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**CHEMICAL FATE PREDICTION FOR USE IN GEO-
REFERENCED ENVIRONMENTAL EXPOSURE ASSESSMENT**

**VOORSPELLING VAN HET GEDRAG VAN CHEMICALIEN
IN HET MILIEU MET HET OOG OP GEOGRAFISCH
GEREFEREERDE BLOOTSTELLINGSBEOORDELING**

door

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Chapter 1

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Geo-referenced Environmental Risk Assessment, the GREAT-ER Project

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Chapter 1

Geo-referenced Environmental Risk Assessment, the GREAT-ER Project

The work described in this thesis was conducted in the framework of the GREAT-ER project (Geography-referenced Regional Exposure Assessment Tool for European Rivers). The objective of this international project was to develop a tool to accurately predict chemical exposure in the aquatic environment, for use in environmental risk assessment. As the techniques which are currently used to assess regional exposure do not account for spatial and temporal variability, and do not offer realistic predictions of actual concentrations, they are merely applicable on a screening level. In GREAT-ER, a software system was developed to predict concentrations of 'down-the-drain' chemicals (e.g. detergents) in surface waters in a more realistic and accurate way. To reach this objective, a Geographic Information System (GIS) was used for data storage and visualization, combined with adequate mathematical models for the prediction of chemical fate.

1. Introduction

1.1. Safety Aspects of 'Down-the-Drain' Chemicals

During the past decades, households have become more and more dependent on consumer chemicals for hygiene and comfort. In first instance, the main safety aspects of these chemicals are related to the potential dangers they may pose to the consumer, either through normal use or through abnormal or accidental contacts with the products.

After consumption, many of these chemical substances are discharged 'down the drain' into domestic sewage (e.g. Woltering *et al.*, 1987). During their conveyance through sewers and purification in waste water treatment plants (WWTPs), they may be transformed or eliminated by several chemical, biological or physical processes. However, a fraction of the chemicals - or their transformation products - may pass through the waste water infrastructure, and be discharged into surface waters. Another fraction can be retained in waste water treatment sludge, and may hence end up in agricultural soil or landfills, and later be transported to ground water. Yet another fraction may volatilize and undergo atmospheric transport, fate and deposition processes.

Here, two more aspects of chemical safety arise. As spent ‘down-the-drain’ chemicals can reach several compartments of the environment, they may pose a risk to the individual organisms present in these compartments, and to the functioning and the structure of the ecosystems as a whole. Moreover, the ‘technological environment’ of biological waste water treatment systems may also be at risk, due to inhibition of the purification processes. Second, the chemicals may enter the human food chain or drinking water supplies through these environmental compartments (ECETOC, 1994a). This way, they may pose a risk to a population which is larger than the individual consumers only.

An overview of the different safety (and risk) aspects of ‘down-the-drain’ consumer chemicals is shown below, in Figure 1.1.

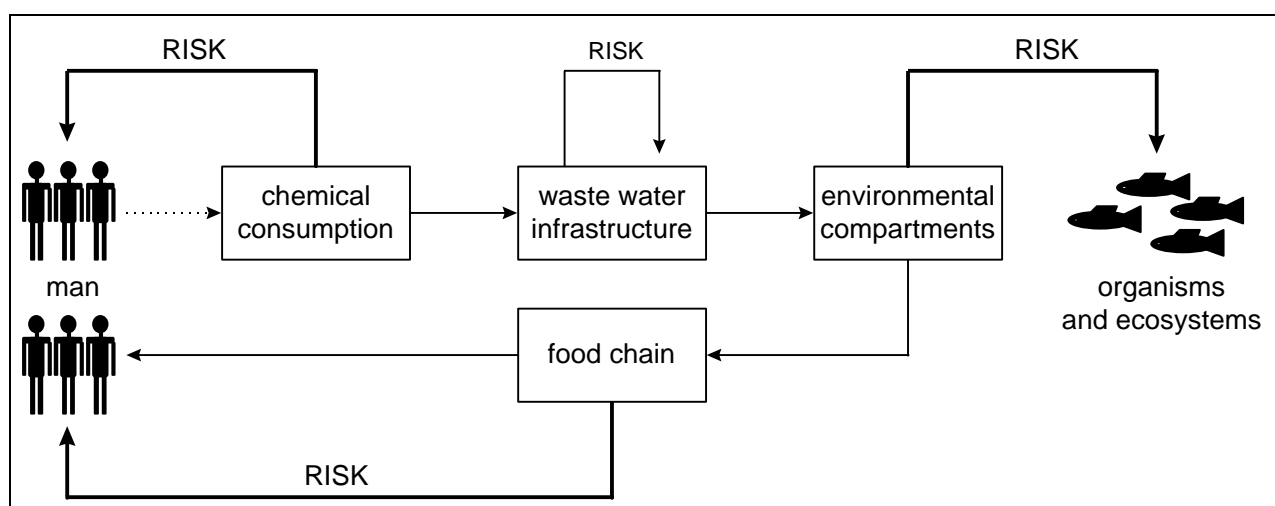


Figure 1.1. Safety aspects of ‘down-the-drain’ consumer chemicals (schematic)

1.2. Environmental Risk and Exposure Assessment

The goal of comprehensive risk assessment is to estimate the likelihood and the extent of adverse effects occurring in man, animals or ecological systems from possible exposure(s) to substances (Feijtel *et al.*, 1997). In this thesis, only the environmental part of chemical risk assessment is considered. The determination whether a substance presents a risk to organisms in the environment is based on the comparison of a predicted environmental concentration (PEC) with a predicted no effect concentration (PNEC) to organisms in ecosystems (ECETOC, 1993). Such assessment can be performed for different compartments (e.g. air, water and soil) and on different spatial scales (local, regional). For application within European Union chemical legislation, this is further captured in a number of European Commission documents (EEC, 1993, 1994a, 1994b), and implemented in the European Union System for the Evaluation of Substances EUSES (Vermeire *et al.*, 1997).

The basic environmental risk assessment scheme is given below in Figure 1.2 (after ECETOC, 1993). Environmental risk assessment typically consists of 3 main steps:

- On the exposure side, a prediction is made of the chemical concentrations in the environmental compartment(s) of concern (ECETOC, 1994b). Hence chemical emissions and releases have to be estimated, as well as chemical fate and distribution. The result of such an exposure assessment is a PEC (Predicted Environmental Concentration).
- On the effects side, the potential impact of the considered chemical on representative organisms is quantified. Generally, data obtained from ecotoxicological tests are extrapolated, to result in a PNEC (Predicted No Effect Concentration).
- Finally, the obtained PEC and PNEC values are compared. If the ratio $PEC / PNEC$ is below 1, the chemical is considered safe under the proposed or current usage pattern. If on the other hand $PEC / PNEC$ is higher than one, safety can not be guaranteed, and a refinement of the assessment is needed.

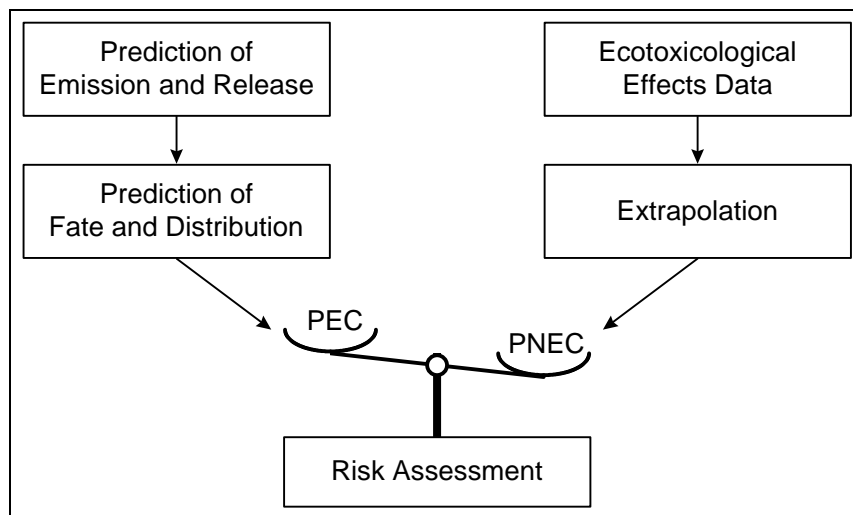


Figure 1.2. Environmental risk assessment process (schematic)

Reliable data on release and emission and reliable physico-chemical data of the substance are key elements for the calculation of relevant PECs for the different environmental compartments. Since the use of more detailed information on the chemical's release in a specific catchment or region may result in a significantly lower predicted environmental concentration, refinement of exposure - rather than effects - will generally be preferred when a risk assessment needs to be refined (Feijtel *et al.*, 1997).

2. Exposure Assessment

The objective of exposure assessment is (1) to identify the relevant environmental compartments which are of concern for a specific chemical, and (2) to provide information about the resulting steady-state concentrations of that chemical in the different compartments. The effect of transport, dilution and transformation processes on the distribution and concentration of chemicals in the different environmental compartments may be predicted by means of mathematical fate models (OECD, 1989; ECETOC, 1992), it may be assessed using simulations in experimental laboratory setups, or - if possible - it may be directly measured in the environment (ECETOC, 1993).

2.1. Current Methods

Exposure estimations can refer to either a regional or a local situation. A regional exposure assessment takes into consideration the fate, transport and distribution of a chemical into different media (air, water, soil and biota) away from the source of emission. Regional PECs can be used as predicted 'background' levels, on top of which site-specific emissions may occur. A local exposure assessment focuses on the environment close to the source of emission (e.g. waste water effluent) and assesses maximum exposure levels (i.e. 'local' realistic worst-case estimates). The decision whether a regional or local assessment is most appropriate depends on the use and release pattern of a substance (Feijtel *et al.*, 1995).

2.1.1. Regional Exposure

As 'down-the-drain' chemicals are typically dispersively used and emitted into the environment, the prediction of regional exposure is a relevant risk assessment tool for these substances. Currently, generic multimedia models are used for regional exposure prediction within the EU risk assessment schemes (EEC, 1993, 1994a, 1994b; Vermeire *et al.*, 1997).

Multimedia models have been developed to estimate fate and behavior of a chemical in the environment on a large (regional) scale. They give an idea of the mass balance of a chemical and identify the compartment(s) in which it tends to partition. They have been introduced for evaluative purposes; they do not exactly represent the real but rather a generic environment which may help understanding the fate and behavior of a substance (ECETOC, 1992). In these techniques, the concept of a 'unit world' evaluative environment (first proposed by Baughman and Lassiter, 1978) is applied. This is supposed to represent the actual environment on a large scale. It is divided in several interconnected compartments with specified volumes (e.g. air, water, soil, sediment, suspended solids and aquatic biota) (Figure 1.3). Within each compartment, the chemical is assumed to be evenly distributed. Several definitions for such a generic environment have been proposed (e.g. Mackay *et al.*, 1992; ECETOC, 1993; RIVM *et al.*, 1994). In the definition by Mackay *et al.* (1992), the 'unit world' has an area of 100,000 km², an atmospheric height of 1,000 m, and water surface area of 10,000 km² (hence 10% of the total area) with a depth of 20 m.

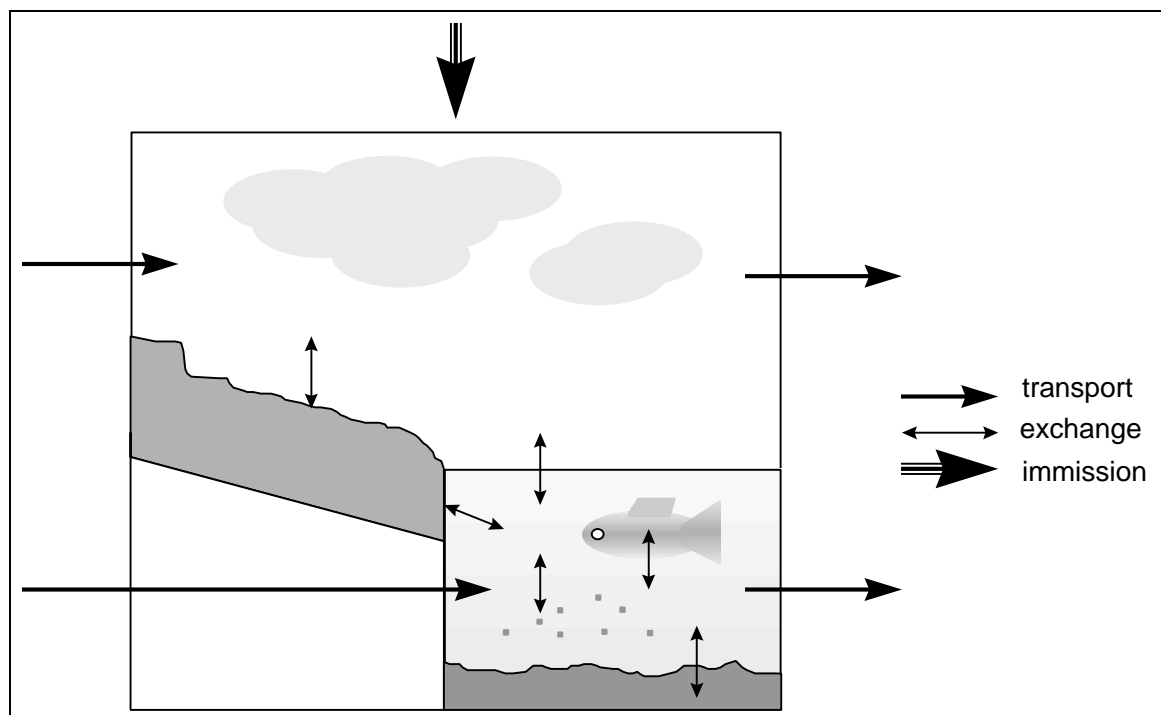


Figure 1.3. Multimedia 'unit world' evaluative environment

Multimedia fugacity chemical fate models are used to predict the environmental partitioning or removal of the chemical within the 'unit world', and its concentrations in the different compartments (Mackay, 1991). Four classes of these models exist (Mackay and Paterson, 1981):

- Level I: equilibrium and steady-state are assumed, and transformation of the chemical is not taken into account. Level I models help in identifying the 'target' compartments which may have to be studied more extensively.
- Level II: equilibrium and steady-state are also assumed, but next to this chemical transformation and advection are considered..
- Level III: since the rate of transfer between compartments is taken into account, not equilibrium but only steady state is assumed. Level III models are built around a system of equations, one for each compartment, which describe all inputs and outputs for each compartment. These models present a more accurate estimate of chemical quantities and concentrations in each environmental compartment, and of the chemical's persistence.
- Level IV: non-equilibrium and non-steady state are assumed. Level IV models allow prediction of the time required for the chemical to disappear from the environment once its use has ceased or, alternatively, the time needed to reach steady-state when chemical releases are continuing. These models use the same set of equations as Level III, but because of the non-steady state assumption, solution becomes more complicated. The use of these models is only recommended for estimating the disappearance of chemicals from the environment (ECETOC, 1992).

The concept of fugacity, which drives these models, is well explained in Mackay & Paterson (1981). Fugacity f can be regarded as the ‘escaping tendency’ of a chemical substance from a phase. It has units of pressure (Pa). In the atmosphere, fugacity is usually equal to the partial pressure of a substance. f can be related to concentrations C using a fugacity capacity constant Z , with units of $mol.m^{-3}.Pa^{-1}$:

$$C = Z \cdot f \quad [1.1]$$

The fugacity capacity Z quantifies the capacity of the phase for fugacity. At a given fugacity, if Z is low, C is also low, and only a small amount of substance is necessary to exert the escaping tendency. Substances thus tend to accumulate in phases where Z is high, i.e. where high concentrations can be reached without creating high fugacities. Z depends on temperature, pressure, the nature of the substance, and the medium in which it is present. Its concentration dependence is usually very limited at high dilutions (which is typical for environmental contaminants).

If there is contact between two phases, equilibrium of a substance will be reached when the fugacities are equal. From this, it can be derived that the dimensionless partition coefficient controlling the distribution of the substance between both phases is merely the ratio of their fugacity capacities.

2.1.2. Local Exposure

Local air, water and soil models are designed to complement regional models, in order to refine the prediction of actual substance concentrations for the compartment of concern, near the source of emission. An overview of existing local fate and exposure models is given in ECETOC (1992). Local models can be used to estimate maximum (initial) levels, and to quantify temporal and spatial variations in concentrations at some distance from the emission, taking into account the relevant fate processes (ECETOC, 1994b).

2.2. Limitations of Generic Regional Exposure Assessment Methods

Representing the environment in the form of ‘unit world’ models constitutes a large simplification. An important drawback is that these models compute only one concentration value for each compartment, whereas actual concentrations in the environment vary spatially and temporally (Mackay & Paterson, 1981). Measurements indicate that this variation may range over several orders of magnitude (ECETOC, 1988). Hence, these models are only suited to provide an indication of concentrations in places far away from the source of emission. Therefore, their quantitative results must be used with care (ECETOC, 1992).

Furthermore, in assessments using generic evaluative environments, regional averages or default environmental characteristics are used, rather than geographically referenced specific information. A typical example which is important for ‘down-the-drain’ consumer chemicals, is the connection degree to domestic WWTPs. In the default European Union case (EEC, 1994b) a connection to

treatment of approximately 70% is put forward, hence leaving 30 % of the discharges untreated. As spatial or temporal variability in environmental characteristics, river flows, degrees of treatment or chemical emissions are not taken into account, the obtained results are not realistic, and are therefore only applicable at screening level (European Science Foundation, 1995).

In Figure 1.4, it is illustrated how PECs are influenced by the connection degree to waste water treatment and by chemical removal efficiency in such treatment. In this example, chemical removal was varied between 80% and 99.9%, the WWTP connection degree was varied between 50% and 100%, the raw sewage chemical concentration was 1 mg/L, and dilution in receiving water was by a factor 10 (assuming instantaneous and complete mixing). It is clear that with 70% waste water treatment (cf. the generic EU case) PECs are much higher than under a situation with > 90% connection. When an average treatment degree is used as the default for an entire region, the resulting high PECs are used for risk assessment in areas where treatment is nearly complete as well as areas where no treatment exists.

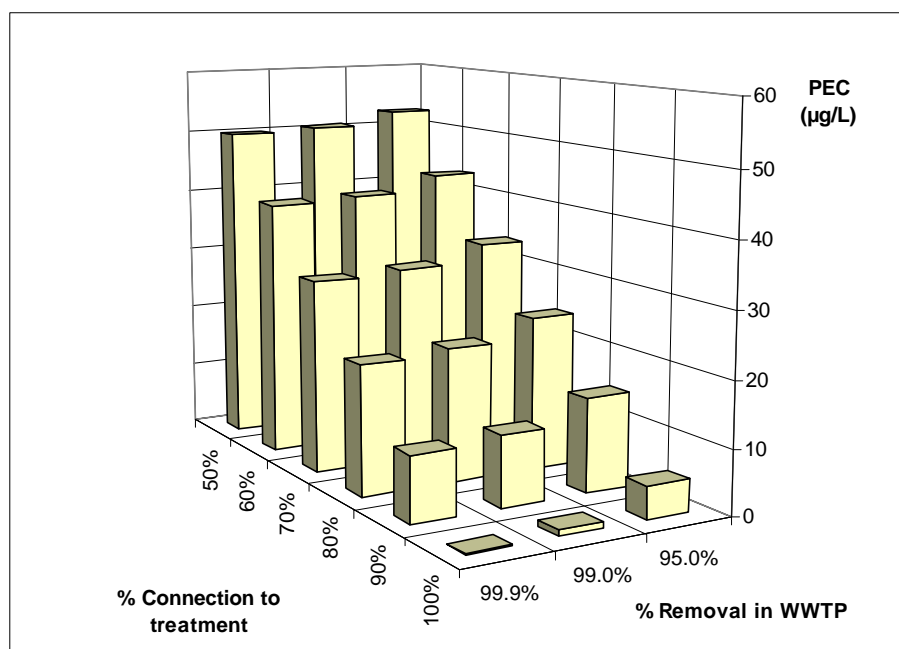


Figure 1.4. PEC as a function of % treatment and removal efficiency

Previous and current legislation and industry strategies have stressed the importance of a high, almost complete removal of consumer chemicals in WWTPs. In a situation where waste water treatment is incomplete, the importance of this very high removal (> 99%) becomes less significant, as even small percentages of directly discharged waste water cause high increases in environmental concentrations. Thus, under these conditions efforts to develop readily biodegradable consumer product ingredients are in part negated by the absence of adequate waste water treatment facilities. Environmental risk and river quality will largely be affected by direct discharges, instead of treated discharges of municipal treatment plants (Feijtel *et al.*, 1997).

It is obvious that the current generic exposure assessment approach causes two problems. For chemicals which are highly removed in WWTPs, there is a large over-estimation of regional PECs in the majority of EU waters, where treatment is adequate and wide-spread. This will lead to environmental risk assessments which are too conservative. On the other hand, for so-called 'hot spots', where no or limited treatment exists, the estimates of regional exposure are expected to be too low. Risk assessments using these PECs can hence not be positioned in respect to the protection goals and ecological quality objectives for the specific ecosystems.

A more detailed regional PEC calculation for geographies with a high connection to waste water treatment should result in more realistic (and lower) PEC values, which correspond better to the actual measured environmental concentrations. For the 'hot spots', a more detailed approach will lead to the calculation of a realistic worst-case PEC, which will be significantly higher than the 'average' regional PEC. Present knowledge about the effects of direct untreated discharges of individual chemicals on the freshwater environment is limited (e.g. Cowan & Masscheleyn, 1997). Typically, no discrimination can be made between the effects of the chemical and of the untreated sewage itself. It is therefore questionable whether the accepted chemical risk assessment procedures can be applied with any confidence in these situations.

2.3. Geo-referenced Regional Exposure Assessment

Realism in regional exposure assessment can only be further introduced by verification of the underlying assumptions of the applied fate models, and by taking into account the specific structure and properties of the receiving environment as well as specific information on the waste water treatment infrastructure (Feijtel *et al.*, 1997). However, the use of specific, geo-referenced information is fundamentally in conflict with the concept of a generic evaluative environment. Hence, a geographically referenced regional exposure assessment methodology is required to improve regional PEC estimation compared to the current generic approach.

