk ratio of a product, when additive toxicity is assumed. The advantage of using the PRR_xs is the fact that the value LTE_{prod} is not known. However, it may easily be calculated using this equation.

It is stressed that no actual risk ratios as used in ERA are considered in the previous equations, but only the product risk ratios as calculated by a chosen product scenario. The actual composition of the detergent ingredients in the rivers is unknown, since some of the substances may also have been discharged due to other applications. Soap is an example for this. In addition, geogenic concentrations exist for some of the inorganic ingredients. Finally, since in reality not only one product is used, but rather a considerable number of different detergents depending on a time-dependent market share, the actual average composition of detergent ingredients is unknown. Therefore, the sole purpose of the assessment of mixture toxicity as conducted in this thesis is the comparison of different detergent alternatives and washing habits.

C. Sodium, salt and silicon contents in model detergents

In order to derive the concentration increases of sodium, silicon, sulfate, and carbonate due to their use in laundry detergents, the formulations of the four model detergents have been changed with respect to the contents of these different compounds in the formulations. These altered detergent formulations are given in Table C.1. In this appendix, the necessary calculations to derive the percentages of these compounds in the adjusted model detergents are given. Since for these hypothetical detergents and subsequently for the substances mentioned below calculations with the GREAT-ER product mode are performed, the necessary substance data concerning wastewater treatment and instream removal are also given.

Table C.1.: **Altered detergent formulations only considering inorganics (%)**

Substance	Heavy-duty	Compact heavy-duty	Tandem system	3-component system	Comment
Sodium	12.65	15.48	14.50	14.88	
Silicon A	3.12	3.18	4.57	6.18	From zeolite A
Silicon B	1.15	1.23	0.93	1.60	From silicates
Carbonate	5.16	7.20	6.51	8.57	
Sulphate	12.85	1.62	2.57	0.07	

Sulphate

The amount of sulphate ions (SO_4^{2-}) present in detergents is derived from the percentage of sodium sulphate. The fraction is calculated from the molar mass. $M(SO_4^{2-})$ = 96.07 g/mol and $M(Na_2SO_4)$ = 142.07 g/mol, which results in sodium sulphate containing 67.62% sulphate. Sulphate is not further eliminated. Therefore, no elimination in the sewers, the WWTPs, and the surface waters is assumed.

Carbonate

The percentage of carbonate ions (CO_3^{2-}) present in detergents is derived from the percentages of sodium carbonate and sodium percarbonate in the detergents and the fractions of carbonate within these salts.

The molar mass of CO_3^{2-} is 60.01 g/mol and the molar mass of sodium carbonate (Na_2CO_3) is 106.01 g/mol, giving 56.61% carbonate content in sodium carbonate. Based on the molecular formula $Na_2CO_3^{2-} \cdot 1.5(H_2O_2)$ for sodium percarbonate, the fraction of sodium carbonate in sodium percarbonate is 68%. This is also the correction factor to be used in the calculation of the EU-points (European Union, 1999c). Combined with the figures above, this gives a carbonate fraction of 38.5% in sodium percarbonate. The total fraction of carbonate in a detergent ($f(CO_3^{2-})$) is therefore

$$f(CO_3^{2-}) = 0.385 \cdot perc(sodiumpercarbonate) + 0.5661 \cdot perc(sodiumcarbonate)$$

where perc is the percentile of sodium carbonate and percarbonate given in the detergent formulation. As in the case of sulphate, no elimination processes are considered here either.

Silicon

The silicon balance in surface waters is influenced by two detergent ingredients, namely sodium silicates and zeolite A. However, these two sources cannot directly be combined since their environmental fate behaviour differs. Therefore, calculations are carried out separately for silicon contained in zeolite A (called silicon A) and in sodium silicate (called silicon B). The concentrations are then added in order to derive predicted silicon concentration increases in surface waters due to the use of silicon compounds in laundry detergents.

Concerning sodium silicate, the same approach as for sulphate is followed, except that the silicon fraction rather than the silicate fraction is used. This is comparable to the calculation of boron, which also occurs in surface waters as borate, but which is measured as boron. The silicon (molecular weight 28.09 g/mol) fraction of sodium silicate ($Na_2O \cdot 4SiO_2$) is 37.16%. This silicon is called silicon B.

The assessment of silicon present in zeolite A is more difficult. In surface waters, zeolite A undergoes hydrolysis (Kurzendörfer et al., 1997). This process is time-dependent, i.e. not all of the silicon discharged as part of zeolite A into the environment will be transformed into water-soluble silicon compounds. This is an example of the formation of a transformation product in surface waters, which is currently not modelled within the GREAT-ER model. Only few studies can be found in the literature analysing the kinetics of this hydrolysis. One study was found reporting a half-life between 1 and 2 months (Schöberl and Huber, 1988).

In order to assess the silicon contribution from the use of Zelithe A in detergents, some studies follow a conservative approach in order to determine an upper bound for the contribution by assuming a complete and instantaneous transformation (Kurzendörfer et al., 1997). This approach is also followed here, which allows a direct application of the GREAT-ER model.

Therefore, firstly the content of silicon in zeolite A is calculated from the molar mass, which is 15.38%. This is based on the zeolite A molecular formula given in the PLA (Grießhammer et al., 1997, appendix p.78), which is $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O$ and has a molecular weight of 2191 g/mol. For the GREAT-ER calculation, this silicon is called silicon A. The substance data regarding transport in the sewers and fate in wastewater treatment are taken from zeolite A (see 4.5), since the assumed instantaneous hydrolysis occurs in the surface waters. As for silicon B, instream removal of silicon A is not taking place.

Sodium

Almost all detergent ingredients are added to the product as sodium salts. In the washing machine, these salts are dissolved immediately. Thus, after the washing process the sodium ions are discharged via the sewerage system and a possible wastewater treatment plant into the surface waters. Elimination processes do not occur.

In order to estimate the sodium loads entering freshwater systems due to their use in detergent formulations, their fractions in the various ingredients (frac$_i$(Na)) have to be estimated based on the molecular weight. In the second step the total percentage of sodium (perc(Na)) in a detergent formulation is derived by adding the products of the sodium fraction in ingredient i and the percentage of the ingredient (perc(i)) in the formulation:

$$perc(Na) = \sum_{Ingredients\ i} (frac_i(Na) \cdot perc(i))$$

The sodium percentages in the detergent ingredients and how these have been derived are given in Table C.2.

Table C.2.: **Sodium (Na) percentages in detergent ingredients**

Substance	MW g/mol	Na %	Comment
LAS	348	6.6	Average German LAS according to Schöberl et al. (1988)
AS	332.2	6.9	Palm cernel-based AS according to Grießhammer et al. (1997, p. 49), molecular weights from Stache (1981)
Soap	277.5	8.3	Mixture of coconut and palm oil as defined in Grießhammer et al. (1997, p. 49), molecular weights from Stache (1981)
Zeolite A	2191.0	12.6	Molecular weight according to Grießhammer et al. (1997, appendix p.78)
Polycarboxylates	m·94.0	24.5	According to the PLA, a homopolymer is applied, the formula of which is $[C_3H_3O_2Na]_m$ (Opgenorth, 1992)
Sodium citrate	258.1	26.7	Based on molecular formula $Na_3C_6H_5O_7$ (Hoyt and Gewanter, 1992)
Sodium silicates	302.4	15.2	Based on molecular formula $Na_2O \cdot 4H_20$ (Grießhammer et al., 1997, appendix, p. 72)
Sodium perborate tetrahydrate	153.8	15.0	Based on molecular formula $NaBO_3 \cdot 4H_20$ (Raymond and Butterwick, 1992)
Sodium percarbonate	155.9	29.5	Based on molecular formula $Na_2CO_3^{2-} \cdot 1.5(H_2O_2)$
Sodium carbonate	106.0	43.4	Based on molecular formula Na_2CO_3
Sodium sulphate	142.1	32.4	Based on molecular formula Na_2SO_4
CMC	433.1	3.3	Based on molecular formula and data given by Bafelaan et al. (1992). For the degree of substitution of OH-groups by carboxymethyl groups the mean of 0.5 and 0.75, values relevant for detergents, is used.
Optical brighteners	925.0	5.0	Based on molecular formula given by Kramer (1992)
TAED			not containing sodium
AE			not containing sodium
PVP			not containing sodium

D. Implementation of the GREAT-ER product mode

In this chapter, different aspects of the graphical user interface (GUI) of the product mode are described. Firstly, implementation principles are given, followed by brief descriptions of the different dialogues. This second part also serves as a short user manual. Finally, a short guide on how to include a new use habit is given.