2.3.1. Geo-referenced Evaluative Environments

For several regions, the 'unit world' concept has been applied in a geo-referenced way. In this approach, large geographical entities (such as countries) are divided into smaller regions, for which the generic environmental parameters are replaced by specific data. Examples are France (CHEMFRANCE: Devillers *et al.*, 1995), Canada (CHEMCAN, applied in e.g. Mackay *et al.*, 1996), and Denmark (Severinsen *et al.*, 1996). Although the accuracy of these region-specific applications of the 'unit world' concept is generally higher compared to the generic methods, they still have to deal with the same fundamental drawbacks as the latter.

2.3.2. Regionalizing of Local Exposure Assessment

Another method of including a geographical aspect in regional exposure assessment, is to develop a regional exposure prediction by means of local exposure models. To achieve this, a region is to be split up into a large number of interconnected 'local' environments, for all of which local PECs are to be calculated. In the ROUT model (Rapaport and Caprara, 1988), information about the location and emissions of individual WWTPs is combined with data on river flows. As this model is linked with several pan-USA databases, geo-referenced chemical fate simulations are possible which result in aquatic PECs for all main rivers in the USA (Caprara and Rapaport, 1991). The ROUT approach has also been applied to the river Rhine (Hennes and Rapaport, 1989). In the US-EPA water quality assessment model BASINS (Whittemore, 1998), a simple river dilution and fate model for performing screening-level assessments of toxic pollutants (TOXIROUTE) was combined with a GIS (Geographical Information System), to allow visualization of geo-referenced predicted exposure in rivers. A simplified simulation of individual chemical fate is also possible in the GIS-based water quality model NOPOLU (Béture-Cérec, France).

3. The GREAT-ER Project

The work described in this thesis (see section 4 of this chapter) was mainly conducted in the framework of the GREAT-ER project. To situate this work, a description of the entire project is given in this section.

The GREAT-ER project (Geography-referenced Regional Exposure Assessment Tool for European Rivers) (Feijtel *et al.*, 1997; Matthies *et al.*, 1997; Boeije & Schowanek, 1997) aims to refine PEC calculations of ‘down-the-drain’ consumer chemicals in the aquatic environment. A new fate simulation concept was developed to obtain more reliable predictions, which are to be applicable at a higher risk assessment tier than the current methods. Geo-referenced ‘real’ datasets are applied instead of generic or average values. To account for temporal variability and uncertainty, PECs were defined as statistical distributions. Predicted concentrations can be visualized and (spatially) analyzed by means of a Geographic Information System (GIS).

Compared to the existing GIS-linked chemical fate models (see higher, 2.3.2), GREAT-ER is more advanced. It is specifically dedicated to chemical fate simulation and allows the use of more complex and detailed fate models. Its built-in analysis tools are focused on environmental exposure assessment and PEC calculations. Finally, it allows to perform uncertainty and variability analyses.

3.1. Modular Approach

The project was approached in a modular way (Figure 1.5):

- Geographical Data Methodology - input data sourced from several data bases (and from the hydrology module) were transformed into appropriate GIS formats, including geographical segmentation
(work performed by the Institute of Environmental Systems Research, University of Osnabrück, Germany)
- Hydrology - several hydrological databases were combined with a hydrological model, to provide the GREAT-ER system with the required flow distributions and river characteristics
(work performed by the NERC Institute of Hydrology, Wallingford, UK)
- Chemical Fate Modeling - prediction of chemical emission, of transformations during conveyance and treatment, and of chemical fate in rivers, resulting in geo-referenced frequency distributions of predicted concentrations
(work described in this thesis)

- GIS / Model Integration - access to and visualization of the data banks and model results was achieved, as well as the linking of the models with the data banks

(work performed jointly with the Institute of Environmental Systems Research, University of Osnabrück, Germany)

- Monitoring - to provide the specific environmental measurements required for model calibration and corroboration

(work performed by a task force of the European Center for Toxicology and Ecotoxicology of Chemicals - ECETOC, the UK Environment Agency, and the University of Milan, Italy)

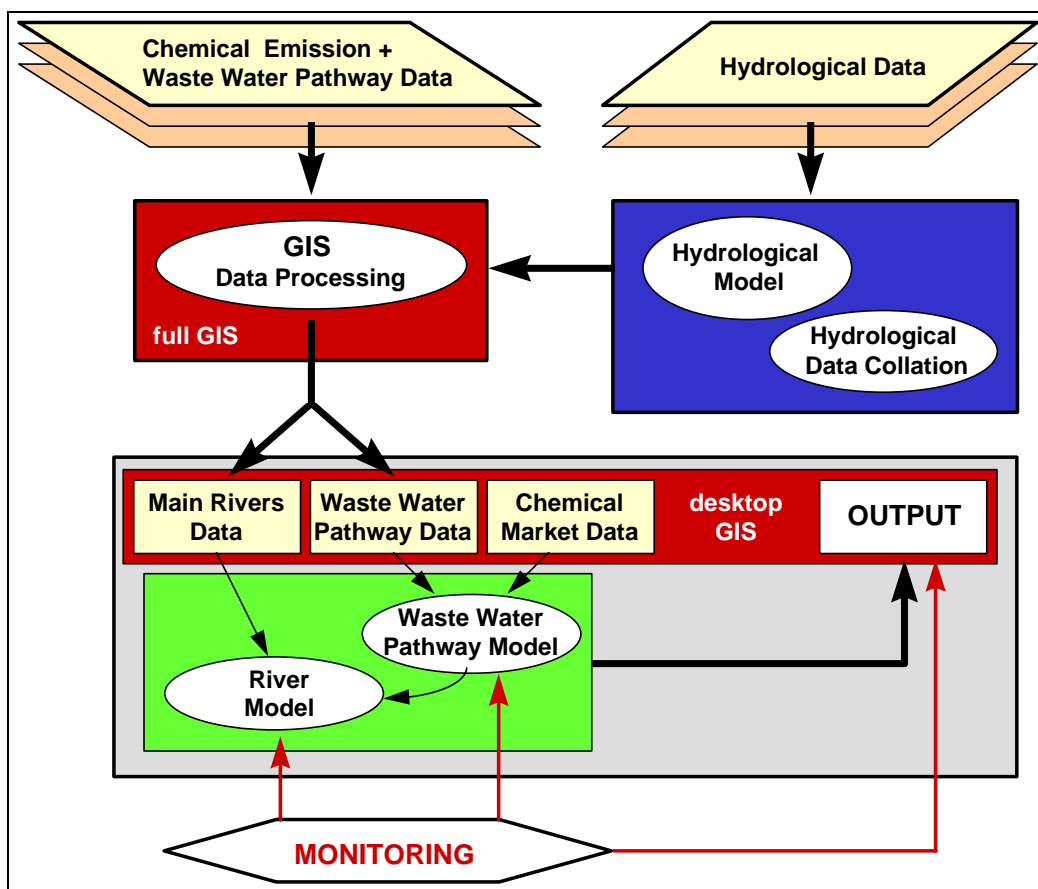


Figure 1.5. GREAT-ER project: modular approach

3.2. Geographical Data Methodology

3.2.1. Scope and Scale

A blueprint system ('prototype') was developed, and applied to 2 main pilot study areas: in northern Europe: UK, Yorkshire Ouse (15,000 km²), and in southern Europe: Italy, Lambro (sub-catchment of the Po, near Milan) (1,000 km²). Next to this, GREAT-ER was also applied to the Itter, Rur and

Untermain (Germany), and the Rupel (Belgium). The ultimate objective is to implement the GREAT-ER system for the entire European Union.

The blueprint system is scale-independent. The scale is only determined by the scale of the used geographically-referenced data bases. Hence, one specific area can be modeled at a small detailed scale or at a large, less detailed scale. Based on the pilot study area experiments, an optimal range of geographical scales for the pan-European application will have to be determined. Typically, such an optimal scale will represent a compromise between data availability, model complexity and desired accuracy.

3.2.2. Geographic Information System (GIS) Data Processing

A GIS approach was used for data storage and visualization. This allows an easy data access by the fate models, and user-friendly interactions. Moreover, it allows spatial analysis and interpretation of model results. A flexible, data-driven approach is followed. The general data structure is based on digital river networks. Both river properties and information on waste water discharges (and emission) are related to river stretches, which are geo-referenced within a network.

For the transformation of various input data sources, specific GIS data conversions and transformations were to be applied (Wagner & Matthies, 1997). The software ARC/INFO (®ESRI, Redlands, Ca., USA) was used for this purpose. Geographical segmentation was also performed using this tool.

3.3. Hydrology

3.3.1. Digital River Network and Hydrological Data

Pan-European river network data can be sourced from the CORINE large scale digital rivers. For the UK pilot study area, the required information was obtained from the Micro Low Flows (® NERC-Institute of Hydrology, Wallingford, UK) database. For the Lambro, detailed river networks were digitized from base maps. Flow distribution curves were derived from time-series flow measurements. These are characterized by their mean and 5th percentile (defined as Q95, the flow which is exceeded in 95% of time). The measured flow information was entered into the geographically referenced hydrological data bank. The principal source of measured pan-European flow data will be the European FRIEND databases, the EEC CORINE river flow database, and the GRDC (Global Runoff Data Center).

3.3.2. Hydrological Modeling

For ungauged river stretches, hydrological model results were used to complement flow data in the hydrological data bank. There is a considerable variation in the behavior of river flows across Europe, depending on climate, physical catchment properties, and artificial influences. A quantitative hydrological model, based on existing methods (Gustard *et al.*, 1992) was used for flow

predictions. These methods were adapted to incorporate seasonality of low flows, local hydrometric data, and different hydrological situations.

In general, a step-wise approach was applied: (1) the average annual runoff and a local estimate of mean flow were calculated from a simple water balance model, where the catchment average values were estimated from maps; (2) the flow distribution curve was derived: characterization of the catchment low flow response by a multivariate regression model, derivation of a dimensionless flow duration type curve characteristic for such low flow response, and re-scaling of the selected curve by the local estimate of mean flow.

Flow velocities were derived from a statistical relation with flow characteristics (Round *et al.*, 1998). Velocities are required for the calculation of the hydraulic residence time in a river stretch, and hence for the estimation of in-stream-removal of chemicals.

3.4. Chemical Fate Modeling

3.4.1. Deterministic Models

Mechanistic chemical fate models were applied (Boeije *et al.*, 1997). These describe the behavior / removal of chemicals in the main compartments of the technosphere and the ecosystem. A distinction was made between chemical sorption, volatilization, biological degradation, non-biological degradation, etc. The fate kinetics for these different processes were estimated from physical / chemical and biological properties of the considered substances, and from relevant environmental parameters.

The chemical fate model consists of two main sections: (1) a waste water pathway model, used to estimate the emission of chemicals, their transport and fate through the waste water conveyance system, and their removal in treatment plants (e.g. Struijs, 1996); and (2) a river fate model, which is used to calculate PECs along 'main' rivers (e.g. Trapp & Matthies, 1996).

3.4.2. Stochastic Aspects

By means of Monte Carlo simulation, a stochastic layer was added on top of the deterministic fate simulation core (e.g. NRA, 1990). This deals with the inherent variability of the environment (seasonality: flow distributions, temperature, wind speed,...) and parameter uncertainty (e.g. uncertainty on chemical consumption, on physical/chemical properties,...). Variability and uncertainty may be captured in statistical frequency distributions. In each Monte Carlo 'shot', discrete samples are taken from these distributions, and used as input for the deterministic fate models. This hybrid approach finally results in statistical distributions of predicted concentrations for each river stretch.

3.5. GIS / Model Integration

The (standardized) GIS data banks and the chemical fate models were integrated into one coherent simulation system (Wagner & Matthies, 1997). Statistical and spatial analysis tools can also be integrated. Data transfer between the GIS and the models can be performed by means of direct or indirect coupling. In the latter approach, a GIS / Model Interchange Server (GMIS) is used to generate the appropriate model input data formats from the data banks, and to convert simulation results back to a GIS format (Figure 1.6).

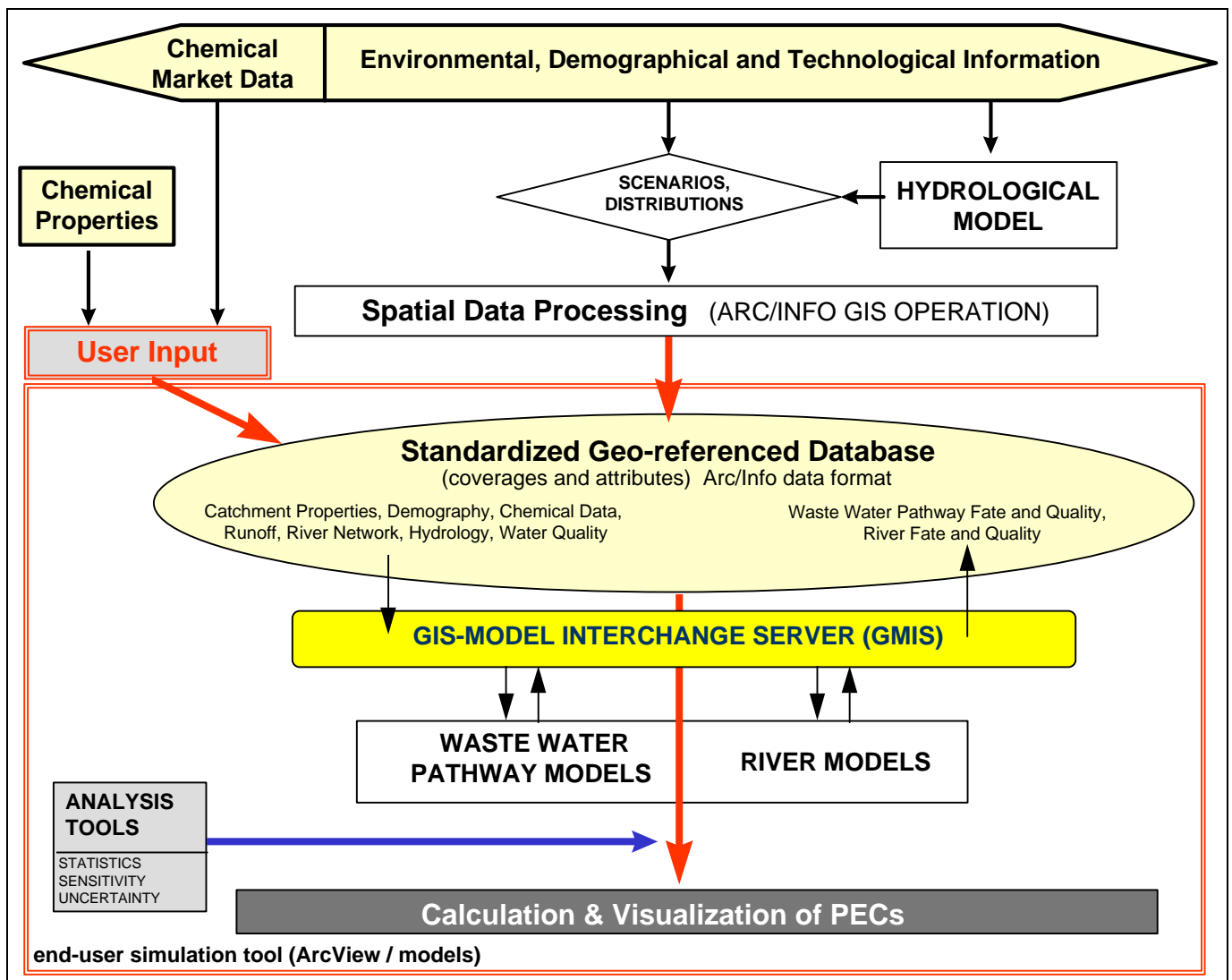


Figure 1.6. GREAT-ER project: GIS / model integration methodology

For the end-user software, the desktop GIS ArcView version 3.0a (® ESRI, Redlands, Ca., USA) was applied. From this easy-to-use front end, simulations can be launched, input data can be reviewed, and results can be visualized and interpreted (Wagner & Matthies, 1997).

3.6. Monitoring - Calibration and Verification

3.6.1. Monitoring Program

Linear Alkylbenzene Sulphonate (LAS) and Boron (B) were used as test chemicals. LAS is a biodegradable surfactant used in consumer detergents, which mainly enters the environment via domestic waste water discharges. The majority of Boron in the freshwater aquatic environment is coming from detergents. Since B is chemically inert and water soluble, this chemical can be used as a convenient tracer. For both analyses, well validated analytical methodologies are available. Particular attention was given to ensure that samples taken for LAS determinations were adequately preserved and stored prior to analysis.

Frequency distributions (time series) of environmental concentrations were measured at several locations in the British and Italian pilot study areas (Holt *et al.*, 1997). Additional studies were performed to analyze the fate of the test chemicals in trickling filter sewage treatment works (Holt *et al.*, 1998). LAS removals during activated sludge waste water treatment have been reported elsewhere (e.g. Waters & Feijtel, 1995; Holt *et al.*, 1995). Experiments to determine the in-stream removal of these chemicals in rivers were also conducted (Fox *et al.*, submitted).

3.6.2. Calibration and Verification

Concentrations in water were calculated using the developed simulation system, and were compared to measured values. Initially, monitoring results were used to calibrate and fine-tune the modeling, to improve the predictive power. Finally, they served to test the reliability of the predictions. An initial target accuracy factor of less than 5 was aimed for within the scope of geographical exposure and risk assessment (Feijtel *et al.*, 1997). This desired accuracy factor should be positioned against the much lower accuracy obtained with the generic multimedia models (of which the predictions may differ from monitoring data by several orders of magnitude), and also against the high variability which is encountered in the environment.

3.7. Summary

The output of GREAT-ER is a distribution of geo-referenced predicted concentrations, on a regional level, including seasonality and / or uncertainty. The chemical-specific input data for the model are the physical/chemical and biochemical parameters, together with geographical consumption patterns or market data. Required environmental information was taken from available geography-linked databases. For the storage and the access of the majority of these data in a user-friendly format, and for results visualization and analysis, a Geographic Information System (GIS) was used.

The final deliverable of this project is a software prototype of the exposure assessment tool. This prototype is applicable globally, and was calibrated and validated for a number of pilot study areas. The resulting PC software was made freely available (under license agreement).

4. Overview of this Thesis

The work described in this thesis was mainly conducted in the frame of the GREAT-ER project. A geo-referenced exposure simulation methodology was developed and implemented in an appropriate software system, which could be linked with the GIS user interface and data base. Chemical fate models of different complexity levels were selected, and if necessary adapted or newly developed. In this thesis, only novel aspects are dealt with; for a complete description of the model selection, reference is made to the GREAT-ER user manual and technical documentation (ECETOC, 1999). Finally, to increase the practical applicability of geo-referenced exposure assessment, a technique to obtain spatially aggregated PECs was worked out and tested.

This thesis can be split up into three main sections: (1) methodology; (2) measurement and prediction of chemical fate; and (3) analysis (Figure 1.7). The methodology and analysis sections are at the highest ‘hierarchical level’, and are an integral part of the GREAT-ER concept. Section (2), on the other hand, is situated at the more detailed level of individual chemical fate processes.

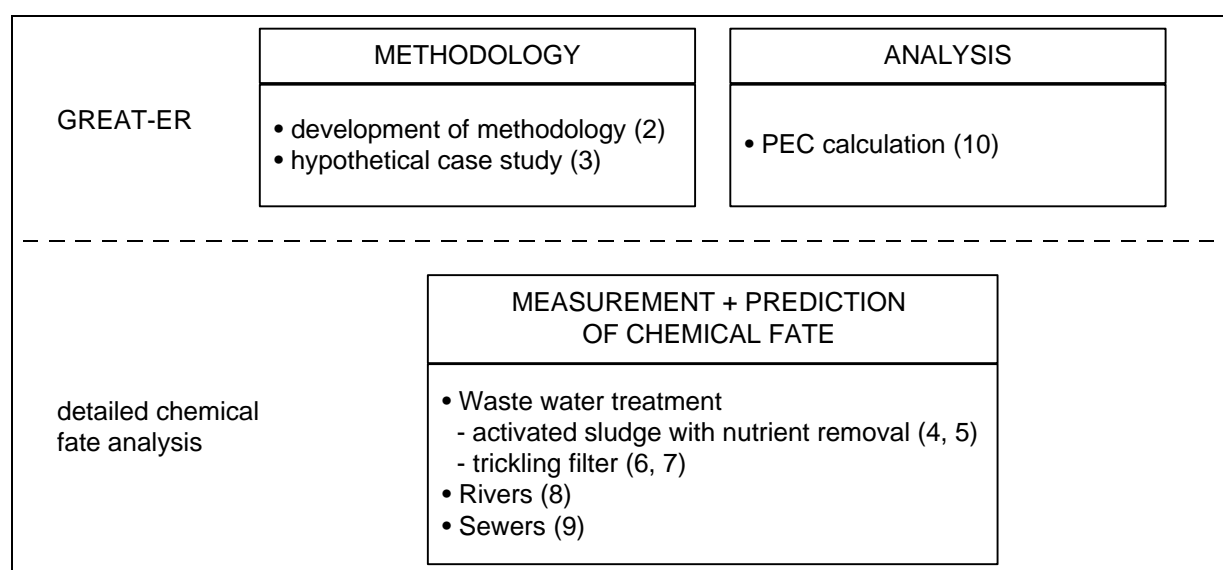


Figure 1.7. Overview of this thesis (chapter numbers between brackets)

Methodology

A new exposure assessment methodology was worked out and implemented. The development of a geo-referenced aquatic exposure prediction methodology for ‘down-the-drain’ chemicals is presented in chapter 2. Steady-state deterministic chemical fate models were combined with a Monte Carlo simulation to obtain statistical frequency distributions of predicted concentrations in the aquatic environment. Issues related to uncertainty and variability are only briefly discussed, as a complete uncertainty analysis was outside the scope of this thesis. The new simulation approach was tested by means of a hypothetical (but realistic) case study, which illustrated its practical applicability and independence of scale (chapter 3).