D.1. Implementation principles

Main structure

The product scenario data structure was developed and implemented on the basis of the existing GREAT-ER scenario concept. While in the GREAT-ER 1.0 software, a scenario is basically defined by a substance and a catchment, the product scenario's main components are a catchment, a product, which mainly consists of a set of substances together with their percentages, and a use habit, whose attributes depend on the kind of product assessed. A currently used definition for the use habit of doing the laundry considers the total amount of laundry per time unit, the average amount of laundry per wash, and the detergent's dosage per wash. A use habit for hair washing, however, would probably only be defined by the two parameters number of hair washes per year and the dosage of the shampoo per wash.

Thus, the implementation of a product assessment needs to be flexible enough to handle different types of use habits, i.e. it must be easily possible to include new scripts and dialogues that allow the assessment of new use habits. This openness is preserved by a short guide on how to include a new use habit given at the end of this appendix. So far, two different use habits for assessing laundry detergents are implemented. One is based on the scenarios defined in the PLA (Grießhammer et al., 1997), and the second reflects the information given in European detergent consumption statistics (Gutzschebauch, 1999).

Once a product scenario is defined, i.e. after having chosen a name, a catchment, a product, a use habit, the model, and environmental parameters, a simulation can be started. Then, annual per-capita consumptions are calculated for all substances that are part of the product, which is the figure needed by the simulator. The equation for calculating the per-capita consumption depends on the definition of the use habit. The per-capita consumptions are written to the results file resultslog.txt, which is stored in the scenario's subdirectory. GREAT-ER then calculates hypothetical concentration increases in the surface waters of the chosen catchment based on the assumptions of the actual scenario. The results are then shown as a theme for each substance, i.e. by showing the mean $C_{\mathrm{sim,internal}}$s. The calculation of the critical lengths CL and the product risk ratios PRR_x can then be carried out. The results are also written to dBase-files, the names of which have to be provided by the user. In addition, the CLs are also written to the file resultslog.txt.

Furthermore, the analysis tools of the original GREAT-ER software have been adjusted to also allow the analysis of GREAT-ER product mode results. Therefore, $PEC_{\mathrm{catchment}}$ and PEC_{initial} values as well as concentration profiles for further plotting can be obtained[1]. Depending on whether the active scenario is a product mode scenario or an ordinary GREAT-ER scenario, the appropriate scripts are invoked.

Definition of products and use habits

The definition of new use habits and products encounters different kinds of difficulties. Typically, product formulations reflect the detergents as they enter the washing machine, while the loads leaving the machine are required for GREAT-ER calculations. Thus, the product formulations are adapted to reflect the loads and substances entering the sewerage system by either substituting some of the substances and/or adjusting their percentages. The substitutions performed in the case study of this thesis are shown in Table 4.1: TAED is substituted by DAED, sodium perborate tetrahydrate is substituted by boron, and sodium percarbonate is included in the sodium carbonate fraction. In addition, the percentage of the whitening agent DAS-1 accounts for the fact that half of the mass remains on the laundry (Richner, 2000). If the definition of other product groups is intended, it must therefore also be assured that the product formulations are given in the composition in which they enter the sewerage system.

In the case of use habits, the complexity depends on the question as to whether the new use habit fits into one of the two currently implemented schemes. If this is the case, the procedure as given in the following section may easily be followed. If, however, a not yet considered type of use habit shall be defined, appropriate scripts and most likely additional dialogues have to be developed. To facilitate this proceeding, guidance is supplied in section D.3.

[1] All these functions are explained in detail in the GREAT-ER user manual (ECETOC, 1999b).

D.2. Main dialogues and User manual

All new functions can be accessed via a new menu called ‘Product’, which was introduced into the GREAT-ER graphical user interface (GUI), see Figure D.1. It is launched when switching to the Product mode or to the Expert mode. In this menu, the main features such as defining, editing, saving, deleting, and closing product scenarios, products, and use habits, as well as importing and exporting the product scenarios are handled. The import and export functions use the same mechanism as the GREAT-ER software. In addition, after having opened many product scenarios, this menu offers the possibility to switch between them. The scripts being invoked from within the other menus such as Substance, Catchment, Model, Analysis, and Display were changed or substituted. Depending on the type of the active scenario, the appropriate script is used. This allows working simultaneously with different types of scenarios. Also, the look-and-feel of the GREAT-ER GUI has remained the same which makes it easy for users familiar with GREAT-ER 1.0 to work with the product mode. The dialogues have been implemented using C++. They are included in the updated dynamic library greater.dll. Their look-and-feel is very similar to the dialogues of GREAT-ER which has advantages both concerning user friendliness and development time.

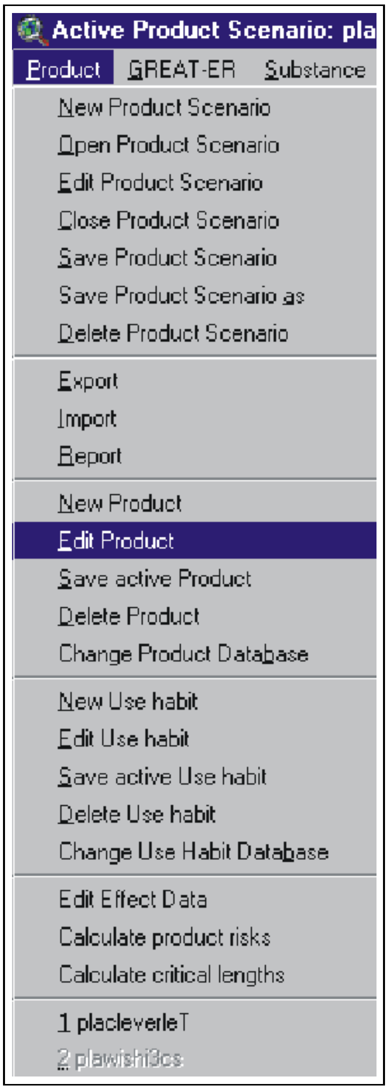

Figure D.1.: The GREAT-ER product menu

The implementation of the dialogues to define, edit, open, and delete product scenarios directly follows the principles of the GREAT-ER 1.0 dialogues. The dialog for defining and editing a product scenario, which is invoked from the entries ‘New Product Scenario’ and ‘Edit Product Scenario’, is shown in Figure D.2. The dialogue for choosing a product scenario is invoked from the ‘Open Product Scenario’ and ‘Delete Product Scenario’ and is shown in Figure D.3. Their functionality and that of a small dialogue invoked by the item ‘Save Product Scenario as’ is identical to that in the GREAT-ER 1.0 scenario dialogues.

The dialogue for editing an existing or defining a new product is the most complex one, since it allows the ingredients and their percentages within the product to be edited (as mentioned above, in the composition the product enters the sewerage system). From within this dialogue, other windows may be opened by either using the appropriate buttons to add a further substance to the formulations or by double-clicking on a substance to alter its percentage. In addition, the name of a product may be edited and a comment may be inserted. It should be noted that altering the name of an existing product implicitly defines a new product, since products are internally identified by their names. The dialogues related to editing a product are given in Figure D.4.