Measurement and Prediction of Chemical Fate

This section deals with measuring and modeling environmental fate of ‘down-the-drain’ chemicals in the three main steps of their aquatic fate pathway: sewers, waste water treatment plants and rivers. Measurements were only conducted for the surfactant LAS, as this was the GREAT-ER project’s main test substance. Although the presented fate models are in principle applicable to any chemical they could only be tested for LAS. Hence, to examine their validity for other substances (e.g. volatile compounds) additional research will be required.

The new developments in environmental fate modeling reported in this thesis mainly focus on the use of site-specific information rather than generic parameters (such as ‘typical’ waste water treatment plants or ‘typical’ rivers). This way, it was attempted to increase the realism of the exposure predictions. The new or adapted fate models can find their application in geo-referenced exposure assessment in general, and in GREAT-ER in particular. However, the presented models may also be useful to increase the realism of non-geo-referenced exposure evaluations using generic evaluative environments.

The standardized Continuous Activated Sludge (CAS) laboratory test system (OECD, 1993) and the mathematical fate model *SimpleTreat* (Struijs, 1996) are used to routinely assess the elimination of substances in activated sludge waste water treatment plants. The effects of biological nutrient removal processes (BNR) on chemical fate are not included in the CAS test nor in *SimpleTreat*. As BNR is rapidly gaining importance in waste water treatment practice, a number of modifications were worked out. The adaptation of the CAS test to include BNR processes is described in chapter 4. The performance of two modified test units, which were fed with an improved synthetic sewage (developed as part of this study), was monitored and compared with model simulations. Similarly, the *SimpleTreat* model was modified to increase its applicability to BNR plants (chapter 5). The adaptations focused on an improved description of sludge recycling and on the presence of different redox zones in the biological reactor. Two updated models were applied to the bench-scale WWTPs developed in chapter 4, and confronted with measurements of LAS removal in these systems.

The development and operation of a pilot-scale high-rate trickling filter waste water treatment plant and removal measurements of LAS in this system are presented in chapter 6. As for trickling filters no standardized chemical fate model existed, a new fate model was developed based on the steady-state non-equilibrium approach used in *SimpleTreat* in combination with an existing biofilm model (chapter 7). To test this model, it was applied to predict the fate of LAS in the lab-scale test unit, and to two full-scale domestic trickling filters in Yorkshire (UK), for which LAS removal had been monitored within the GREAT-ER project (Holt *et al.*, 1998).

In chapter 8, modeling chemical fate in rivers was worked out, supported by artificial river experiments. To predict the in-stream biodegradation, a mathematical model was developed which considers both biofilm and suspended biomass activity. To calibrate this model for LAS, experimental data were obtained in a small lab-scale artificial river system. The model was further tested by comparing its predictions to a detailed field study in the Red Beck, a small Yorkshire river (Fox *et al.*, submitted).

A tentative fate measurement of biodegradable surfactants in the sewer system is presented in chapter 9.

Analysis - calculation of Predicted Environmental Concentrations (PEC)

The direct results of GREAT-ER simulations are digital maps with predicted concentrations for individual river stretches. As this output may contain too much local detail for practical risk assessment applications and decision making, a spatial aggregation is desirable. In chapter 10, the development of new PECs based on the spatial aggregation of local predicted concentrations is discussed, as well as issues related to scale-dependency and stretch selection. Tests for 2 pilot study catchments (Calder and Went, Yorkshire, UK) are also presented in this chapter.

Chapter 2

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A Geo-referenced Aquatic Exposure Prediction Methodology for 'Down-the-Drain' Chemicals

a condensed version of this chapter was published as:

Boeije, G., Vanrolleghem, P. & Matthies, M. (1997). *A geo-referenced aquatic exposure prediction methodology for 'down-the-drain' chemicals (Contribution to GREAT-ER #3)*. Water Science and Technology, 36(5), 251-258.

Chapter 2

A Geo-referenced Aquatic Exposure Prediction Methodology for ‘Down-the-Drain’ Chemicals

A geo-referenced simulation methodology for the prediction of aquatic exposure to individual ‘down-the-drain’ chemicals (consumer chemicals which mainly enter the environment via the domestic waste water route, e.g., detergents) was developed. This method uses real-world data, including their spatial and temporal variability. It results in statistical frequency distributions of predicted concentrations in the aquatic environment. A stochastic / deterministic simulation approach is used. Steady-state deterministic models, which describe chemical fate, form the system’s core. A stochastic (Monte Carlo) simulation is applied on top of this. From chemical market data, combined with information on the location of consumers and their emission habits, geo-referenced domestic chemical emissions are predicted. These emissions are further processed in sewer and treatment models, to obtain predicted chemical fluxes to rivers. The emission fluxes are entered into a river model, resulting in (geo-referenced) predictions of chemical concentrations in the considered river systems.

1. General Simulation Approach

To deal with statistically distributed inputs and outputs, a hybrid simulation approach is used, involving both stochastic and deterministic techniques. The model core is deterministic. By means of Monte Carlo simulation, a stochastic layer is added on top of this core. A large number of ‘shots’, which are discrete samples from the distributed data set, are generated. For each distributed input parameter, there exists a discrete counterpart in the ‘shot’, which was sampled at random from the input distribution. For each of these ‘shots’, the deterministic model is called, which contains a mechanistic description of the considered processes in the rivers and in the waste water drainage areas. Process rates are derived from knowledge about chemical properties and process specifics. Finally, the (discrete) results from each ‘shot’ are statistically analyzed, to obtain distributed results as simulation output.

For reasons of model and data set simplicity and computation performance, only steady-state model formulations are applied. Hence, a number of fundamental assumptions are made: (1) constant chemical emissions: diurnal patterns in product and water consumption are disregarded, as well as variations between different days of the week; (2) constant flows within each steady-state model calculation run; (3) constant environmental properties.

To allow a straightforward mass-balancing approach, all determinands (chemical levels, water flows) are expressed as fluxes. Chemical mass fluxes F (*mass/time*) are applied to describe chemical loads. Water flows are expressed as volumetric fluxes Q (*volume/time*). In the models, chemical concentrations C (*mass/volume*) are not used, because they are not independent of water flows, and they do not describe chemical transport. Chemical mass fluxes, on the other hand, are independent of dilution or flow (unless this dependency is implicitly included in the models which are used to calculate chemical mass fluxes). When concentrations are explicitly required, they are derived from the chemical mass fluxes and the hydrological volumetric fluxes: $C = F / Q$.

Simulations can be performed for different scenarios (i.e., evaluations of different chemicals and chemical consumption patterns). The simulation input consists of a scenario-independent and a scenario-dependent data set. These data are expressed as statistical frequency distributions, incorporating seasonality and parameter uncertainty. Environmental characteristics are constant, and hence non-scenario-dependent. These include the river network structure, flow and flow velocity distributions, discharge point locations, treatment plant information, emission data, properties of sewers and small surface waters, etc. Chemical-specific information is scenario-dependent: chemical properties (i.e., biological, chemical and physical properties, specific process rates,...), and chemical market data (i.e., per capita product consumption rates). Market data are geo-referenced in the same way as the waste water information (i.e., related to waste water discharge points).

The simulation input data are expressed as statistical frequency distributions. This allows to include both seasonality effects and parameter variability and/or uncertainty into the simulation input. For river flows and flow velocities, the lognormal distribution is used (after NRA, 1995). For hydrological information this distribution is described by the mean and the 5th percentile. In the case of flows, there is a 95% probability that the 5th percentile low flow (also referred to as Q_{95}) is exceeded: $P(Q > Q_{95}) = 0.95$.

The simulation results are frequency distributions of chemical concentrations, incorporating temporal variability. For risk assessment purposes, these can be expressed as lognormal distributions, defined by their mean and 95th percentile values. Predicted concentrations are geo-referenced in the same way as the input data set: river concentrations are associated with a river network structure, and waste water drainage area concentrations are associated with discharge points. Within one location, a further differentiation is made between the maximal predicted concentrations (i.e., upon discharge), the minimal predicted concentrations (i.e., after degradation processes), and an 'internal' average value. For the calculation of the latter, specific algorithms have to be provided in the deterministic models.

2. Segmentation

2.1. General

A strict segmentation is applied at all levels (Figure 2.1). Geographies are divided into geographical segments, which are connected in parallel or in series. In each geographical segment, one or more processes occur. Each process further consists of one or more sub-processes. Each sub-process has an input and an output terminal. Input and output operations, as well as model calculations, are performed at the sub-process level.

Processes can be independent from each other (e.g., different emission types), or they can depend on upstream processes (e.g., treatment, which depends on emission). Independent processes are connected in parallel, while dependent processes are connected in series. The sequence of the different processes is upstream to downstream. Sub-processes are used to describe several options which can be followed within one process. For each flow fraction, only one option can be selected (e.g., in waste water treatment: either treated or untreated). It follows that within a process, different sub-processes are always independent from each other and hence connected in parallel.

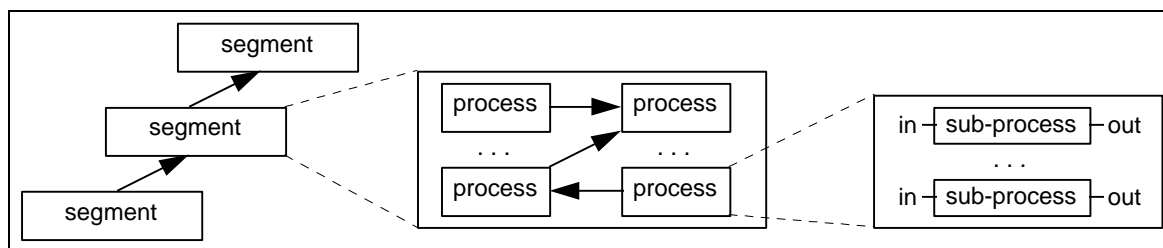


Figure 2.1. System segmentation at different levels (geographical vs. process)

A river system is represented by means of a digital river network, which consists of an interconnected set of 'main river' stretches. The segmentation is determined by the occurrence of homogeneous environmental conditions and constant flow distributions within each stretch, and by the location of discharge points. The selection of 'main rivers' depends on the applied geographical scale (see below). With each waste water discharge point into the river, a waste water drainage area is associated, where chemicals are emitted, transported and possibly removed. The total drainage area of a river is segmented into Geographic Units (GU), each of which represents the drainage area of one discharge point, and is associated with one river stretch (Figure 2.2).

Hence, a geographical segment consists of a river stretch, and - if a discharge occurs - a Geographic Unit. All waste water drainage area processes upstream of a discharge point, are lumped into a single GU. These processes can be real (e.g., a single treatment plant) or hypothetical (e.g., multiple untreated domestic discharges grouped into a single 'aggregated discharge').

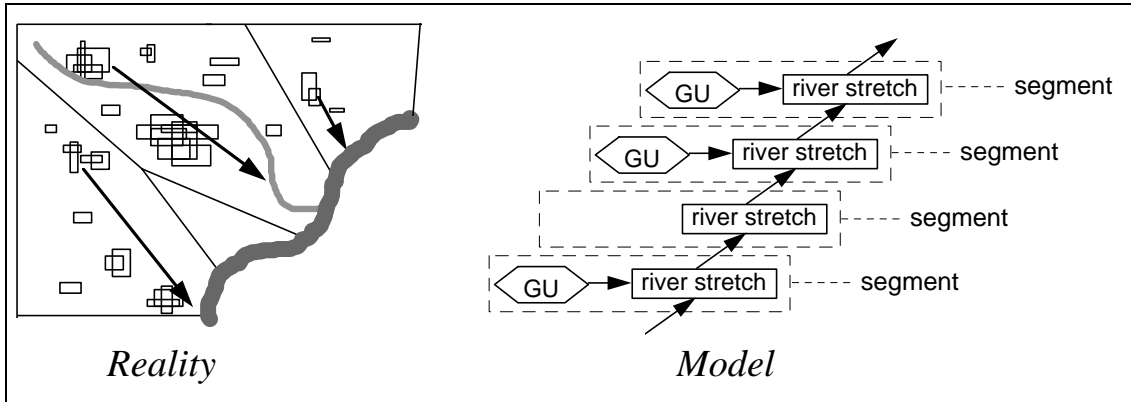


Figure 2.2. Geographical segmentation methodology used in GREAT-ER

The modeling and simulation methodologies, as well as the GIS data methodology, are scale-independent. In the upscaling process (i.e., moving from a smaller, detailed scale to a larger, less detailed scale), multiple discharge points can be aggregated into single (hypothetical) discharges; several smaller rivers are no longer considered as ‘main rivers’, but are transferred to the waste water discharge model and aggregated into a single (hypothetical) ‘small surface water’. In the large scale approach, the mouth of a small rivers’ catchment into a large river is represented by a discharge point. Hence, for different scales, only the geo-referenced data set is different; the applied models are identical. In Figure 2.3, a system is modeled at a small (left) and at a large scale (right). In this example, a complex system of ‘main rivers’ is used for the small scale, each with individual waste water discharges. In the large scale approach, the system is reduced to a single ‘main river’ with a single discharge point.

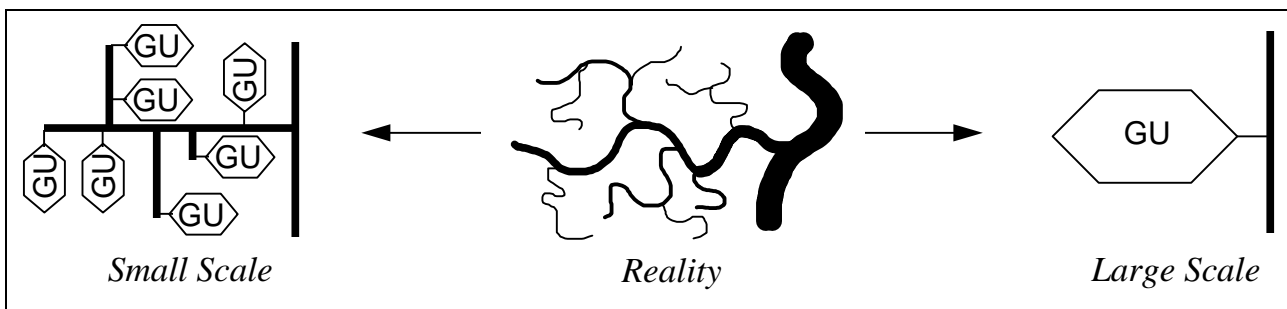


Figure 2.3. Geographical scale flexibility (illustration)

2.2. Geographical Database Structure

A set of five separate databases are used to store all required geo-referenced information:

- a river database, in which river stretch specific information is stored (e.g., flow and flow velocity)
- a waste water pathway (discharge) database, which contains information about the GUs (population, sewer network) and links to the information about treatment infrastructure,

- a river class database, which contains data that are specific for groups of rivers, but not for individual stretches,
- a WWTP database, in which treatment plant specific data are stored, and
- an emissions database, with information about market data and non-domestic emissions.

The river network segmentation is the 'backbone' of the geographical data structure. Each river stretch which receives waste water is directly related to its GU, as the same identification code is used for both. Each river stretch belongs to one specific river class, of which the identification code is known in the river database. Each waste water discharge segment is associated with an emission data point. If a GU contains a WWTP, then there is a link to the WWTP database.

The following example clarifies this data structure concept. The catchment shown in Figure 2.4 consists of two rivers: a main river, divided into 6 segments, and a tributary, divided into 2 segments. There are 3 waste water discharge points: a large city (AS waste water treatment, segment 5), a first small city (TF waste water treatment, segment 3), and a second small city (TF waste water treatment, segment 8). Suppose that several river classes have been defined, and that the main river (segments 1..6) belongs to river class 1, and the tributary (segments 7..8) to another river class 3. Assume that we have exact information on the activated sludge plant (AS) in segment 5, but no exact information on both trickling filter (TF) plants. Further, assume that chemical market data for the entire catchment belongs to the emission category 2. The associated data structure, with the links between the different databases, is shown below in Figure 2.5.

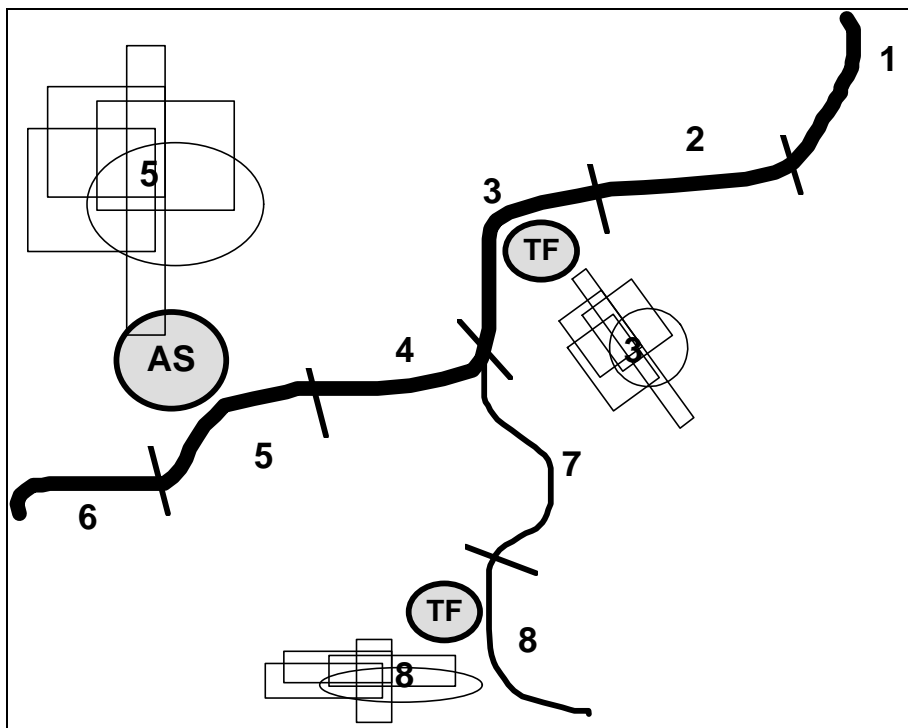


Figure 2.4. Data structure example (catchment)

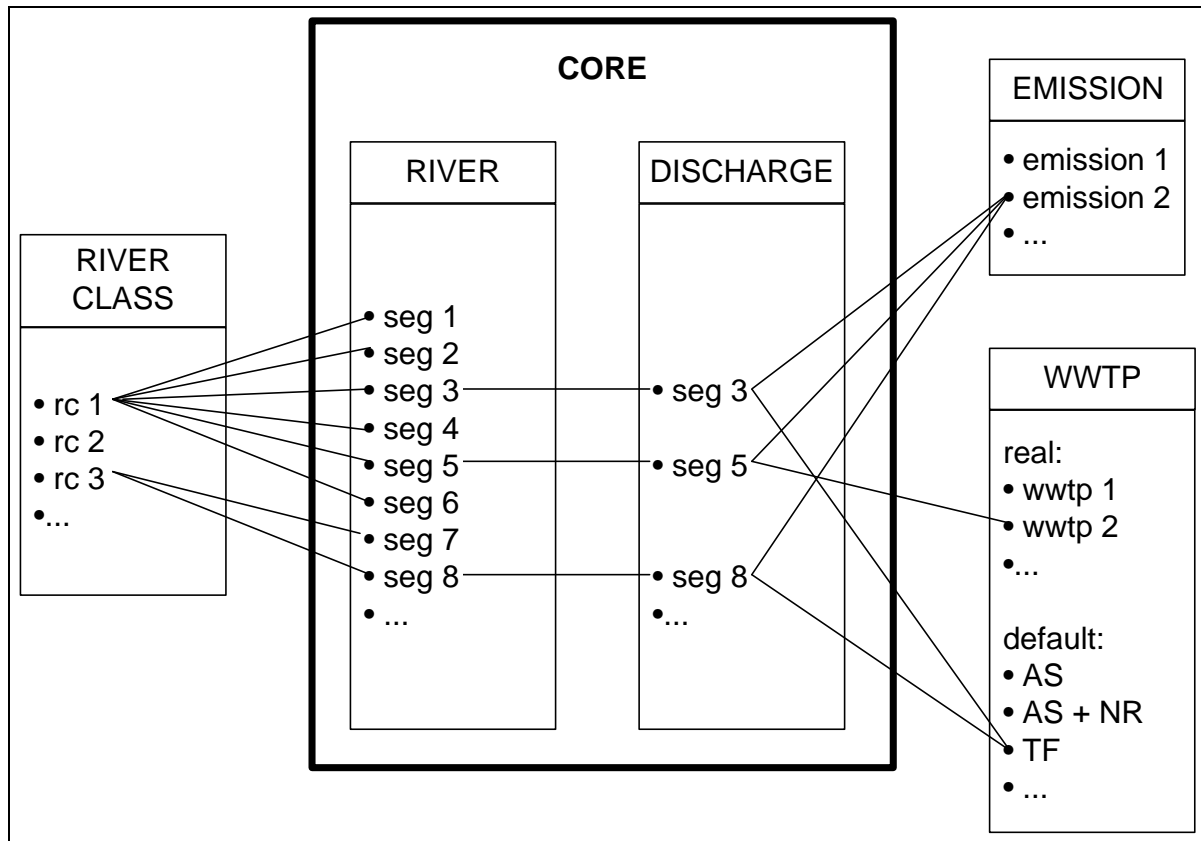


Figure 2.5. Data structure example

3. Deterministic Model

In environmental exposure assessment, several applications are related to ‘new’ chemicals, of which the safe use is to be assessed. Since these chemicals are generally still in a development phase, or have not been marketed yet, environmental concentration measurements, which are required for statistical modeling (e.g., Helsel and Hirsch, 1992), can not be obtained. Hence, knowledge-derived deterministic models need to be applied. In such models, the chemical, physico-chemical and biological properties of a substance are combined with the properties of the receiving environment and with information about emissions, to predict the environmental fate and distribution of the substance (Feijtel *et al.*, 1995).

In the deterministic model, all geographical segments are sequentially simulated (upstream to downstream). For each segment, the influent (from upstream segments) is calculated; if required the waste water pathway simulation is performed; the ‘main river’ processes are simulated; and finally the effluent (flowing to downstream segments) is calculated.

3.1. Segment Selection

A recursive tree-walking algorithm is used to find the correct segment sequence. The algorithm climbs up into the river network from the most downstream segment (i.e., the root of the tree), until the most upstream segments (i.e., the leaves of the tree) are detected. At confluences, both upstream directions are climbed, one after the other. At bifurcations, the upstream climbing is ended if the upstream part has already been climbed before, i.e., when coming from the other side of the bifurcation. Next, the network is again descended. Each segment which is encountered during the descent is selected and simulated. This way, influent data (from upstream) are always available to downstream segments. An example of the selection methodology is shown in Figure 2.6 (the numbers indicate the sequence in which the segments are called for simulation).

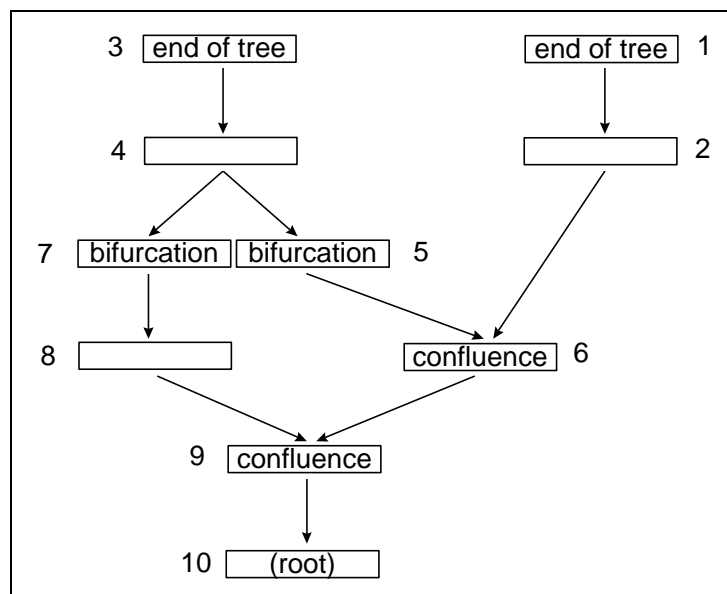


Figure 2.6. Sequential segment selection

3.2. Influent and Effluent Calculation

Segment influents and effluents are discrete values, as they are only required within each 'shot'. For the influent, only chemical fluxes are calculated. Each segment's influent flow is set to the segment's 'main river' flow, which is taken as such from the (hydraulically consistent) geo-referenced data set. In the 'normal' case (with only one upstream segment), a segment's influent chemical mass flux is set to the upstream segment's effluent. At a confluence, complete and instantaneous mixing is assumed, hence the influent is equal to the sum of the upstream effluents. At a bifurcation, the upstream segment's effluent is split into two fractions, proportional to the (known) river flows in each stretch downstream of the bifurcation. The effluent of a segment is identical to the effluent of the segment's 'main river' stretch. Hence, no effluent calculations are to be performed as such.

3.3. Individual Process Modeling Concept

3.3.1. General

Each process model exists at two levels: at the detailed process rate calculation level, and at the conceptual segment level. At the detailed level, different models can be used in different software implementations. At the conceptual level, described in this chapter, the model format is implementation-independent. Models are considered as ‘open boxes’, each of which applies to one sub-process. The general model expression for one determinand within each sub-process is:

$$x_{out} = a \cdot x_{in} + b \quad [2.1]$$

with

a	chemical conversion factor
b	emission value
x_{in}	sub-process input value
x_{out}	sub-process output value

Emissions and conversion factors are obtained at the detailed model level. At this level, several model formulations (e.g., Monod or first-order kinetics describing biodegradation) and solution algorithms (e.g., analytical or numerical) can be applied. Emission models are described by one emission value for each determinand. Their output is this set of emission values. Obviously, no input is required. Chemical fate is simulated by means of transport / conversion models. These are described by the chemical removal fraction R , which is calculated at the detailed model level. A ground water leakage fraction L can also be applied. L is part of the sub-process outflow fractionation, taken as such from the geo-referenced data set. The input vector of a transport / conversion model, as well as the output vector, is a set containing a value for each simulated determinand.

3.3.2. Waste Water Pathway Model

The waste water pathway model is used to predict the properties of discharges into ‘main river’ stretches. It consists of both emission and transport / conversion processes. A (simplified) overview of what is meant with the ‘waste water pathway’ concept is given below in Figure 2.7. The waste water pathway model focuses on the fate of ‘down-the-drain’ chemicals. These consumer chemicals are (mainly) emitted via the domestic sewage pathway. After use in the households, they are flushed down the washing machine’s drain, the kitchen sink, the bathroom drain, or the toilet. Next to these domestic emissions, industrial and / or agricultural emissions may occur in exceptional, site-specific and chemical-specific cases. Emission to water by land runoff is very unlikely.

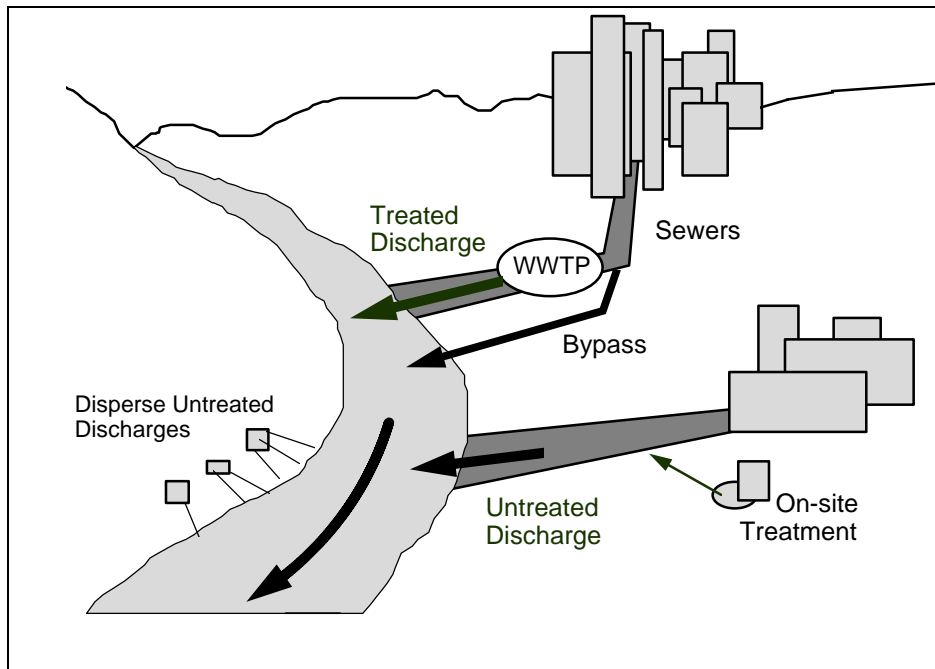


Figure 2.7. Waste water pathway of 'down-the-drain' chemicals (illustration)

Three types of chemical emission into the waste water pathway are considered:

- domestic emission (blackwater, i.e., chemicals together with sanitary waste; and greywater, i.e., chemicals discharged separately);
- non-domestic emission (industrial and agricultural); and
- land runoff.

Five transport / conversion processes are considered along the pathway:

- domestic on-site treatment (e.g., septic tanks);
- sewers (combined sewers or separate sewers);
- waste water treatment;
- ground water leakage; and
- small surface waters.

Process interconnection

The outflow of each sub-process is split into a number of fractions, each of which is connected to one downstream sub-process. One or more downstream steps can be 'skipped', e.g., a domestic emission outflow fraction can be connected directly to the 'main river' discharge point. Emission processes are always at the most upstream level - they do not receive any inflow. The sequence of the transport / conversion processes is: on-site treatment → sewer → treatment plant → ground water → surface water. The architecture of the interconnection between processes is identical for each segment. The (simplified) interconnection for domestic waste water pathway processes is shown in Figure 2.8.

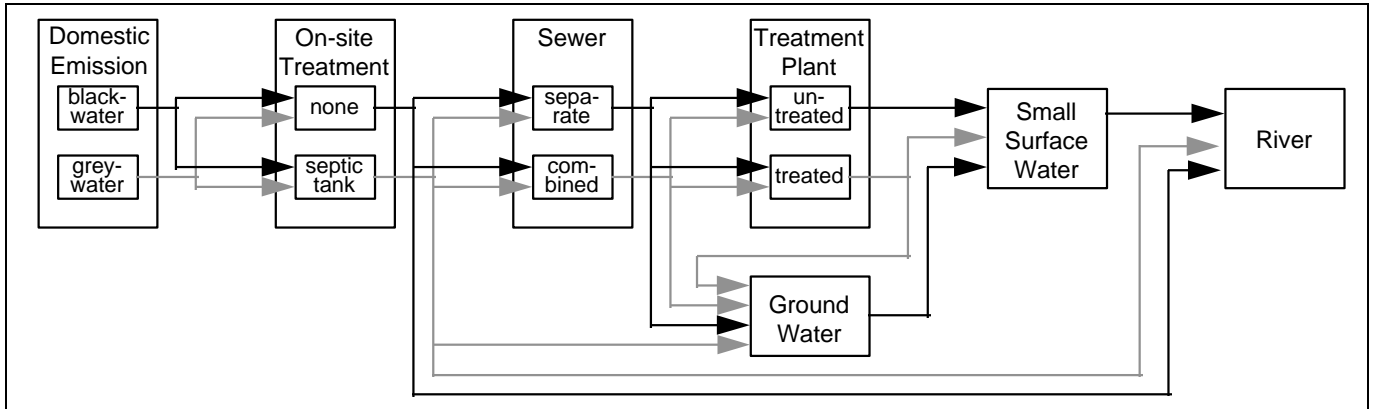


Figure 2.8. Domestic waste water pathway process interconnection within a segment (simplified)

3.3.3. River Model

The river model is used for the ‘main river’ process in all segments. The model’s inflow is the sum of the segment influent (from upstream segments) and the segment’s waste water discharge (if applicable). The river model is a transport / conversion model, without leakage step. Water flows are not simulated but are taken as such from the geo-referenced data set. Hence, the process is completely determined by the chemical removal fraction, which is obtained at the detailed model level (e.g., Cowan *et al.*, 1993a; Trapp & Matthies, 1996).

3.4. Calculation Approach

For each determinand (i.e., flow, chemical flux, etc.), the system of steady-state model equations for an entire segment consists of one equation [2.1] for each sub-process. The system can be expressed as:

$$X_i = A_i \cdot X_i + B_i \tag{2.2}$$

with:

- A_i (square) transport/conversion matrix for determinand i , with elements $a_{k,l}^i$
- B_i emission vector for determinand i , with elements b_k^i
- X_i state variables vector for determinand i , with elements x_k^i

The vectors X_i and B_i are partitioned per process, within a process per terminal, and finally within a terminal per sub-process (e.g. sewer - outputs - combined sewer). The process sequence in the arrays is from upstream to downstream; the terminal sequence is first input, then output. Hence, determinand values at a specific situation are only dependent of values at more ‘upstream’ situations. Consequently A_i is a lower triangular matrix with zero-diagonal. In A_i the element $a_{k,l}^i$ is the conversion factor of x_l^i to x_k^i . In an input to output conversion, this represents the non-removed fraction. In a transport step, this is the fraction of x_l^i (upstream output) which is sent to x_k^i (downstream input).

Emission values are taken as such from the B_i vectors, hence the A_i rows referring to emissions are all-zero.

The A_i rows referring to transport/conversion inputs are partitioned into:

- a first set of columns (relating to upstream processes), which contain the upstream outflow fractions directed to the current process; and
- a second set of columns (relating to the current and to downstream processes), which is all-zero.

Outputs only depend on the (sub-)process inputs. The A_i rows referring to these outputs are partitioned into:

- a first set of columns (relating to upstream processes) which is all-zero;
- a second set (relating to the inputs of the current process) which is a diagonal matrix, with the input to output conversion factors for each sub-process on the diagonal; and
- a third set of columns (relating to the outputs of the current processes and to further downstream situations) which is again all-zero.

The equations can not be solved using matrix inversion:

$$X_i = (I - A_i)^{-1} \cdot B_i \quad \text{with: } I \text{ the unity matrix} \quad [2.3]$$

as in some cases the elements of the A_i matrices may only be obtained as the calculations proceed. Values in A_i at row k may be derived from (previously calculated) values of any determinand in any upstream process:

$$a_{k,l}^i = f(x_{1..k-1}^1, \dots, x_{1..k-1}^m) \quad \text{with: } m = \text{the number of determinands} \quad [2.4]$$

Hence, a sequential solution (from the 'top' of the system to the 'bottom', or in other words: from upstream to downstream) is required:

$$x_l^i = \sum_{k=1}^{l-1} a_{l,k}^i \cdot x_k^i + b_l^i \quad \text{with: } \lambda \text{ varying from 1 to the total number of rows} \quad [2.5]$$

4. Stochastic Aspects

4.1. General

The stochastic simulation takes into account seasonality of the determinands or parameter uncertainty. Seasonality deals with major environmental variation throughout the year(s). Parameter uncertainty deals with the difficulties to estimate model parameters, and with the inherent variability in specific processes.

By means of Monte Carlo simulation, discrete 'shots' of the data and parameter set (e.g. flows, process parameters, market data,...) are generated. With these discrete values, the entire geography is simulated, using the deterministic model (Figure 2.9). In particular, discrete segment inputs and

outputs are applied. The main advantage of this approach, is that no correlation analysis between flows and chemical fluxes is needed. In an alternative approach (NRA, 1995), individual Monte Carlo simulations are performed for each segment. Hence, segment inputs and outputs are distributions. As flow and chemical flux are not necessarily independent, the correlation between them must be known to allow correct Monte Carlo sampling. However, for ‘new’ chemicals, this information may not be obtainable.

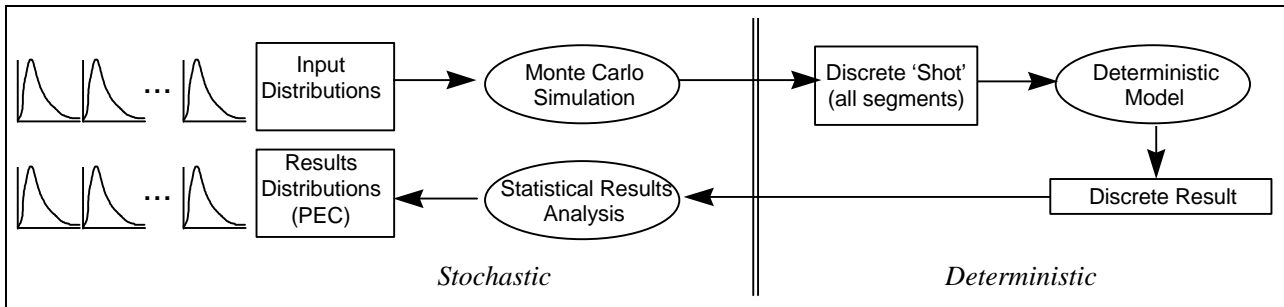


Figure 2.9. Stochastic simulation concept used in GREAT-ER

4.2. Seasonal Variability: Flow Scenarios

In each river stretch, a range of flows can occur, due to (seasonal or non-seasonal) variations in weather and climate. The probability of each individual flow within this range is given by the flow distribution, which is approximated by a log-normal distribution (NRA, 1995). This distribution is typically described by its mean flow and 5th percentile flow (Gustard *et al.*, 1992).

A flow scenario is defined as a percentile from a flow distribution. In the scenario with flow percentile P , the flow associated with the P^{th} percentile of its distributions will occur. Flow scenarios exist both at the river level and at the waste water pathway level. A correlation may exist between segments (i.e., from upstream stretches to downstream stretches), and within segments (i.e., between waste water flows and river flows). Other parameters - such as river flow velocity, depth, water quality, etc. - are also correlated to flow and are hence related to the flow scenario. River flow may also be correlated to weather parameters such as temperature and wind speed.

A total correlation is assumed for flow percentiles between segments as within one Monte Carlo shot, a single flow scenario is applied to all river stretches. For each shot, a flow percentile value is sampled from a uniform distribution $U(0,1)$, from which the flows and flow velocities in all segments are derived. This assumption does not imply that the same flow percentile occurs simultaneously in each segment; it means that the flow percentile ‘follows’ the water flow from upstream to downstream. For very large river systems, the validity of this approach may be limited. When different climatological circumstances occur simultaneously along the river’s length, flow percentiles between upstream sections and far away downstream sections may be uncorrelated. A (hypothetical) example of such a system is given in Figure 2.10. In late spring, flows may be very high in the mountains due to snow melt. In the same season, low flows may occur in the continental region due to a long dry period, while average flows may be found in the coastal region.

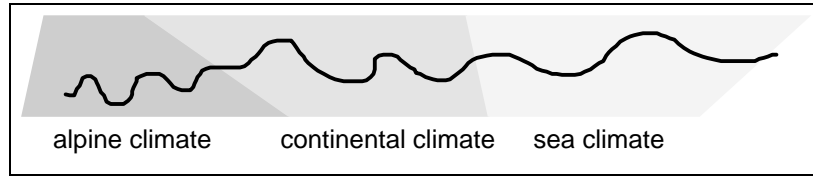


Figure 2.10. Climatological differences in large river systems (example)

Within segments, the correlation between the waste water discharge flow and the 'main river' flow is to be specified in the data set. For large rivers, it will generally be assumed that these flows are uncorrelated. Dry weather waste water flow is obviously independent of the 'main river' flow. Wet weather flow in combined sewers depends on short-term rain events, rather than longer-term climatological conditions. One can expect the highest chemical fluxes to occur at high waste water flows (e.g. due to treatment plant bypassing and combined sewer overflows). Hence, for chemical risk assessment, the uncorrelated approach is probably the most appropriate, as it does not overlook this worst-case scenario (high chemical loads combined with low river flows). For small rivers, on the other hand, correlation of river flows with waste water discharge flows may become significant.

4.3. Uncertainty and Variability Analysis

4.3.1. Types of Uncertainty and Variability

The stochastic simulation in GREAT-ER deals with the major environmental variabilities throughout the year(s) (especially focusing on river flows and climate) and the intrinsic variability of parameters. Alternatively, it can also deal with parameter uncertainty within a fixed (i.e., non-variable) scenario. Within the discussed simulation approach, four kinds of uncertainty and variability can be discerned (Figure 2.11):

- Parameter Uncertainty and Variability. In reality, parameter values may vary considerably both in time and in space, due to natural variability. Next to this, the actual parameter values and/or distribution shapes are not known exactly. This uncertainty and/or variability may lead to uncertainty and/or variability in the model results.
- Model Uncertainty. The applied model equations are not a full and completely correct description of reality. Moreover, in the case of a geo-referenced model, the geographical structure and segmentation of the simulated system may contain errors or strong simplifications.
- Simulation Uncertainty. In practice, the number of Monte Carlo shots is limited, due to the required computation time. However, to obtain 'perfect' distributions, an infinite number of shots would be needed. Even with more efficient sampling methods, the results distribution will always be an approximation of the 'true' distribution. Next to this, specific mathematical / numerical errors may occur during simulation.

- Measurement Uncertainty (for model corroboration). The number of environmental samples, which are used to develop temporal and spatial distributions of concentration, is necessarily limited. Hence, the resulting measured distributions will only be an approximation of the true distributions. Moreover, sampling and analytical variability will introduce further noise.

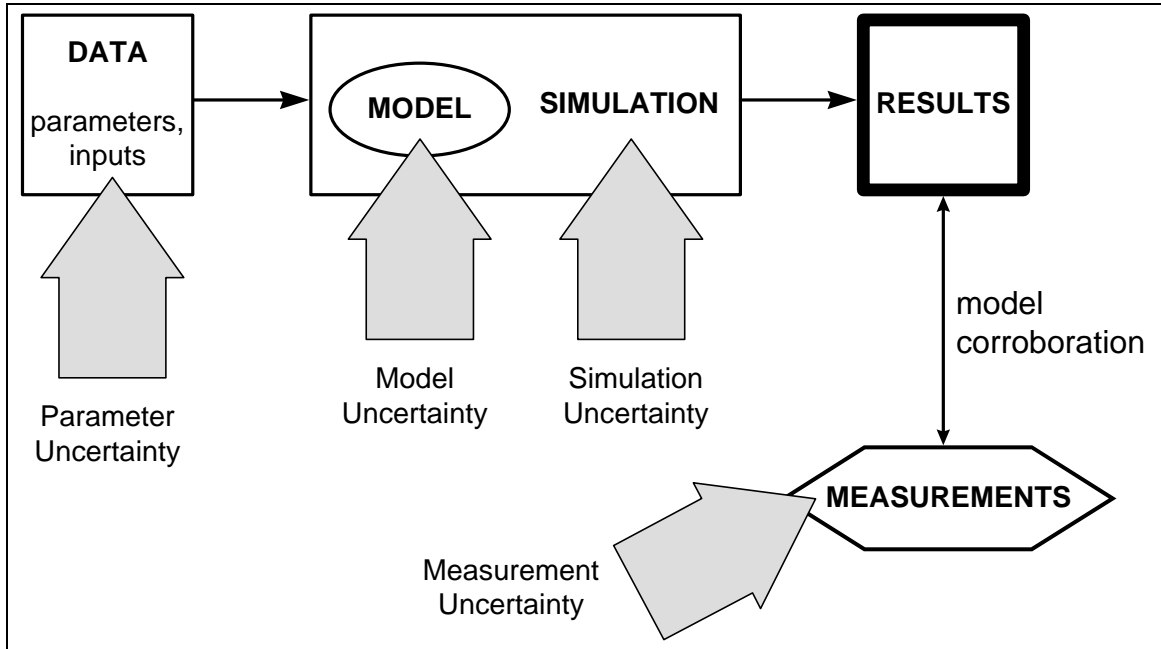


Figure 2.11. Types of uncertainty encountered in GREAT-ER (schematic)

In the example below (Figure 2.12), the shift and the difference in shape between the true environmental concentration C_{ENV} and ‘ideal’ predicted concentration C_{PRED} distributions can be due to both parameter uncertainty and to model uncertainty. The fact that the real environmental concentration C_{ENV} is a distribution rather than a single value, is due to natural variability. The latter also determines (or at least influences) the shape of the measured \hat{C}_{ENV} and computed \hat{C}_{PRED} distributions. Simulation uncertainty can be seen by comparing the ‘perfect’ C_{PRED} with the Monte Carlo simulation \hat{C}_{PRED} . Measurement uncertainty is illustrated by the difference between the ‘real’ C_{ENV} and measured \hat{C}_{PRED} .