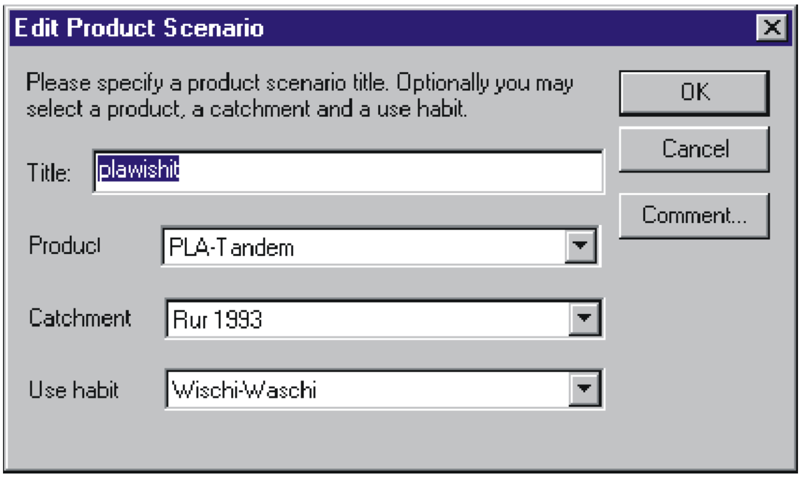

Figure D.2.: **New/Edit product scenario dialogue**

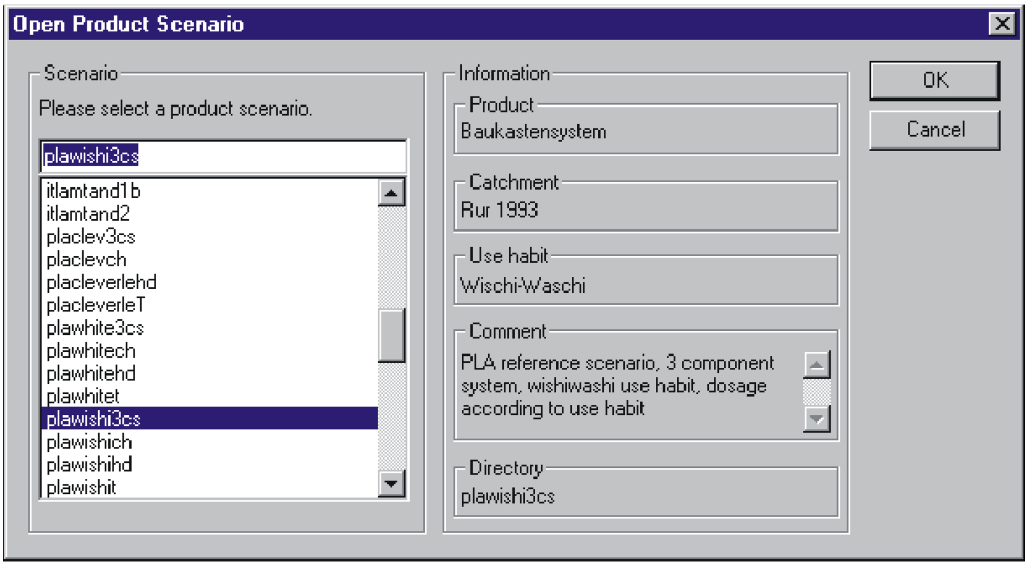

Figure D.3.: **Open/Delete product scenario dialogue**

Further dialogues are required for selecting a product, either for the purpose of editing or deleting the chosen product, and for changing a product database. Both dialogues are identical to corresponding dialogues from the GREAT-ER 1.0 GUI's substance menu and are therefore not explicitly shown.