In the stochastic simulation method described in this chapter, only parameter variability or uncertainty are dealt with. Hence, neither model and simulation uncertainty, nor measurement uncertainty are analyzed in the calculations.

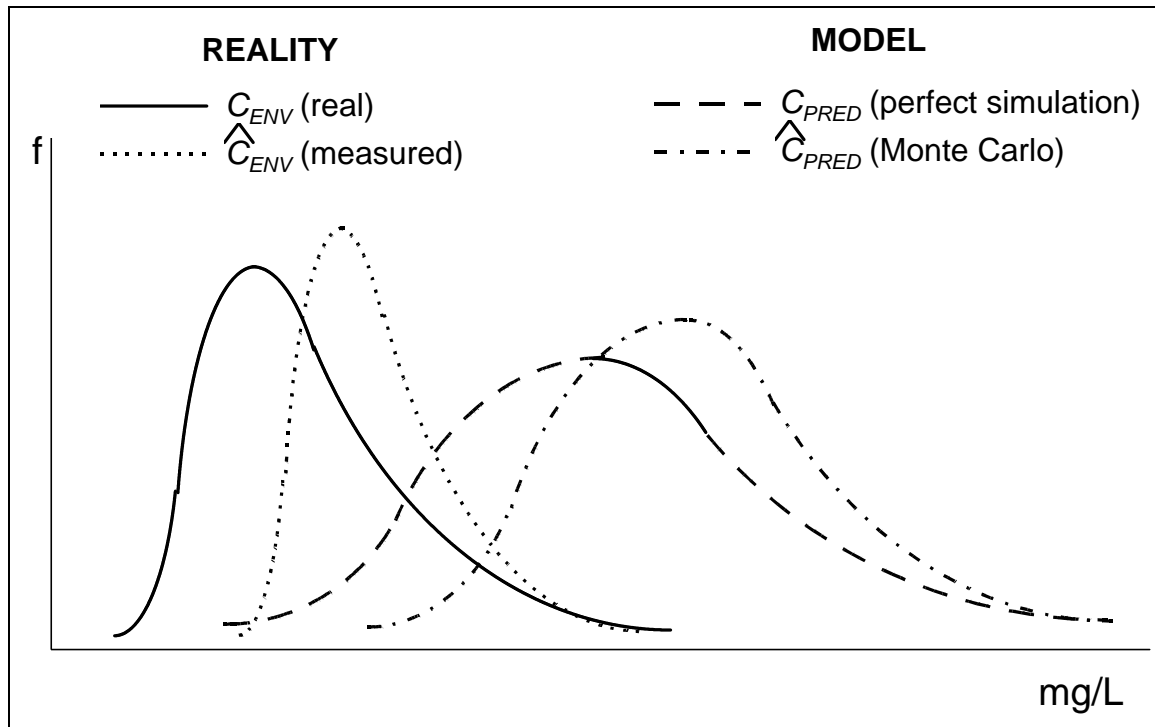


Figure 2.12. Measurement and predictive uncertainty (example frequency distributions)

4.3.2. Variability versus Uncertainty

Four classes of parameters can be defined, based on their degree of variability and/or uncertainty.

- **Fixed Parameters.** These parameters are constant in reality (i.e., they never change over time or space). Moreover, their exact value is known. Hence, these parameters have no statistical distribution. Typical examples are constants that are defined by laws of nature (e.g., the universal gas constant R).
- **Known Variability.** These parameters have a natural variability in the environment. The exact shape of their distributions is known, as well as the exact parameter values. Hence, the uncertainty is negligible. Assuming that perfect measurements are available, a river flow distribution built from a very long time-series of flow data could be an example of this class.
- **Uncertainty.** Some parameters are constant in reality (cf. the fixed parameters). However, their exact value is not known. Their statistical distribution represents this uncertainty. An example is the connection degree to waste water treatment in a specific area.
- **Uncertainty and Variability.** These parameters show a natural variability in the environment, just like the 'known' variability parameters. But, neither the exact shape of their true distribution nor the exact parameter values are accurately known. Hence, the parameters used to describe the distributions of these parameters are distributions themselves. An example could be river flow distributions predicted by a hydrological model.

Variability analysis

One of GREAT-ER's objectives is to provide high and low percentiles next to mean predicted concentrations. The resulting frequency distribution at one point in a river represents the natural variability of concentrations which is predicted to occur at that location. Such variability analysis can be performed by means of a Monte Carlo simulation where all parameter variability is captured in the parameters' frequency distributions, and where the correlation between different parameters has been accounted for. The resulting mean and percentile predicted concentrations are in themselves point values, without any information about their confidence limits.

Uncertainty analysis

An uncertainty analysis can not be conducted simultaneously with a variability analysis using the same Monte Carlo simulation (Ellis, 1998a). If the parameter frequency distributions include both uncertainty and variability, this merely increases the spread of the distribution. It gives no extra information about the confidence limits of the mean predicted concentration, and it gives an under(over)estimation of low (high) percentiles. To conduct a combined uncertainty and variability analysis, a two-stage approach is required (e.g. Cohen *et al.*, 1996). In a first Monte Carlo simulation, uncertainty is dealt with. For each uncertain parameter a point value is sampled from its uncertainty frequency distribution. After this first Monte Carlo stage, a realization of the parameter set has been created which is no longer influenced by uncertainty. This set is subsequently used in a second variability Monte Carlo simulation. Finally, mean and confidence limits can be obtained for mean predicted concentrations as well as for high and low percentiles. In a simplified way, this method was implemented by Ellis (1998b) in the GUAVA approach.

A tentative theoretical uncertainty analysis for GREAT-ER simulations was worked out by Galoch *et al.* (1998).

5. Simulation Software Design

The general software structure is shown in Figure 2.13. The simulator consists of the three sections: Control Section, Data I/O Section and Model Section.

5.1. Control Section

The Control Section consists of two different hierarchical levels. In Level 1, the Monte Carlo simulation is performed. First, the input parameters are obtained (by calling the Data I/O Section). Second, a number of Monte Carlo simulation shots is generated. For each shot, a random 'flow percentile' scenario is determined, discrete values are sampled from each parameter's distribution, and Level 2 of the simulation is called. After the Monte Carlo loop, the distribution parameters of the results (e.g. mean and standard deviation) are calculated, from the 'summary information' provided by Level 2, and the simulation output is stored (by calling the Data I/O Section).

Level 2, the Segments Loop level, applies to one discrete shot of the parameters set, which was generated in Level 1. All segments are sequentially simulated, from the river network's source to its mouth. Influent data are prepared for each selected segment (from the interface variables), the input parameters associated with the current segment are selected, and the current segment is simulated (by calling the Model Section). After the segment's simulation, its 'summary variables' are calculated (WWTP influent and effluent concentration if applicable; river concentrations: start of stretch, end of stretch, average value in stretch). Finally, the summary variables' distribution moments, which are needed to calculate the distribution parameters in Level 1, are updated.

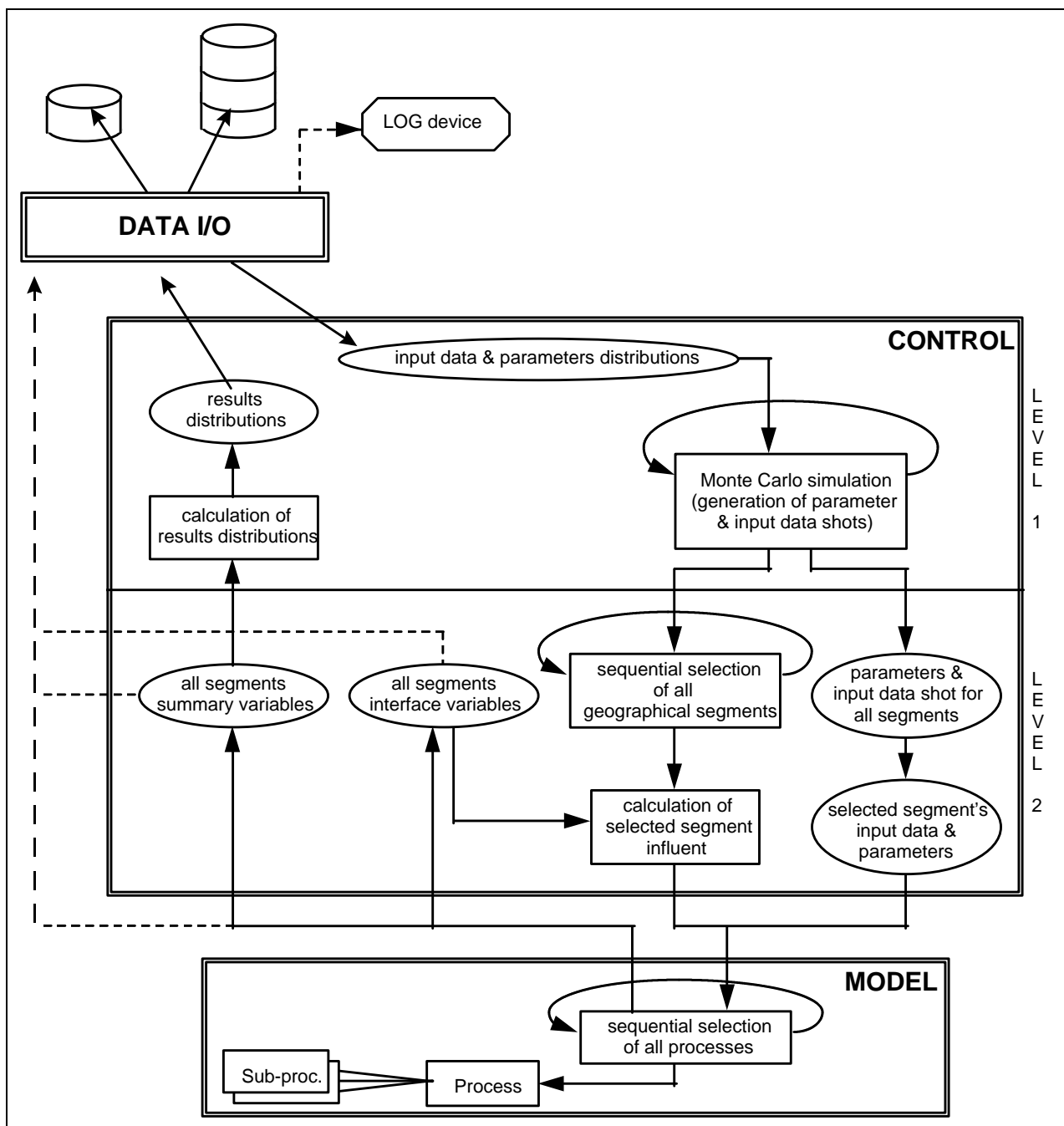


Figure 2.13. General software structure of the GREAT-ER chemical fate simulator

5.2. Data I/O Section

The Data I/O Section is called from the Control Section. It is mainly used to read and interpret the input provided by the geo-referenced and non-geo-referenced data banks, and to write the output back to a geo-referenced results data bank. Also communication with the user (either through a log file or via the user interface), and the processing of error messages are performed in this section.

5.3. Model Section

The Model Section is applied independently for each geographical segment. It is called from the Control Section, from which it also receives all required input information and model parameters. These represent a discrete case - no stochastics are incorporated here. The Model Section consists of a Segment Control Section and one or more Processes. Each Process further consists of one or more Sub-processes.

The Segment Control Section controls the simulation of an individual geographical segment. First, it receives segment-specific input from the 'main' Control Section (see above). Then sequentially all models applying to the different Processes and Sub-processes are called. Interface and summary variables are calculated for the current segment, from the model state variables. Finally, the results (i.e., the interface and summary variables) are sent back to the Control Section.

In Processes, which relate to individual processes occurring in a geographical segment, process-specific input is received from the Segment Control Section, and sequentially all the required Sub-Processes (one or several, depending on the process) are called. Model calculations are performed (i.e., emission or removal are calculated), and the results (i.e. the model state variables) are sent back to the Segment Control Section.

Sub-Processes relate to individual sub-processes within a specific Process. Here, sub-process-specific input is received from the associated Process, process rate calculations are performed, and the results (i.e., sub-process removal efficiencies) are sent back to the Process.

6. Concluding Remarks

A geo-referenced simulation method for the prediction of aquatic exposure to individual 'down-the-drain' chemicals was developed. The fate of these chemicals, taking into account emission, sewage transport, treatment and river processes, is simulated by means of deterministic models. The natural variability, and/or the uncertainty in the required information, is dealt with via a Monte Carlo simulation. This finally results in statistical distributions of predicted concentrations, which can be used for risk assessment.

A prototype of the presented simulation system was tested by means of a large sample data set, containing 16,000 geographical segments. A 1,000 shot Monte Carlo simulation took less than 1.5 hours on a Windows NT workstation (Pentium, 150 MHz). Typical simulations for the GREAT-ER pilot study catchments generally took less than 15-30 minutes. This indicates the feasibility of the approach for detailed regional or large-scale pan-European simulations.

Chapter 3

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Geo-referenced Prediction of Environmental Concentrations of Chemicals in Rivers: a Hypothetical Case Study

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Chapter 3

Geo-referenced Prediction of Environmental Concentrations of Chemicals in Rivers: a Hypothetical Case Study

1. Introduction

For use within environmental risk assessment, a new tool for chemical fate prediction, GREAT-ER (Geography-referenced Regional Exposure Assessment Tool for European Rivers), was developed. In this chapter, the practical applicability of the GREAT-ER simulation methodology is illustrated by means of a hypothetical but realistic case study. Temporal distributions of predicted concentrations in the aquatic environment were calculated and analyzed. For the analysis of seasonality (i.e., the variability of river flows through the year), the Monte Carlo simulation technique was compared to a discrete ‘flow scenario’ approach. Finally, the scale-independent character of the approach was investigated, by upscaling from a detailed to a larger geographical scale.

The objectives of this hypothetical case study were: to demonstrate the practical applicability of the GREAT-ER simulation approach, by modeling a virtual but realistic catchment; to analyze the statistical distributions of predicted concentrations and to test the validity of the assumptions used in the simulation approach; to compare the results of the Monte Carlo simulation approach with a discrete flow scenario approach; and to investigate the options for upscaling the detail of a catchment data set, from a small geographical scale to a large (aggregated) scale.

2. Model Implementation

A simple implementation of the simulation approach described in Boeije *et al.* (1997) was developed to perform this hypothetical case study. A simplified waste water pathway structure and low-complexity models were selected, as the objective was to demonstrate the feasibility of the approach and its general behavior, rather than to analyze the potential accuracy of the predictions.

2.1. Waste Water Pathway Structure

The following processes were considered: domestic emission, combined sewers, waste water treatment, and the river. Within one segment, these processes were interconnected as shown in Figure 3.1.

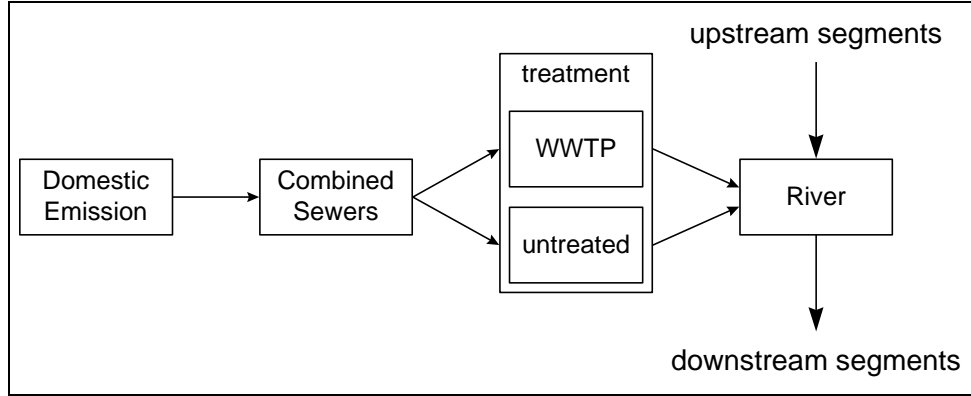


Figure 3.1. Overview of processes within one segment

2.2. Models

2.2.1. Domestic Emission

Chemical mass fluxes were calculated from market data (product sold per person per year) and population data. Domestic waste water flows (i.e. dry weather flows) were similarly derived from daily water consumption and population.

$$\Phi_{out}^{dom} = \left(M \cdot \frac{1000}{365 \cdot 24 \cdot 3600} \right) \cdot Pop \quad Q_{out}^{dom} = Q_{dwf} = \left(W \cdot \frac{1}{1000 \cdot 24 \cdot 3600} \right) \cdot Pop \quad [3.1]$$

2.2.2. Combined Sewer

No chemical elimination processes in the sewer system were considered. The combined sewer flow was assumed to be related to the (calculated) dry weather flow. A correction factor a was used to derive the sewer flow from this dry weather flow. If $a < 1$, leakages (out of the sewer) occur; if $a > 1$, the waste water is diluted by rainfall or by infiltration of groundwater. It was further assumed that a can be described by a log-normal distribution. For the given hypothetical case, the mean was set to 1.5, while the 5th percentile was set to 1. This implies that the mean combined sewer flow is 1.5 times its dry weather flow, while the 5th percentile low sewer flow is equal to the dry weather flow.

$$\Phi_{in}^{sewer} = \Phi_{out}^{sewer} = \Phi_{out}^{dom} \quad Q_{in}^{sewer} = Q_{out}^{sewer} = a \cdot Q_{dwf} \quad [3.2]$$

2.2.3. Waste water treatment

The treatment process consists of an untreated discharge model and a waste water treatment plant (WWTP) model. The inflows are calculated as shown below:

$$\begin{aligned} \Phi_{in}^{untreat} &= \Phi_{out}^{sewer} \cdot f_{untreat} & Q_{in}^{untreat} &= Q_{out}^{sewer} \cdot f_{untreat} \\ \Phi_{in}^{wwtp} &= \Phi_{out}^{sewer} \cdot f_{wwtp} & Q_{in}^{wwtp} &= Q_{out}^{sewer} \cdot f_{wwtp} \end{aligned} \quad [3.3]$$

In the untreated discharge model, no chemical elimination or changes in flow were assumed:

$$\Phi_{out}^{untreat} = \Phi_{in}^{untreat} \quad Q_{out}^{untreat} = Q_{in}^{untreat} \quad [3.4]$$

The WWTP consists of a bypass model and an actual treatment model. In the bypass model, a plant's maximal hydraulic capacity is assumed to be $3 \cdot Q_{dwf}$. The treated fraction is calculated as:

$$\text{if } Q_{in}^{wwtp} > 3 \cdot Q_{dwf} \text{ then } f_{treated}^{wwtp} = \frac{3 \cdot Q_{dwf}}{Q_{in}^{wwtp}} \text{ else } f_{treated}^{wwtp} = 1 \quad [3.5]$$

The actual treatment model describes chemical elimination based on a given (chemical-specific) removal percentage. Flow is assumed constant through the plant.

$$\Phi_{out}^{wwtp} = \Phi_{in}^{wwtp} \cdot [1 - f_{treated}^{wwtp} \cdot R_{wwtp}] \quad Q_{out}^{wwtp} = Q_{in}^{wwtp} \quad [3.6]$$

2.2.4. River

The chemical mass flux into a river was calculated as the sum of the different inputs. Flows were not calculated, but were taken as such from the hydrological dataset (which was assumed to be hydraulically consistent). Hence, no flow mass balancing was required.

$$\Phi_{in}^{river} = \Phi_{upstream}^{river} + \Phi_{out}^{wwtp} + \Phi_{out}^{untreat} \quad Q_{in}^{river} = Q_{out}^{river} = Q_{river} \quad [3.7]$$

A 1st order elimination model was applied to describe chemical in-stream removal (equation [3.8]). The river stretch travel time was calculated from length and flow velocity. The latter was estimated from actual and mean river flow, according to a method developed for English catchments by Round & Young (1997), which is given in equation [3.9].

$$\Phi_{out}^{river} = \Phi_{in}^{river} \cdot e^{-k \cdot (HRT \cdot 3600)} = \Phi_{in}^{river} \cdot e^{-k \cdot \frac{l}{v}} \quad [3.8]$$

$$v = 10^{-0.599} \cdot (Q_{actual}^{river})^{0.286} \cdot \left(\frac{Q_{actual}^{river}}{Q_{mean}^{river}} \right)^{0.165} \quad [3.9]$$

2.2.5. Calculation of Predicted Concentrations

Concentrations were calculated for waste water after the treatment step, and for the start (C_{start}) and the end (C_{end}) of each river stretch. Next to this, so-called 'internal' values were calculated for each river stretch ($C_{internal}$). These were defined as the average value of the exponential decay curve between the maximal and the minimal value in the stretch, and calculated as follows in equation [3.10] (for $k \neq 0$). Note that $C_{internal}$ is equal to C_{start} when the decay rate coefficient is zero.

$$C_{end} = C_{start} \cdot e^{-k \cdot (HRT \cdot 3600)}$$

$$\begin{aligned} \Rightarrow C_{internal} &= \frac{1}{(HRT \cdot 3600)} \cdot \int_0^{(HRT \cdot 3600)} C_{start} \cdot e^{-k \cdot t} \cdot dt \\ &= \frac{C_{start}}{(HRT \cdot 3600)} \cdot \left[\frac{1}{-k} \cdot e^{-k \cdot t} \right]_0^{(HRT \cdot 3600)} \\ &= \frac{C_{start}}{(HRT \cdot 3600)} \cdot \left(\frac{1}{-k} \cdot e^{-k \cdot (HRT \cdot 3600)} - \frac{1}{-k} \cdot 1 \right) \\ &= \frac{C_{start}}{k \cdot (HRT \cdot 3600)} \cdot \left(1 - e^{-k \cdot (HRT \cdot 3600)} \right) \end{aligned} \quad [3.10]$$

2.3. Monte Carlo Simulation

By means of a 1,000 shot Monte Carlo simulation, the variability of the parameters mentioned in Table 3.1 was incorporated into the simulation. The correlation between the river flow and the combined sewer flow was assumed to be 0.6. This value was taken from the defaults used in the SIMCAT model (NRA, 1995).

Table 3.1. Parameters used in Monte Carlo simulation

Parameter	Description	Distribution	Correlation to river flow
Q^{river}	river flow	lognormal	1
R_{wwtp}	chemical elimination percentage in a WWTP	normal	0
a	combined sewer flow correction factor	lognormal	0.6

3. Description of the Hypothetical Case Study

3.1. Hypothetical Catchment

A hypothetical but realistic catchment was constructed, which consists of a main river and one tributary. Along the main river, there are two large cities (A and B), which discharge their waste water into the river, after treatment or untreated. The tributary runs through a rural area with disperse population, which discharge their untreated waste water directly into the tributary. A representation of this catchment is given in the left half of Figure 3.2. The right half of the same Figure shows the applied segmentation. A schematic representation, including segments identification numbers (Segment ID), is given in Figure 3.3. Segments containing a waste water input were labeled with 'D'. The river stretches and waste water discharge properties are shown in Table 3.2. For all discharges, the per capita water consumption was assumed to be 200 L/cap.day.

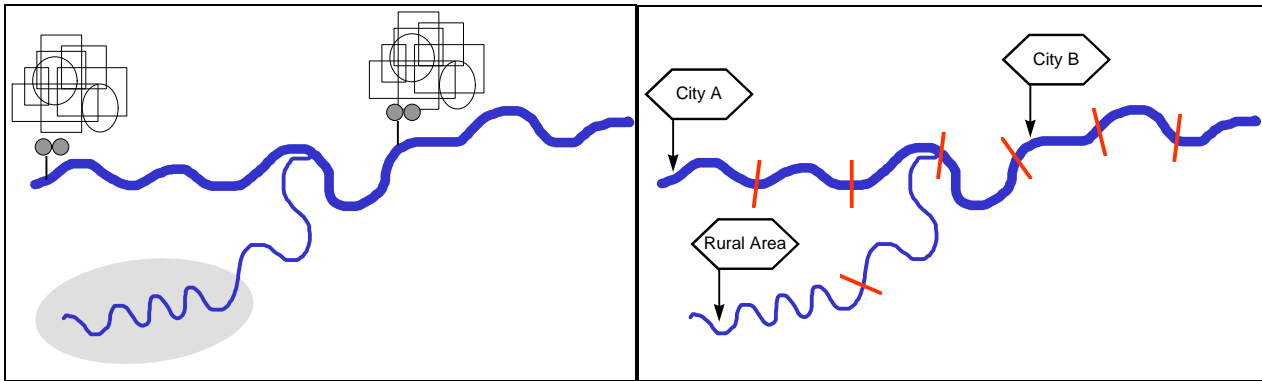


Figure 3.2. Hypothetical catchment (left: illustration - right: structure)

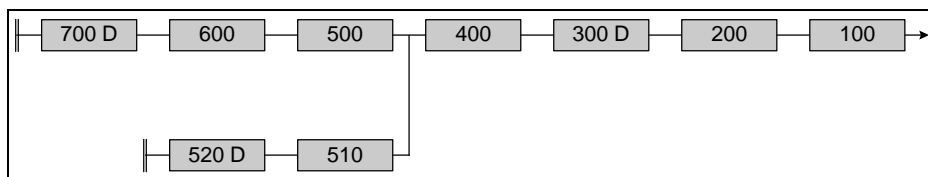


Figure 3.3. Hypothetical catchment (schematic representation)

Table 3.2. River and discharge properties

Segment ID	River stretches				Discharges	
	Length (km)	Distance* (km)	Mean flow (m ³ /s)	Q95 flow (m ³ /s)	# people (cap)	% treated (-)
Main river						
100	10	10	66.00	49.50	-	-
200	10	20	65.00	48.75	-	-
300	10	30	64.00	48.00	750,000	50 %
400	10	40	63.00	47.25	-	-
500	10	50	52.00	39.00	-	-
600	10	60	51.00	38.25	-	-
700	10	70	50.00	37.50	500,000	75 %
Tributary						
510	25	65	10.00	6.00	-	-
520	25	90	8.00	4.80	100,000	0 %

* distance from the most upstream point of the stretch to the end of the catchment

3.2. Hypothetical Chemicals

Two hypothetical chemicals were defined: a conservative chemical A and a degradable chemical B. The chemical properties and market information are given in Table 3.3.

Table 3.3. Chemical properties and market data

	Chemical A	Chemical B
Product consumption	2 kg/cap.year	2 kg/cap.year
In-stream removal rate coefficient	0 h ⁻¹	0.069 h ⁻¹ (t _{0.5} = 10 h)
WWTP elimination %	0 % ± 0 %	95 % ± 5 %

4. Results and Discussion

4.1. Predicted Concentrations

4.1.1. Main River Predicted Concentration Profiles

The main river predicted concentration profiles resulting from the hypothetical case simulation, are shown in Figure 3.4.

The impact of the discharges of both cities is obvious. The tributary (at 40 km) results in a slight decrease of the concentrations, which suggests that the tributary has a dilution effect on the main river. The decrease after both cities is caused by increasing dilution and by in-stream-removal (for Chemical B only).

4.1.2. Tributary

The mean and 95th percentile concentrations for the tributary mouth (and for the main river at the same location) are given in Table 3.4 below.

Table 3.4. Tributary: predicted concentrations at the tributary mouth
(and in main river at same location)

	Chemical A		Chemical B	
	Tributary	Main River	Tributary	Main River
<i>C</i> _{mean} (mg/L)	0.699	0.627	0.082	0.085
<i>C</i> _{95thile} (mg/L)	1.082	0.816	0.086	0.109

The tributary's dilution is sufficient to reduce its relative impact on the main river predicted concentrations, as is shown for Chemical A. For Chemical B, concentrations are further reduced by in-stream removal, and - even though the tributary receives the untreated waste water of 100,000 people - the tributary dilutes the main river.

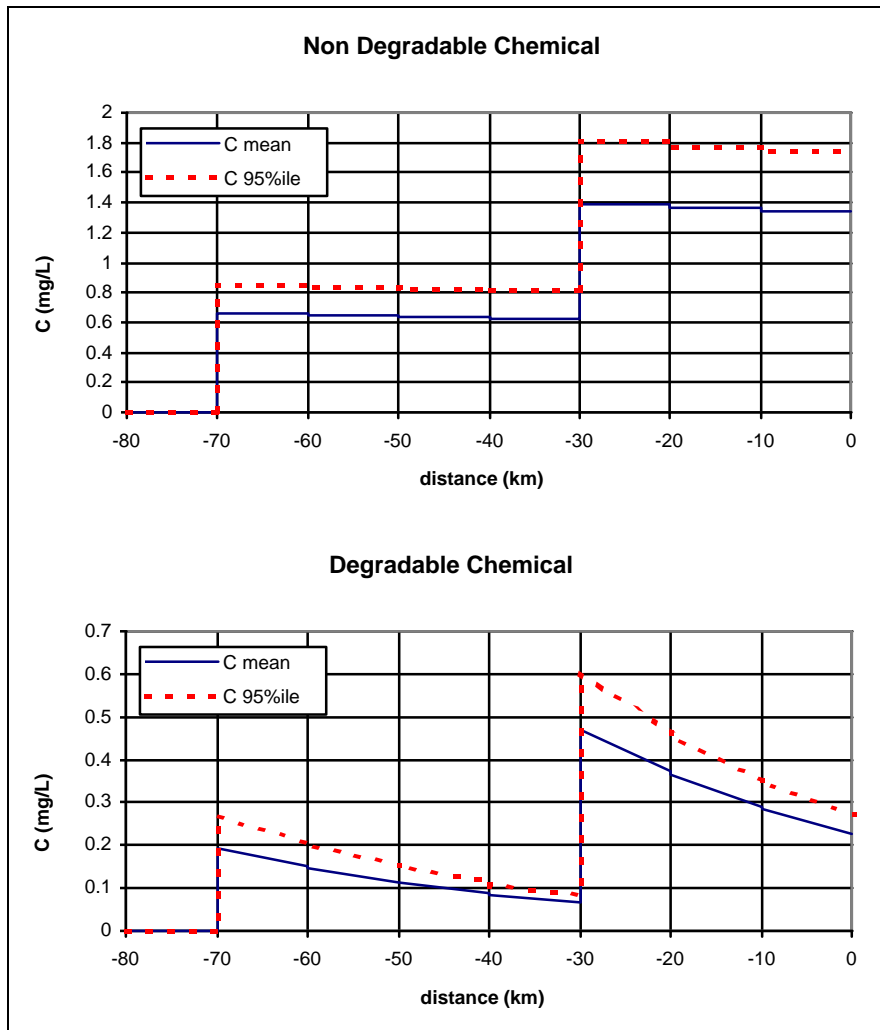


Figure 3.4. Main river predicted concentration profiles

4.1.3. Discharges of Cities A and B

The mean and 95th percentile concentrations and chemical mass fluxes for both cities are given in Table 3.5 below.

Table 3.5. Discharges of Cities A and B: concentrations and chemical mass fluxes

		Chemical A		Chemical B	
		City A	City B	City A	City B
Predicted concentrations C					
mean	(mg/L)	27.4	27.4	7.69	13.9
95%ile	(mg/L)	62.3	62.3	17.7	32.0
Predicted chemical mass fluxes Φ					
mean	(g/s)	31.7	47.6	9.43	25.3
95%ile	(g/s)	31.7	47.6	12.0	27.9

For the conservative Chemical A, the concentration distributions are identical for both cities, as these values only depend on - assumed identical - market data and domestic water consumption. For Chemical B, the uncertainty of the mass fluxes can be explained by the variability of WWTP removal and plant bypassing.

Plant bypassing occurred in 82 of the 1000 Monte Carlo shots. As this is above the 5% threshold, the 95th percentile concentrations of chemical B were influenced by these extreme flow events.

4.2. Analysis of Predicted Concentration Distributions (Chemical B)

For 3 locations in the study area, an analysis of the predicted concentration distributions of the degradable Chemical B was made: the discharge (effluent) from City A, the mixing zone of this discharge in the river, and the end of the catchment (segment 100) (see Figure 3.5).

Predicted concentration distributions are described by their mean and 95th percentile values. The latter were obtained in 2 ways: (1) by assuming log-normality (using the method of moments), and (2) by complete statistical analysis of the results dataset. Skewness of the distributions was also determined. (Table 3.6). These distributions are illustrated by the histograms in Figure 3.5, together with their geographical locations.

Table 3.6. Description of predicted concentration distributions

		City A discharge	City A mix. zone	End of Catchment
C_{mean}	(mg/L)	7.69	0.193	0.226
$C_{95^{th}ile}$	assuming log-normality (mg/L)	17.75	0.269	0.271
$C_{95^{th}ile}$	from statistical analysis (mg/L)	18.22	0.278	0.275
skewness	-	2.37	0.76	0.39

The 95th percentile Cs calculated using the log-normality assumption corresponded well with the true 95th percentiles. The skewness in the river was lower than in the discharge, due to leveling out of high sewage concentrations by high river flows (the correlation between river and sewer flows was 0.6). The lower skewness at the end of the catchment can be explained by leveling out due to multiple discharges and the effect of in-stream removal.

A one-sample Kolmogorov-Smirnov test (SPSS Software version 7.5) for normality (on the logarithms of the concentrations), using a significance threshold $\alpha = 0.05$, showed that the log-normality assumption for all three C distributions was valid.

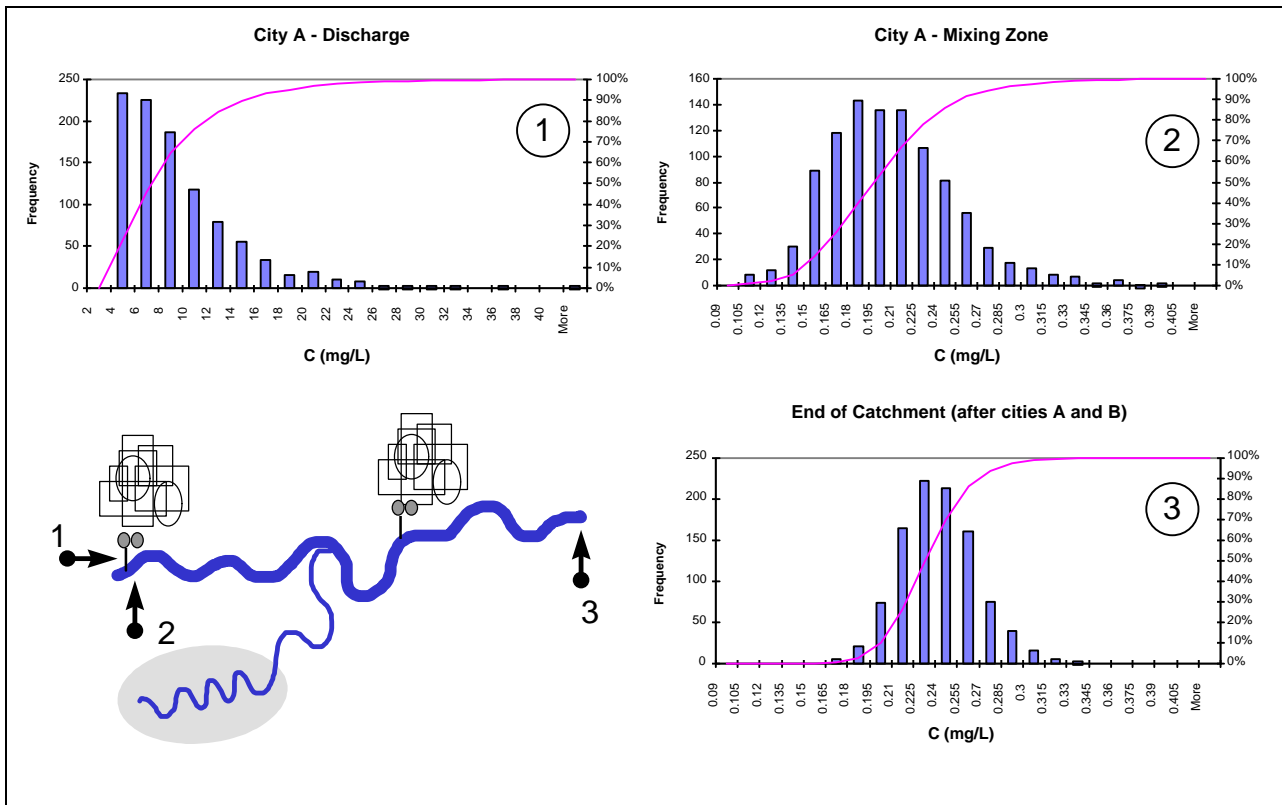


Figure 3.5. Predicted concentration distributions (histograms + geographical location)

4.3. Monte Carlo Simulation versus Flow Scenario Approach

An alternative to Monte Carlo simulation for dealing with flow seasonality, is the calculation of Cs from discrete Flow Scenarios. In this case, one obtains a predicted concentration from a single simulation at mean flow: $C(Q_m)$. From another simulation, at the 5th percentile flow, one obtains $C(Q_{95})$. Both calculation approaches were compared (using $C_{internal}$ values). The relative difference of the discrete Cs at these two Flow Scenarios and the corresponding Monte Carlo simulation Cs is shown in Figure 3.6.

Mean C and C at mean flow were very similar for all segments. In some cases, the predicted concentrations at Q95 significantly under-estimated the 95th percentile C (10 - 15 % deviation). From this, one can derive that the Flow Scenario approach can provide quick initial results (especially for the means). For more detailed simulations, and especially for 95th percentiles, Monte Carlo approach was better-performing. Note that for a complete uncertainty analysis, Monte Carlo simulation is also required.

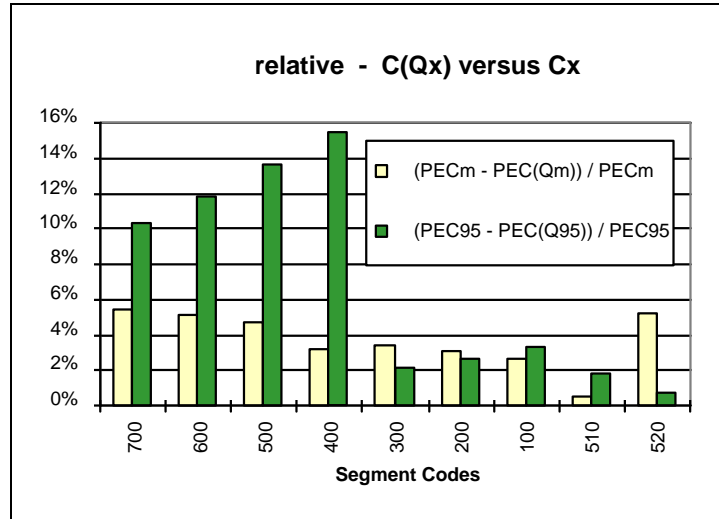


Figure 3.6. Relative difference between results of flow scenario and Monte Carlo approach

4.4. Spatial Aggregation

The entire catchment was represented by a single (aggregated) segment (Table 3.7). The river flow was taken from the final stretch in the detailed approach (segment 100). The aggregated stretch length was calculated as the weighted average (by population) of the distances from each discharge to the end of the catchment. For the aggregated discharge, the number of people was equal to the sum of all three discharges, and the WWTP connection degree was calculated as the average of the discharges, weighted by population.

Table 3.7. Spatial aggregation: aggregated segment properties

river flow	(m^3/s)	mean = 66.0 5 th %ile = 49.5
river length	(km)	49.25
population	(cap)	1350000
% connected to treatment	(-)	55.56 %

In Figure 3.7, the average and output C values are shown for the large scale approach, as well as the corresponding small scale results. The small scale average values were calculated as the weighted average (by stretch length) of the $C_{internal}$ in all stretches.

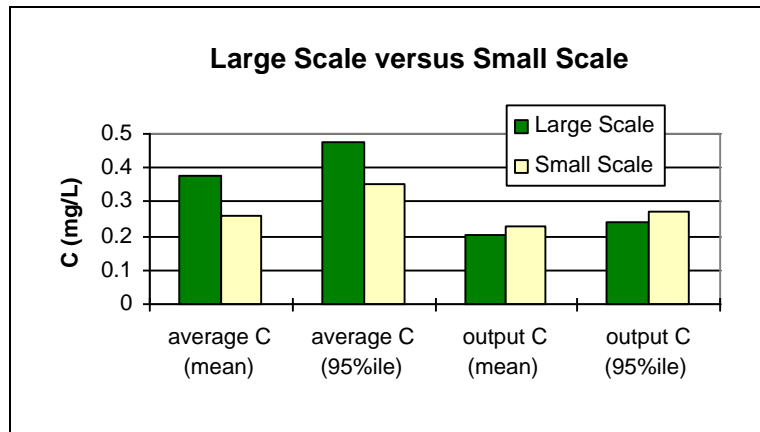


Figure 3.7. Comparison of large scale versus small scale results

The large scale prediction for the catchment's output C approximated the more detailed small scale value within 12% (under-estimation). For the average predicted concentration of the entire catchment, on the contrary, the large scale approach over-estimated the mean by 45% and the 95th percentile by 36 %.

5. Conclusions

The GREAT-ER simulation approach allowed to analyze the impact of different discharges and tributaries on the temporal and spatial distributions of predicted concentrations in a hypothetical (but realistic) catchment. The resulting distributions were log-normal. For the prediction of 95th percentile concentrations, Monte Carlo simulation was superior to the discrete Flow Scenario approach. Also for a complete uncertainty or variability analysis, Monte Carlo simulation is needed. However, to quickly obtain initial results, the Flow Scenario approach may be useful. Finally, it was found that the GREAT-ER methodology allowed spatial aggregation of the simulated hypothetical catchment, from a small detailed scale to a larger scale.

Chapter 4

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Adaptation of the CAS Test System and Synthetic Sewage for Biological Nutrient Removal

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Chapter 4

Adaptation of the CAS Test System and Synthetic Sewage for Biological Nutrient Removal

1. Introduction

Accurate exposure predictions are required for the environmental risk assessment of chemicals. Determining the degree of elimination in waste water treatment plants is a crucial step in the environmental exposure assessment of down-the-drain chemicals. To predict such removal efficiencies, chemical fate models or laboratory simulation tests can be used. Even if mathematical models are employed, laboratory tests are needed to provide the data necessary for model calibration. In this chapter, an adaptation to the standard OECD CAS (Continuous Activated Sludge) test (OECD, 1993; ISO, 1995) is presented, which incorporates biological nutrient removal.

In the scope of biodegradability testing of industrial chemicals, the EC directives 67/548/EEC (CEC, 1967), 73/405/EEC (CEC, 1973) and their subsequent amendments specify the CAS test system as one of the valid testing methodologies. The CAS system is probably the most widely applied laboratory model for the simulation of activated sludge systems. Yet, many modern full-scale wastewater treatment plants (WWTPs) can no longer be approached as a single aerated reactor. The EU Urban Waste Water Treatment Directive 91/271/EEC (CEC, 1991) imposes WWTP effluent criteria for nitrogen and phosphorus in nutrient sensitive areas. Full-scale biological nutrient removal (BNR) designs such as the UCT, Bardenpho, Bardenpho, A/O, A2/O process, etc., are being built with increasing frequency (Bowker & Stensel, 1990). Alternatively, existing plants are retrofitted for BNR (e.g. Matsché, 1987; Randall *et al.*, 1992; Kayser, 1994).