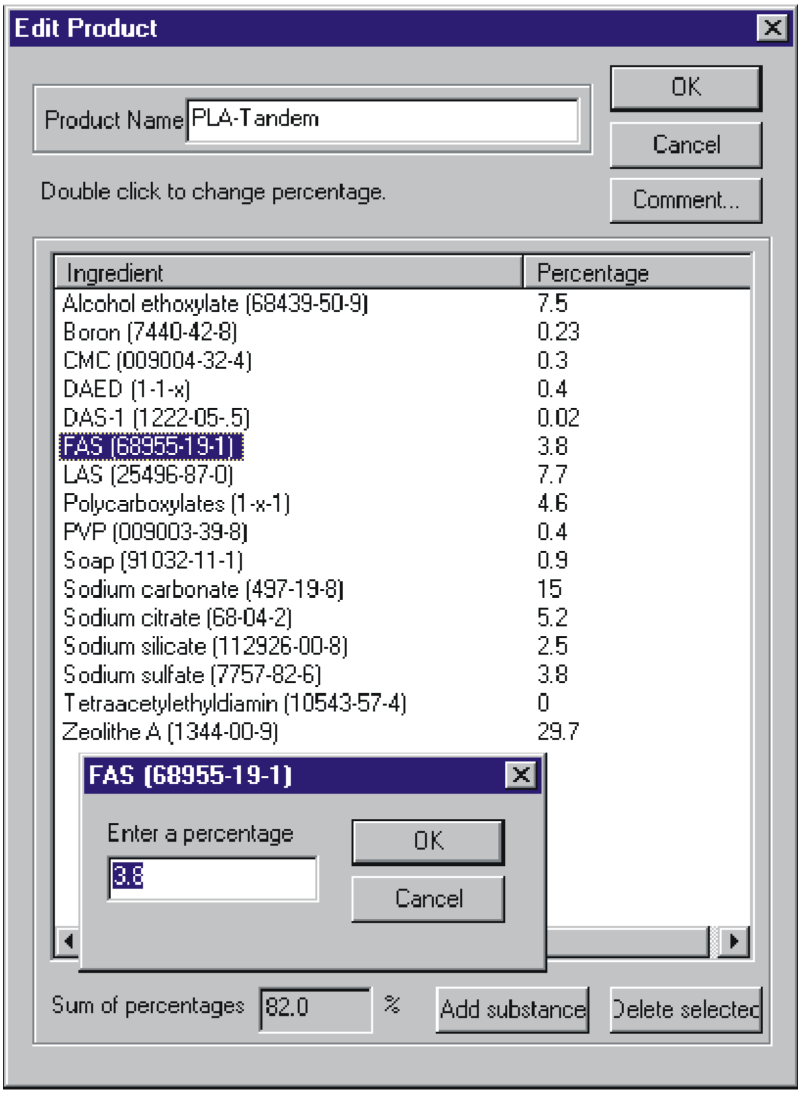

Figure D.4.: **New/Edit product dialogue**

The dialogues for working with use habits can be divided into those that are used for working with any type of use habit and those whose shapes depend on the use habit. The former are developed for selecting a use habit to either edit or delete this use habit and for changing a use habit database. In all these cases, the dialogues are the same as for the corresponding product and substance dialogues. The dialogue to edit or define a use habit depends on the shape of the use habit. Currently, two types of use habits exist, one having two and the other having three parameters. Both dialogues are given in Figure D.5.

If a new use habit is to be defined, the user first gets a list of available use habit types. Depending on the user's choice, an appropriate dialogue will be opened. Thus, the 'New Use Habit' item only allows the definition of a new use habit, which is of an existing type. If a use habit of a not yet implemented type is to be defined, first the new use habit type has to be incorporated into the system. This incorporation has to be performed according to the guidance given in section D.3.

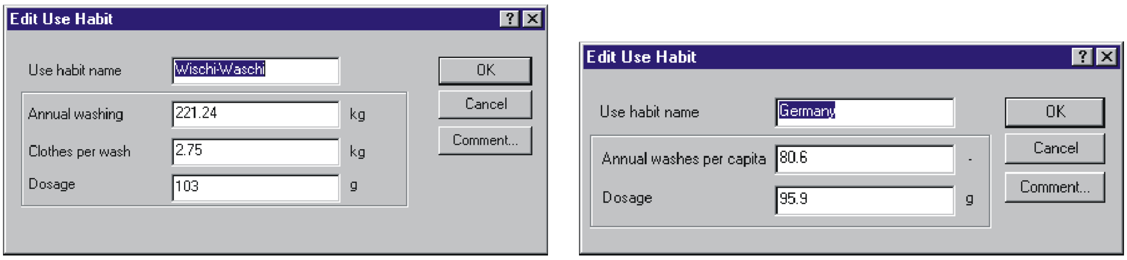

Figure D.5.: **New/Edit use habit dialogues**. The left dialogue is based on the washing habits as defined in the PLA, while the right dialogue is based on studies concerning detergent usages in different European countries.

Use habits may be stored in different files, which are object database files (*.odb). Different types of use habits may be stored in the same file. However, a use habit belongs explicitly to one type of use habit. Internally, this type is represented by an identifier.

Performing a simulation and investigating results

Once a scenario is defined, a simulation can be started. Firstly, a data check is performed. If this test passes, the hypothetical annual consumption is calculated for each substance of the product. The results are automatically stored in the file resultslog.txt. Then GREAT-ER simulations are carried out. The result screen looks similar to the GREAT-ER screen, except that not only one, but one result theme per ingredient exists (see Figure D.6). They can all be investigated using the Identify tool (see Figure D.7) known from GREAT-ER 1.0.

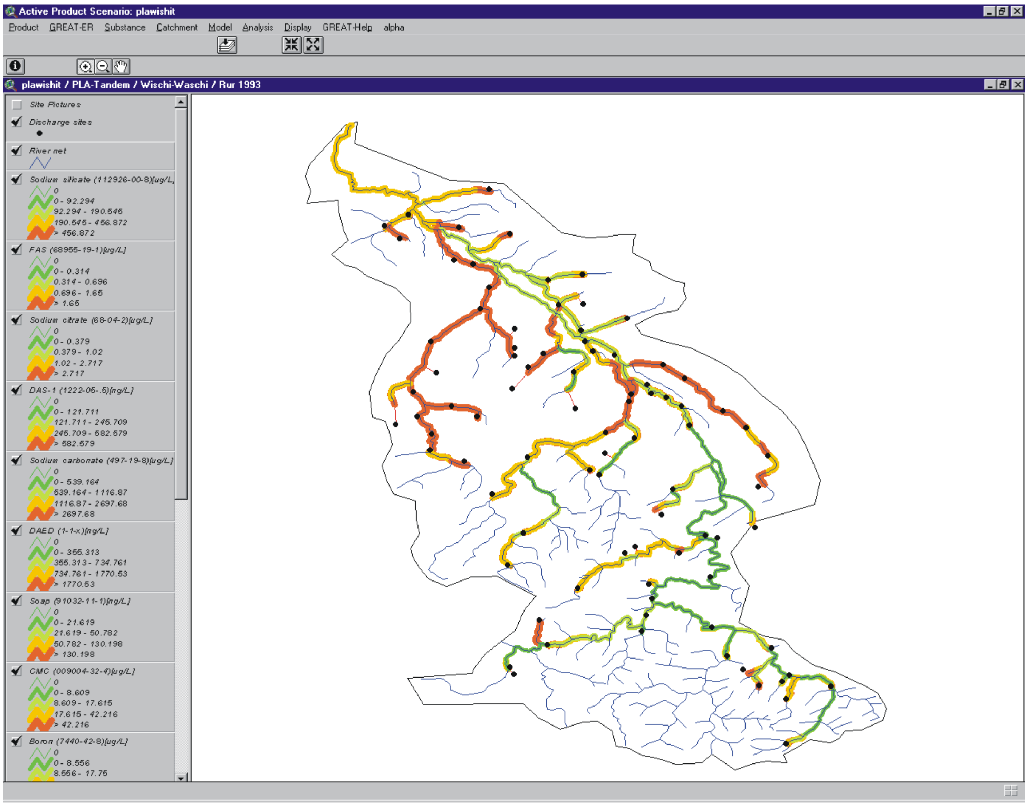

Figure D.6.: **Result screen of the GREAT-ER product mode**

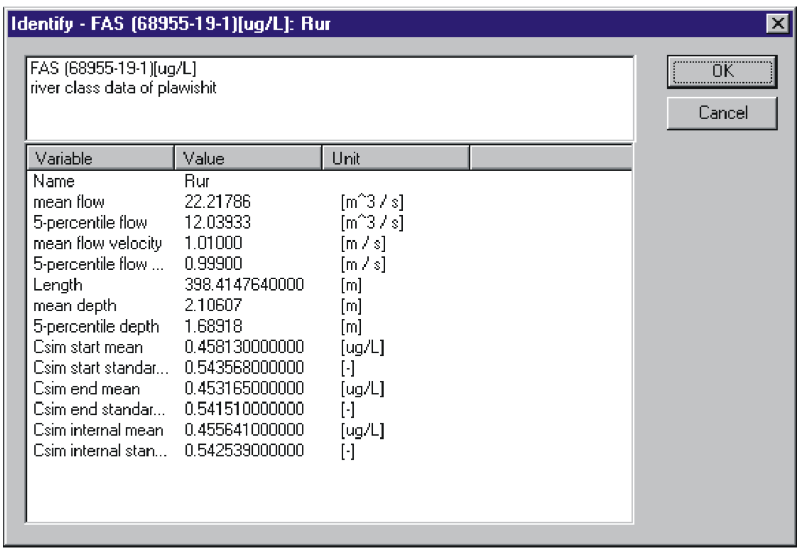

Figure D.7.: **Identify dialogue of the GREAT-ER product mode**

Evaluating the results

As defined in the thesis, evaluation is carried out using the two quantities critical length (CL) and product risk ratio (PRR_x). Both depend on toxicological information, which have to be given for all product ingredients. In addition, they have to be comparable. As outlined in section 4.5, within the case study the LTE concentrations as given in the DID-list are used. The dialogues for editing these data are not complex. A list dialogue is used for choosing the substance, and a text entry dialogue is invoked for editing the effect concentration of the chosen substance. Due to their easy structure, they have been developed in Avenue rather than in C++.