An improved laboratory-scale WWTP simulation system in which BNR is included would permit to routinely study the degree of elimination of industrial chemicals, their biodegradation pathway(s) in the different compartments, and potential effects on plant operation. Two aspects are of particular interest:

- 1) the presence of alternative electron acceptors in addition to oxygen may lead to other degradation pathways and/or kinetics under anoxic/anaerobic conditions.
- 2) two additional essential biological processes take place, i.e. excess phosphorus uptake, and biological nitrogen removal via nitrification/denitrification. This may imply an increased sensitivity of the plant to inhibitory substances (Kroiss *et al.*, 1992, Strotmann & Eglsäer, 1995).

In this chapter, two systems are evaluated and compared to the traditional CAS unit. In selecting the test unit's design, a number of factors were taken into account. The units were to be simple, flexible, require little control, and be able to mimic most full scale plants built to meet the EU Urban Waste Water Treatment Directive (CEC, 1991). To allow in-depth testing of the fate of chemicals in activated sludge systems, they should also be fit for the use with radiolabeled test compounds.

The OECD 303A protocol prescribes a synthetic sewage with a pre-established composition as influent for the activated sludge units, whilst the latest ISO 11733 protocol permits the use of real sewage. Although the results obtained from units run on synthetic sewage are intended to be highly reproducible due to a minimized variability of the medium, the opposite is often seen in practice.

Despite close supervision of the units, the peptone and meat extract based OECD synthetic influent often leads to a number of operational problems, such as frequent sludge bulking (AISE-CESIO report, 1990, unpublished). The OECD feed has also been criticized that it is not an accurate reflection of real domestic sewage due to its unbalanced composition, and therefore may result in a decline in microbial diversity in the system (Kaiser *et al.*, 1997). As such, not all catabolic enzyme systems normally present in an activated sludge community would be expressed. With the use of real domestic sewage the above problems can generally be overcome. However, domestic sewage is prone to strong temporal variations in strength, and to occasional toxic pulses.

Recognizing the advantages a synthetic sewage can have in principle, this chapter introduces an improved type of synthetic sewage. The starting point for its development was that it should be a better simulation of real (pre-settled) sewage than the OECD medium, and that it should reduce the latter's inherent issues. A key success criterion for this new synthetic sewage was that it should sustain the operation of a broad range of pilot scale wastewater treatment plants (WWTPs), specifically those with biological nutrient removal (BNR), since these systems will increasingly need to be simulated in the laboratory.

2. Adapted Test Units

2.1. Test Unit Selection

The 'single sludge' approach (i.e., the same activated sludge biomass circulating through all tanks and redox zones) was selected, since this approach is by far the most popular for full-scale BNR systems treating domestic sewage (Brett *et al.*, 1997; Wentzel & Ekama, 1997).

The first unit, the commercially available Behrotest KLD4[®] (Behr unit) (Behr Labortechnik, Düsseldorf-Reisholz, Germany), consists of an anoxic tank (4.2 L) in front of the aeration tank (4.5 L) (Figure 4.1). There is one sludge recycle, from the settler to the anoxic reactor. In this study the sludge recycle rate was set at 2.5 times the influent flow. This system was initially designed for biological nitrogen removal (Albertson & Stensel, 1994; Gronenberg & Schöberl, 1994), but luxury P-uptake is not excluded (Kernn-Jespersen & Henze, 1993; Henze *et al.*, 1995a; Barker & Dold, 1996). The Behr unit is not a sealed system, but it can be adapted for use with radiolabeled chemicals.

The second unit was designed in-house, based on the University of Cape Town process (Ekama *et al.*, 1984; Carucci *et al.*, 1996; Barker & Dold, 1997; Brett *et al.*, 1997). This unit was named CAS-UCT. It consisted of three reactors in series: an anaerobic, an anoxic and an aerobic reactor (Figure 4.1). The UCT process can be seen as a template for many single sludge BNR systems. Full scale UCT plants have been built in several continents (Wentzel *et al.*, 1988; Wentzel *et al.*, 1992; Randall *et al.*, 1992; McClintock *et al.*, 1993). The separation of the different redox zones in distinct tanks makes this system attractive as a test unit.

Next to these BNR test units, the standard OECD CAS test unit was used as a reference.

2.2. Dimensioning of the CAS-UCT Test Unit

The CAS-UCT unit consists of an anaerobic, an anoxic and an aerobic tank, placed in series. There are three recycle flows, which can be independently controlled. In designing the CAS-UCT unit, the dimensions of the traditional CAS unit were taken as a starting point, i.e. the volume of the aerated unit was set at 3.0 L. To determine the volumes of the other two tanks two scenarios were compared, based on literature data (Ekama *et al.*, 1984; Randall *et al.*, 1992; Johanson, 1994): (1) an anaerobic tank volume of 0.75 L and an anoxic tank of 1.5 L, and (2) both tanks with equal volumes of 1.5 L.

Both scenarios, in combination with six different sludge recycling regimes, were evaluated mathematically by means of the IAWQ Activated Sludge Model N° 2 (ASM2) (Henze *et al.*, 1995b). As the ASM2 was primarily used as a design tool, the default parameter set (supplied by Henze *et al.*, 1995b) was used and no calibration of the model was performed. The model was slightly modified: 50% of X_S (the fraction of COD which biodegrades slowly) was assumed to be in solution (i.e., not to be removed with settled sludge). For the settler, a simple mass-balance point settler model was used. The fraction of solids washed out with the effluent was fixed at 0.5%. The results of the ASM2 simulations (after having reached steady-state) are presented in Figure 4.2 below.

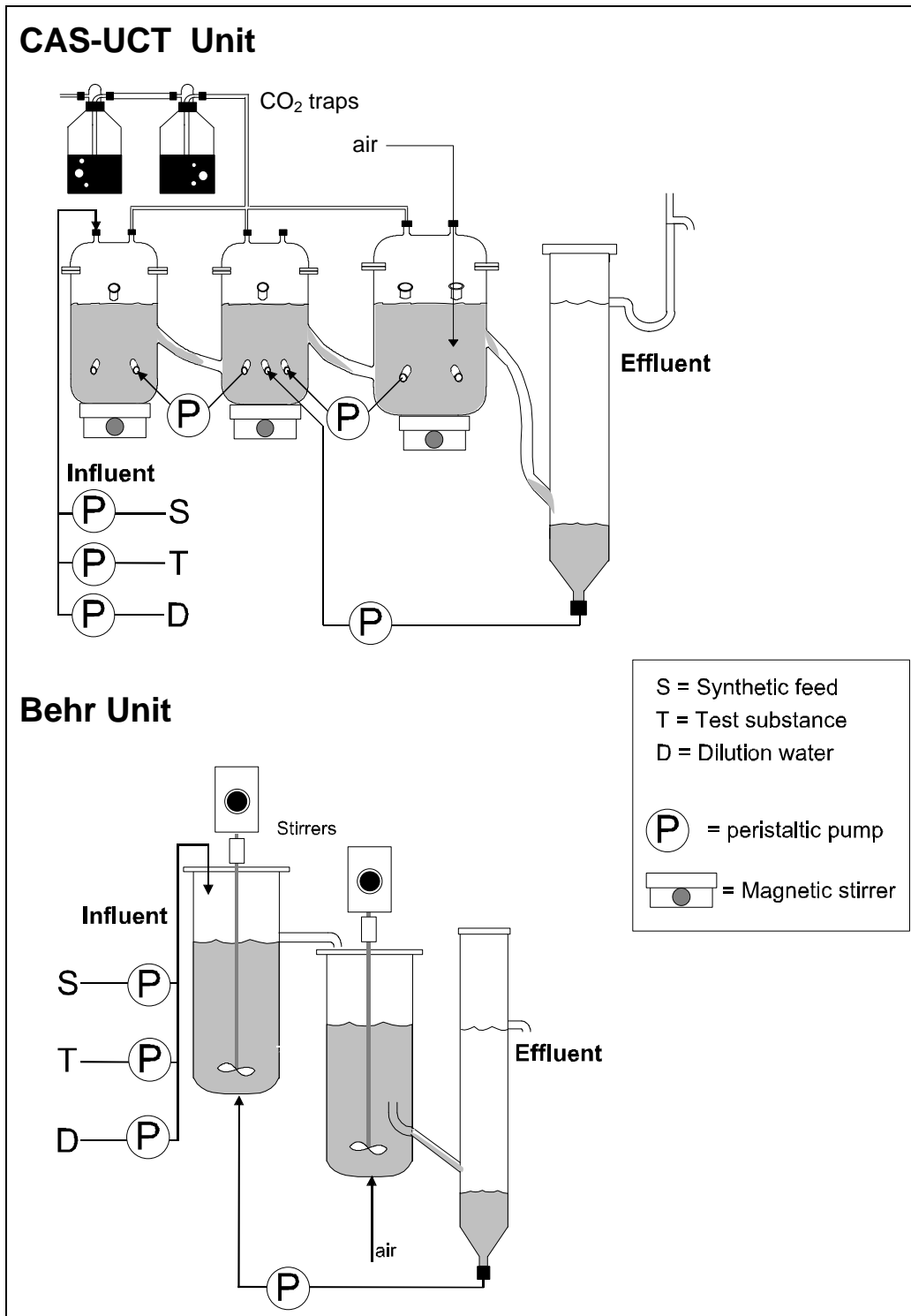


Figure 4.1. Schematic drawing of the CAS-UCT and Behr units

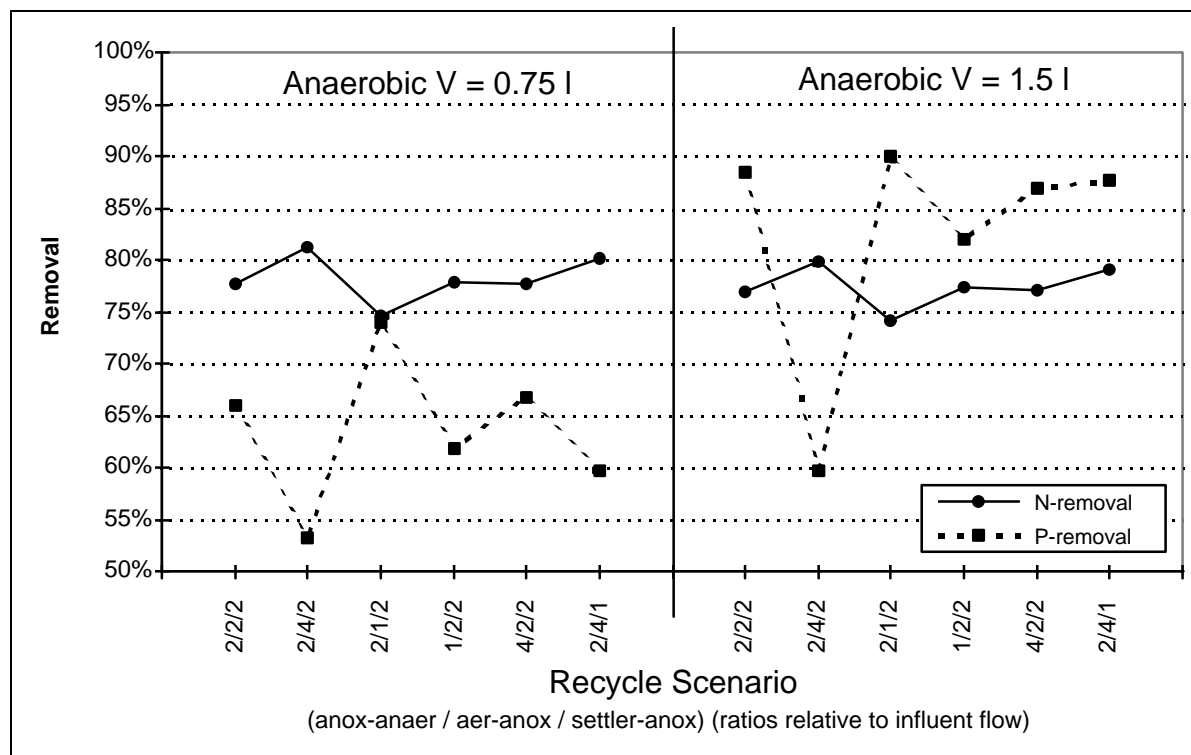


Figure 4.2. Influence of different design scenarios in the UCT unit on N and P removal

Based on the simulation results, the best performance was expected for scenario (2) with anaerobic and anoxic volumes of each 1.5 L, together with a 2/2/2 recycle regime (i.e., the recycle flows from the anoxic to the anaerobic tank, from the aerobic to the anoxic tank and from the settler to the anoxic tank were all set to 2x the influent flow). The volume of the anaerobic tank was predicted to have an important effect on P-removal, while the predicted impact on N-removal was very limited. The recycle regime was expected to influence removal efficiency of both nutrients.

2.3. Test Unit Operation

2.3.1. Operating Conditions

The operating conditions for the BNR units are summarized in Table 4.1. The standard CAS unit was operated in the uncoupled mode according to ISO (1995).

Influent flows were selected to have an HRT (Hydraulic Residence Time) in the aerobic tank of 6 hours (cf. the standard CAS test). The SRT (Sludge Residence Time) in the Behr and CAS-UCT units was set at 15 or 20 days, to allow the development and maintenance of an adequate microbial population (Focht & Verstraete, 1977; Henze *et al.*, 1995a). At this SRT there still was sufficient sludge wastage to ensure stable phosphorus (poly-P) removal with the sludge (CIWEM, 1994).

The sludge loading rate (B_x) followed from the combination of reactor volumes, Mixed Liquor Suspended Solids (MLSS) level, influent characteristics and flow rate, and was typically in the range of 0.20-0.30 gCOD/gMLSS.day for the BNR systems.

The sludge recycle ratio in the Behr unit (from the clarifier to the anoxic tank) was set to 2.5 times the influent flow. For the CAS-UCT unit, the recycle regime presented in section 2.2 above was used.

The dissolved oxygen (DO) concentration in the aeration tank of the Behr and CAS-UCT units was aimed at 3.5 mg/L by tuning the aeration intensity. The safe working range was approximately 2.5 to 4.5 mg/L. A lower DO value would lead to anoxic conditions in the settler, resulting in sludge rising due to denitrification, and P-release into the effluent. Higher DO levels were equally undesirable, as the sludge was recycled to the anoxic and anaerobic tanks. DO levels above 0.2 mg/L in the latter would inhibit denitrification and P-release (Isaacs *et al.*, 1994; Brett *et al.*, 1997). Under the operating conditions employed in this investigation, the DO concentration in the anoxic/anaerobic tanks remained mostly below 0.1 mg/L.

All tests were performed at room temperature (18-23 °C). The influent pH was set at 7.25, and the effluent pH was typically ranged between 7.5-7.9.

Table 4.1. Operating conditions for the BNR units

	Volume (L)	HRT (h)	Run #	MLSS (g/L)	SRT (d)	B_x (g/g.d)
Behr						
- Ax	4.2	5.6				
- A	4.5	6				
			#1 ^(a)	4.1	20	0.25
			#2 ^(a)	3.0	20	0.25
			#3 ^(b)	3.6	20	0.1-0.3
			#4 ^(a)	3.6	15	0.24
UCT						
- An	1.5	3				
- Ax	1.5	3		3.5	15	0.22
- A	3	6				

A = aerobic tank, Ax = anoxic tank, An = anaerobic tank, C = clarifier

^(a) synthetic medium, ^(b) real domestic sewage

2.3.2. Influent Characteristics

For most of the experiments with these units, synthetic sewage was used. As this was concurrently under development during the experimental period, the units were operated using the precursor of the *Syntho* medium (which is described later in this chapter). To compare the performance of a Behr unit fed with synthetic sewage versus domestic waste water, the unit was also operated using real domestic sewage as influent. The sewage used in this study was collected biweekly from the Duffel domestic WWTP (Belgium) (passed through a sieve, mesh 0.5 mm). Average influent characteristics for synthetic and domestic sewage are given in Table 4.2.

Table 4.2. Characterization of *Syntho* (precursor) and Duffel domestic sewage (values in mg/L)

Components	<i>Syntho</i> (precursor)	Domestic Sewage
Total COD	390 *	460 ± 200
Total Phosphorus	7.9	7 ± 3
Total Nitrogen	34.6	25 ± 7
pH	7.25	6.9 - 7.5

* calculated value

3. Development of a New Synthetic Sewage

3.1. Concept and Composition

Syntho was designed to mimic real pre-settled domestic wastewater. As it was intended to be used as a standard influent to the Continuous Activated Sludge system (CAS), its components should be commonly available and at a relatively low cost. In addition, the feed should be easy to prepare and dose. The composition was chosen such that the use of *Syntho* would support excess N and P removal, without aiming to maximize nutrient removal performance per se.

Syntho was conceived as a mixture of synthetic wastewater and a minor fraction (10% v/v) of pre-settled real domestic wastewater. The selection of ingredients for the synthetic part was based on the expected composition of domestic sewage. *Syntho* therefore differs considerably from classic bacterial growth media. It was based on two fractions, a "sanitary" and a "household" wastewater fraction. The sanitary fraction (black water) was based on the average composition and quantity of sanitary wastewater, i.e. the combination of urine and feces (e.g. Hendericks, 1991; Yamada *et al.*, 1991; Haubrich *et al.*, 1994; Isselbacher *et al.*, 1994). The household fraction (gray water) was harder to define given its variability. A typical trait is that it contains biodegradable surface-active agents.

The amount of biodegradable COD needed to transform 1 mg of NO₃-N to N₂ is 5.5-8.6 mg, and the amount of biodegradable COD needed during biological P removal is 50-59 mg per mg of phosphorus (Randall *et al.*, 1992; US EPA, 1993; Henze *et al.*, 1995a; Smolders *et al.*, 1996). Hence, to optimize the synthetic medium for biological nutrient removal, a COD:N:P ratio of approximately 100:7:2 was chosen. A slight variability in this ratio occurs in practice due to the mixing with real domestic sewage. Short chain volatile fatty acids such as acetate have a direct impact on N and P removal (Isaacs & Henze, 1995; Zhao *et al.*, 1995; Barker & Dold, 1996; Brett *et al.*, 1997), and their level can be used to tune N and P removal to a desired level.

The synthetic part also contains lyophilized sludge, mainly to act as a starter for floc formation. Real sewage contains a particulate fraction which is inert or mineral. This fraction is simulated by diatomaceous earth, which helps to increase sludge floc density. The type and concentration of trace metals added to the medium is based on typical concentrations found in sewage (Kempton *et al.*, 1987; Stephenson & Lester, 1987). An overview of the synthetic fraction (90%) of the *Syntho* medium is given in Table 4.3.

Table 4.3. *Syntho* medium composition (values in mg/L)

C-source		N-source		P-source		Sewage simulation	
Peptone	15	Urea	75	MgHPO ₄ .3H ₂ O	25	LAS *	10
Na-acetate**	120	NH ₄ Cl	11	K ₃ PO ₄ .H ₂ O	20	AE *	10
Dry meat extract	15	Uric acid	9			Lyophilised act. sludge	50
Glycerol	40					Diatom. earth	10
Potato starch	50					Diet fibers	80
Milk powder	120						
<i>Minerals & Trace Metals</i> ***							

* C12-C14 Linear Alkylbenzene Sulphonate (LAS) and Alcohol Ethoxylate (e.g. C12-C14AE5) or any other readily biodegradable surface active agents. For cost reasons the use of a commercial rather than a pure grade is recommended (e.g. Fluka 48750 and 44200).

** Na-acetate can be varied to adjust the C/N/P ratio, to fine-tune N/P removal

*** CaCl₂, 5 mg/L; NaHCO₃, 25 mg/L; FeSO₄.7H₂O, 10 mg/L; Trace metals: CuCl₂.2H₂O, 480 µg/L; CoCl₂.6H₂O, 50 µg/L; ZnCl₂, 180 µg/L; MnSO₄.H₂O, 100 µg/L; K₂MoO₄, 20 µg/L; Cr(NO₃)₃.9H₂O, 680 µg/L; NiSO₄.6H₂O, 300 µg/L; EDTA, 0.22 µg/L.

Domestic sewage provides a constant influx of bacteria and spores which act as an inoculum for the activated sludge plant (Mara, 1974; Curds, 1975). The broad range of substrates in real sewage will also ensure a diverse microbial population and enzymatic activity. To reduce the variability in composition to a minimum, the amount of real sewage is limited to 10% v/v.

The total calculated and measured COD of the medium (without the 10% domestic sewage) are approximately 470 and 508 mg/L., respectively. The alkalinity of the synthetic sewage was determined by titration with 0.01 N HCl. At a set pH of 7.25, the alkalinity was 3.5 meq HCO₃⁻/L.

In practice, a concentrated feed stock (e.g. 25 times) was prepared once, divided and frozen in small portions, which were thawed and diluted with deionized water before use. All ingredients of the feed stock were dissolved/mixed with deionized water. The lyophilized activated sludge and the diet fibers were ground in a coffee mill prior to the mixing with water in order to avoid that particulate materials would block the dosing pump. A stock solution of EDTA / trace metals in deionized water (1000 times more concentrated) was prepared separately, stored in a refrigerator, and mixed with the synthetic sewage to the required concentration on the day of use.

The cost of *Syntho* in terms of chemical ingredients is low, ca. 0.03 Euro per liter, or 3.5 - 4.5 Euro per week of testing for a CAS test.

The concentrated feed and the dilution water / real sewage were dosed separately. Although separate dosing of a concentrated stock solution is technically more complicated, this procedure was preferred because it enabled to keep the synthetic feed stock stable for several days on the laboratory bench, resulting in a constant and well defined organic load to the test units. Compared to the traditional OECD feed, the absence of bad odors produced by degrading constituents was an additional advantage.

The experiments with the test units were conducted using the precursor of *Syntho* as influent. This medium contained (in *mg/L*): urea 75; ammonium chloride 11; uric acid 9; dried yeast 45; lauric acid 25; Na-acetate 68; diet fiber 35; LAS 10; AE 10; meat extract 15; peptone 15; starch 70; low fat milk powder 80; mineral salts and trace elements as in *Syntho*.