The calculation of the CLs and PRR_xs can directly be invoked using the appropriate menu entries. CLs and PRR_xs may be derived from any result's percentile. Therefore, when invoking either script, the user is asked to choose between mean predicted concentration increases per stretch or any other result's percentile. Then, CLs or PRR_xs are calculated after having chosen a results filename. The results are stored in dBase files in the product scenario's directory. In addition, the results of the CL evaluation are also written into the file resultslog.txt. For the PRR_x calculation, further Avenue scripts have been developed, which allow the evaluation of typically large tables. The columns represent the ingredients, while in the rows the different stretches of the catchment are represented. Within the new Avenue scripts, the stretches in which a defined PRR_x is exceeded by different numbers of substances are counted. Results are again stored in a dBase file.

Besides these new evaluation methods, the GREAT-ER 1.0 analysis tools accessible via the Analysis menu have been extended for use within product scenarios. The features 'Calculate River $C_{sim}X$', '$PEC_{initial}$', '$PEC_{catchment}$', 'Concentration Profile' and 'Export Profile' have been extended to also function with product scenarios. Due to the fact that these calculations are performed for all substances, they may be time-consuming, which depends on the catchment size and the hardware. The calculation of the river percentiles has not changed, except that not only one, but as many new themes as substances in the product are generated for each percentile. The results of the PEC calculations, however, are no longer printed on the screen, but are written directly into the file resultslog.txt, which is stored in the base directory of the corresponding product scenario. The calculated per capita consumptions are also stored in this file. The Report item in the Product menu allows the display of the contents of this file.

D.3. Steps to incorporate a new type of use habit

Some programming is necessary to incorporate new use habits. In any case, some Avenue scripts have to be extended. In some cases, new dialogues have to be developed, which can be done using Avenue, C++ or any other language, depending on the users preference. It only has to be assured that the dialogues can be invoked from within Avenue. The main steps are 1) writing the dialogue and embedding it into the GREAT-ER product mode scripts, 2) writing an Avenue script that calculates the predicted per-capita consumption, and 3) including the new code within the current GREAT-ER product mode scripts. In the last step, it is also described how to include new kinds of products.

Writing the dialogue and embedding it into GREAT-ER

The current edit use habit dialogues have been developed in C++. They are stored in the dynamic library greater.dll and are called from the script f_EUDetHabitDlg.ave and f_DetHabitDlg.ave. A new dialogue should also be wrapped by an appropriate script. These scripts are invoked from within the scripts EditHabit.ave and NewHabit.ave for either editing or defining a new use habit (of already known shape). Incorporating a new type of use habit requires adding some code to these scripts. The corresponding places in the scripts are marked by asterisks (*******).

Firstly, in the script NewHabit.ave the list availHabits has to be extended by a name of the new type of use habit. Secondly, in the same script, a further if-clause has to be included, in which the script wrapping the use habit is started. Thirdly, this new script has to be written. The currently existing scripts f_EUDetHabitDlg.ave and f_DetHabitDlg.ave may be used as a reference for developing this new script. Fourthly, the script has to be included in the file scripts.lst, which is located in the same directory as the Avenue files. Finally, the second step has to be repeated in the script EditHabit.ave. Please note that this has to be done at two places in the script (see the asterisks). Example syntax of the code may be taken from the code of the incorporated use habits, which is self-explanatory.

Writing a script to calculate per-capita consumptions

Depending on the characteristics of the new use habit, the per-capita consumption is calculated differently. Therefore, an Avenue script that is similar to the currently used scripts f_CalculateDetergentCons.ave and f_CalculateEUDetergentCons.ave has to be developed, which calculates on the basis of both active use habit and active product per-capita consumptions for all ingredients, and creates the internal dictionary Consumptions, in which the calculated per-capita consumptions are stored. In addition, the calculated per-capita consumptions shall be written to the file resultslog.txt. The main structure of this script can be taken from the aforementioned two scripts.

Inclusion into the GREAT-ER scripts

The script to calculate per-capita consumptions is invoked from the script f_StartProdSim.ave. Therefore, in this script, a further if-clause also has to be added at the appropriate place. Within this if-clause, the new script that calculates the per-capita consumptions of all ingredients is invoked. Within this if-clause it is also checked whether product and use-habit fit together. Each product has an identifier describing the kind of product. Currently, all products are of type ‘Laundry’. If a new product group is to be included, the if-clause in the script f_StartProdSim.ave has to be altered to account for this. The product identifier is defined at the end of the script f_DetergentDlg.ave. Therefore, if a new product group is also to be modelled, the script NewProduct.ave needs to be extended by an if-clause and a dialogue prompting for the kind of product.