3.2. Simulation Experiments

3.2.1. ASM2 Parameterization

The ASM2 (Henze *et al.*, 1995b) was used to predict the operation of the test units fed with the proposed medium composition. The same modifications as described in section 2.2 were applied. The ASM2 model components are divided into solubles (*S*) and particulates (*X*), which are further subdivided into easily biodegradable, fermentable and other components. The different constituents of *Syntho* were assigned to an ASM2 component based on the degradation steps they are assumed to undergo in the units (Table 4.4). These were derived from literature data (Mandelstam & Halvorson, 1960; Eastman & Fergusson, 1981; Henze & Mladenovski, 1991; Elisosov & Argaman, 1995; Mino *et al.*, 1995).

To further characterize the *Syntho*-related input parameters for ASM2, a respiration test was carried out with the synthetic sewage according to the methodology described by Spanjers (1993), Spanjers *et al.* (1994) and Henze *et al.* (1995a). Endogenously-respiring sludge was fed with a pulse dose of *Syntho*. The calculations were made according to the methodology described by Spanjers & Vanrolleghem (1995) and Henze *et al.* (1995a). The readily and slowly biodegradable fractions could be derived from the respiration curve. The inert fraction was obtained from the difference between the calculated COD and the actual oxygen demand. It is then further subdivided into a soluble inert fraction (S_i), which was obtained from the effluent COD values of a test unit operating on *Syntho* and an inert particulate fraction (X_i).

The respiration curve obtained for the synthetic medium *Syntho* is shown in Figure 4.3. This compares well with the respirograms obtained by Spanjers & Vanrolleghem (1995) for real domestic sewage. Based on the respirogram, a characterisation of the synthetic medium was carried out, as presented in Table 4.4 (column '*Syntho* - measured'). The main differences between *Syntho* and real sewage are that the fraction of 'heterotrophic bacteria' is larger in real sewage, while *Syntho* contains somewhat more 'soluble fermentation substrate' (e.g. glycerol, surfactants, uric acid, and possibly part of the peptone and meat extract) as well as 'soluble fermentation products' (i.e. acetate). The amount of 'heterotrophic bacteria' in *Syntho* might be underestimated, since the medium was freshly prepared and the lyophilized biomass was probably not fully active when added to the respirometer. The OECD medium has a predominant (estimated) component of X_s , which is not truly particulate, but refers to the easily accessible colloidal peptone and meat extract fraction.

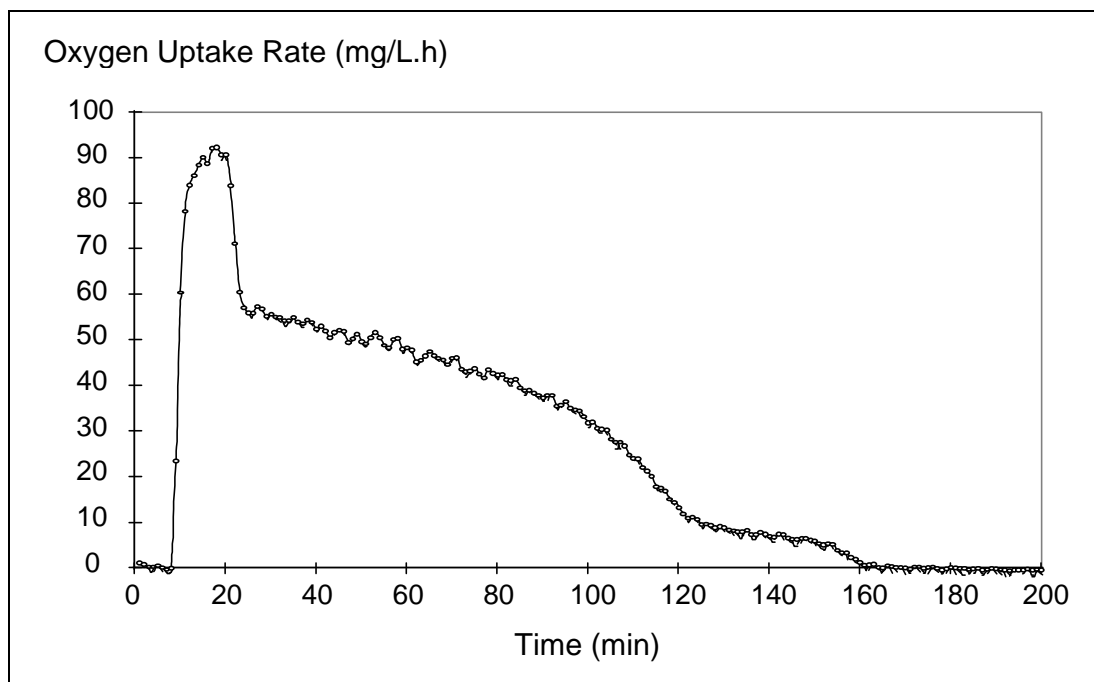


Figure 4.3. Respiration curve obtained with the *Syntho* medium

Table 4.4. Estimated and measured ASM2 parameters for the *Syntho* medium

	Description	<i>Syntho</i> (measured)	<i>Syntho</i> (estimated)	OECD (estimated)	Real sewage**
S_i	Inert soluble matter	0.00	0.04	0.00	0.06
S_a	Soluble fermentation products	0.14	0.18	0.00	0.08
S_f	Soluble fermentation substrate	0.21	0.25	0.19	0.16
X_s	Slow biodegradable partic. matter	0.52	0.43	0.81	0.50
X_{aut}	Autotrophic bacteria	*	0	0	0
X_{pha}	Cell internal storage	*	0	0	0
X_{pao}	P-accumulating organisms	*	0	0	0
X_h	Heterotrophic bacteria	0.04	0.03	0.00	0.10
X_i	Inert particulate matter	0.09	0.07	0.00	0.10

* not measured; ** from range given in Henze *et al.* (1995b)

3.2.2. ASM2 Simulation

A simulation with the ASM2 was carried out to illustrate the expected differences in unit performance when a laboratory UCT system is fed with the OECD medium versus *Syntho*. The composition of the sewage, and in particular the COD:N:P ratio as well as the quantity of readily biodegradable matter, is the main factor in determining whether a UCT unit will perform well (Ekama *et al.*, 1984; Tam *et al.*, 1992; Fass *et al.*, 1994; Henze *et al.*, 1995a; Qasim *et al.*, 1996; Randall *et al.*, 1992).

To evaluate the performance of the new medium, ASM2 simulations were carried out for the UCT test unit described higher in this chapter. For this simulation, a sludge loading rate of 0.25 kgCOD/kgMLSS.day was used. The sludge residence time was set to 15 days, and all three sludge recycles were fixed at 2.5 times the influent flow. The experimentally determined model components were used for *Syntho*. The simulation results are presented in Figure 4.4.

Treating domestic sewage a full-scale UCT will typically give an efficiency in the range of 87-90% P-removal, and up to 75-80% N-removal (Randall *et al.*, 1992). The ASM2 predicts that a UCT test unit operated on *Syntho* could achieve a similar performance. When comparing *Syntho* with the OECD medium, it appeared that the OECD medium supports a predicted N removal in the order of 65-70%. This is slightly lower than the 70-75% predicted with *Syntho*. The OECD medium would support only 55-60% biological P removal, while with *Syntho* this was predicted to reach 85-90%. These differences can be ascribed to the improved COD:N:P ratio of *Syntho*, and the presence of acetate to stimulate BNR processes.

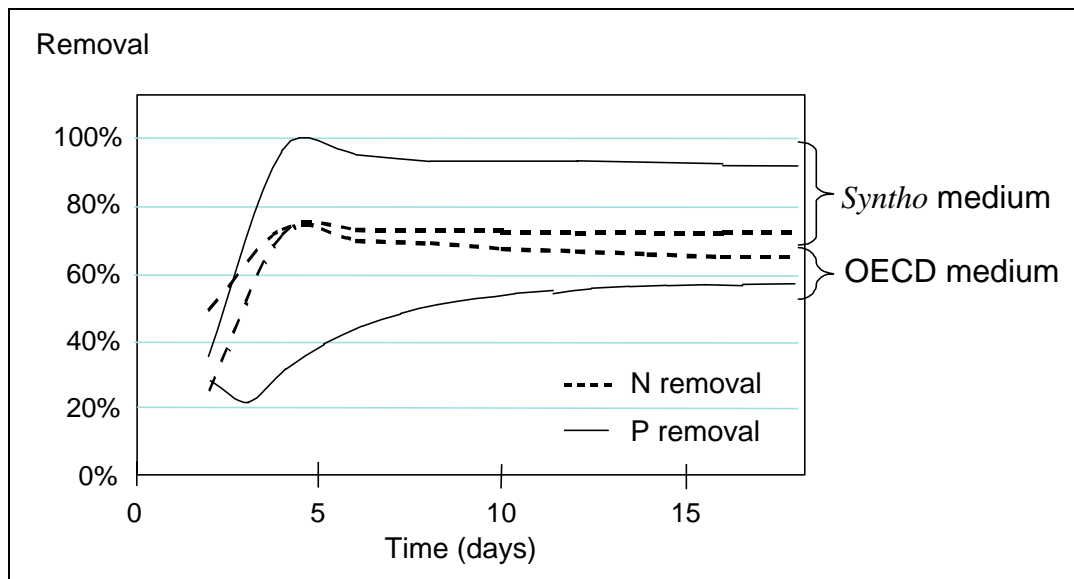


Figure 4.4. ASM2 simulation: predicted N and P removal in a UCT unit during startup

4. Analytical Methods

The parameters outlined below were monitored on a daily basis during working days. Samples were taken from the influent and the effluent of the units. The effluent was collected over a period of at least one hour.

For COD, nitrogen (total, ammonia, nitrate and nitrite) and phosphorus (total phosphate) measurements the Dr. Lange spectrophotometric analytical test system LASA 20 (Dr. Bruno Lange GmbH) was employed.

Mixed liquor suspended solids (MLSS) were measured according to the Dutch NEN-norm 6445; both the aeration tank and the anoxic/anaerobic tanks were sampled. The Sludge Volume Index (SVI) was measured in a 1-litre Imhoff cone over a period of 30 minutes with sludge from the aeration tank. Dissolved Oxygen (DO) was measured on a daily basis in the aeration tank, in the anoxic tank and in the sludge layer of the settler. pH was monitored in all reactors as well as in the influent tank to ensure that the acidification of the sewage did not result in an excessively low pH of the influent. The temperature in the aeration tank was measured each working day. Influent flow rates and the sludge recycling flow rates were verified at least once a week.

LAS was measured by a specific HPLC method according to Matthijs & De Henau (1987).

5. Results and Discussion

5.1. Reactor Performance

In a first series of tests the Behr-, CAS-UCT and standard CAS units were compared in terms of COD, N and P removal, as a validation procedure for the BNR systems. No test chemicals were dosed in this round of testing. ASM2 predictions were used to cross-check the observed test units' performance.

5.1.1. Reactor Performance with Synthetic Medium

Figure 4.5 compares the average COD, N and P removal performance for the three units fed with *Syntho* (precursor) synthetic medium. The test conditions are given in Table 4.1 (Run #1 for the Behr unit). Results relate to a measurement period of minimum three weeks of steady-state operation after initial start-up and equilibration. After inoculation of the units with nitrifying activated sludge it typically took 2-4 weeks to obtain stable reactor performance in terms of nutrient removal.

As the graphs indicate, both the Behr and the CAS-UCT unit are capable of excess nitrogen and phosphorus removal, while the standard CAS unit does not achieve more than ca. 30% N and P elimination. The measured removal in the BNR units is in line with the expectations of what can be achieved with laboratory-scale units (Carucci *et al.*, 1996) and what is seen in full-scale plants (Bowker & Stensel 1990; Randall *et al.*, 1992; Kuba *et al.*, 1993).

The ASM2 predictions (Figure 4.5) concur with the experimentally obtained values. ASM2 was very accurate at predicting the level of N and C removal in all systems. The P removal rate was slightly underestimated for the Behr and CAS-unit, and slightly overestimated for the UCT. In terms of residual COD levels in the effluent, the CAS, Behr and CAS-UCT performed similarly, with average concentrations of 15.8, 16.2 and 13.0 *mg/L* respectively.

The observation of a high degree of P-removal in the Behr-unit, which was considered in first instance a nitrogen removal system, is noteworthy. It should be seen in the light of the recent literature (e.g. Barker & Dold, 1996), which indicates that a significant fraction of the poly-P bacteria can use nitrate as electron acceptor and develop into an active population in the anoxic reactor.

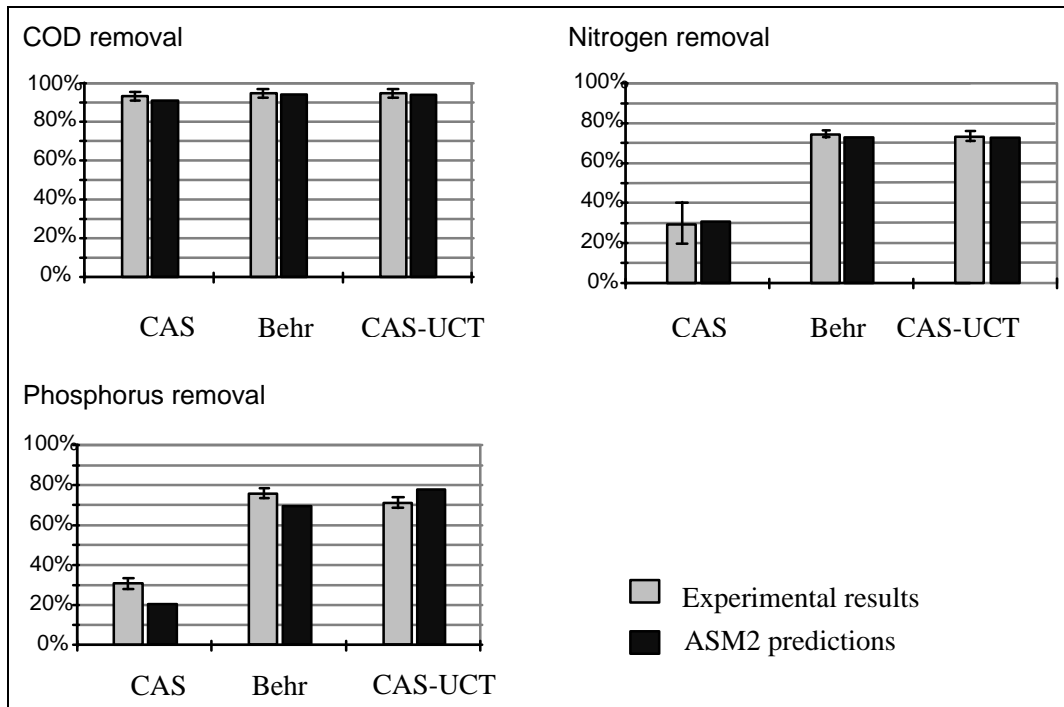


Figure 4.5. Test unit performance using the Syntho (precursor) medium

5.1.2. Behr Unit Performance: Domestic versus Synthetic Sewage

For the Behr unit, a comparison in terms of BNR and reactor stability was made between real domestic sewage and the precursor of the *Syntho* medium. The operating conditions are given in Table 4.1 (Behr: Run #2 and #3).

Reactor performance

The COD, N and P removal data are shown in Figure 4.6, for the period after day 30 of each experiment. Average removal values are given in Table 4.5. For COD and N-removal, the Behr-unit performed on average quite similarly on synthetic and real sewage. However, the synthetic feed showed a lower P-removal. The COD:N:P ratio for the Duffel raw sewage was in the range of 100:6:1.5 while that for *Syntho*'s precursor was ~100:9:2. Hence, for the unit operating on domestic sewage more volatile fatty acids were available for phosphate removal, which would otherwise be used during denitrification (Fass *et al.*, 1994).

Table 4.5. Performance of the Behr unit: % COD, N and P removal

	<i>Syntho (precursor)</i>	<i>Duffel sewage</i>
COD	95.0 ± 3.0	92.5 ± 5.0
N	76.0 ± 8.0	73.0 ± 6.0
P	70.0 ± 9.0	91.0 ± 8.0

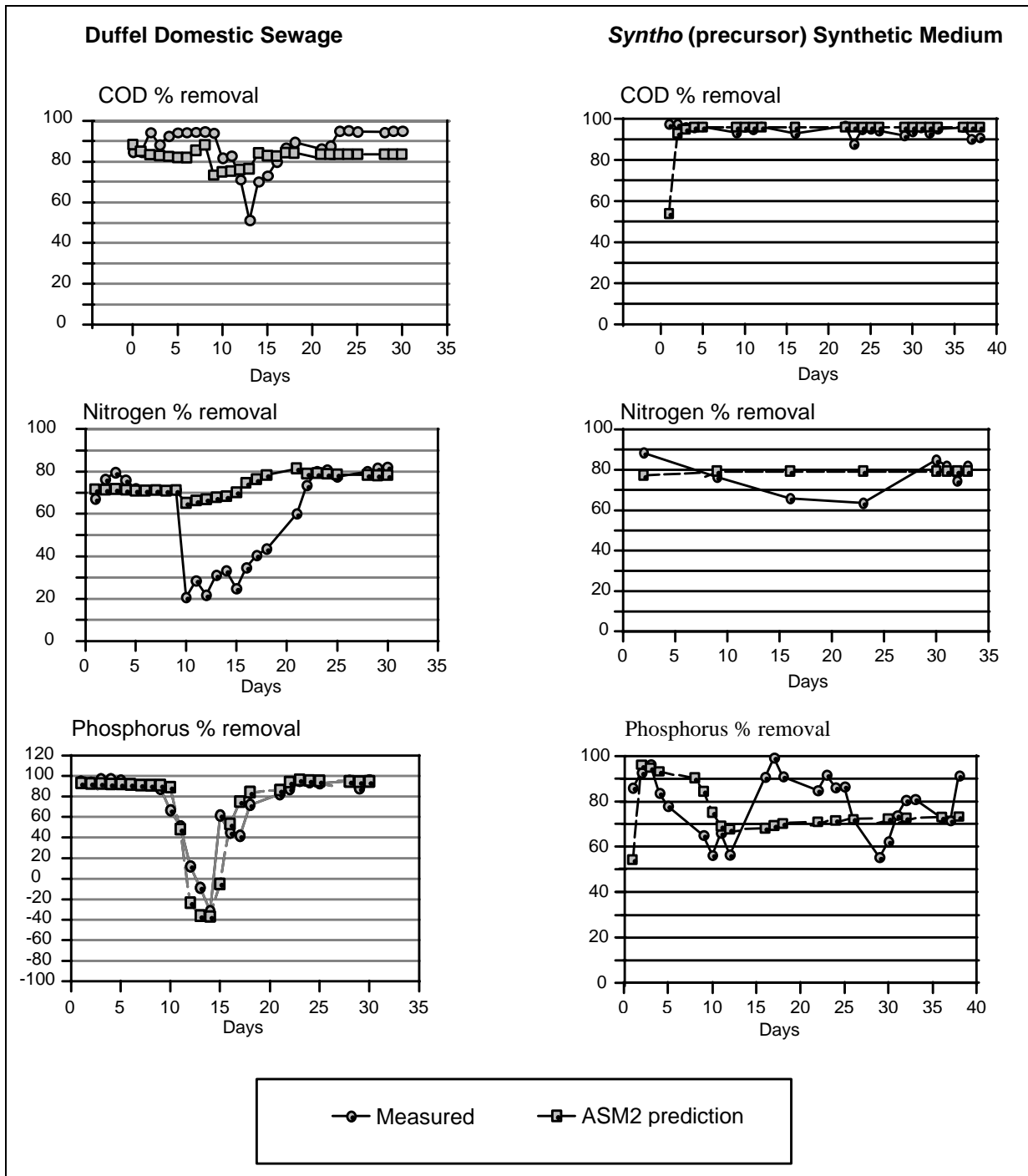


Figure 4.6. Performance of the Behr unit: synthetic medium vs. Duffel sewage

The drop in performance of the unit fed with Duffel sewage (after ten days) was probably caused by a toxic pulse, in combination with a rainy period (causing a low-strength influent). A similar performance upset was also recorded in the Duffel treatment plant itself. The temporary high dilution caused a low level of easily biodegradable carbon and resulted in a net phosphate release, as predicted by the ASM2. However, the drop in nitrogen and COD removal cannot be ascribed to dilution, and was hence not predicted by the ASM2. This event illustrates the vulnerability of the N-removal sub-process (i.e. nitrification/denitrification) to occasional presence of toxic substances, and the relative time frame needed for the BNR processes to recover. It also illustrates an inherent disadvantage of using real sewage.

While the N- and P-removal were relatively well predicted by the ASM2, COD removal seemed to be underestimated systematically. Although the Duffel wastewater is mainly domestic, it also contains the effluent of an ice cream factory. Because of this, there may have been a larger than typical fraction of readily biodegradable organic matter, leading to a somewhat higher COD removal. Note that this may also explain the excellent P-removal.

Sludge settling

Bulking sludge is a major concern in waste water treatment, and can also disturb laboratory tests. It may lead to a severe reduction in unit performance as sludge is lost in the effluent and the system becomes operationally unstable. The sludge settling properties were compared between the synthetic medium and real sewage (Figure 4.7).

A different SVI trend was observed for the two feeds. The SVI of sludge fed with real sewage only rose slightly during the test (from ca. 140 to 180 mL/g). The SVI of the sludge fed with synthetic medium remained stable within a similar range for ca. 1 month, but afterwards it deteriorated to ca. 270 mL/g . This caused no operating problems, but it suggested that the medium could still be improved to prevent sludge bulking. It should be mentioned here that full scale BNR plants have been reported to suffer frequently from bulking and/or foaming sludge (Casey *et al.*, 1992; Urbain *et al.*, 1993). Randall *et al.* (1992) quoted an SVI of 120 mL/g as typical for a well functioning full-scale system with N and P removal.

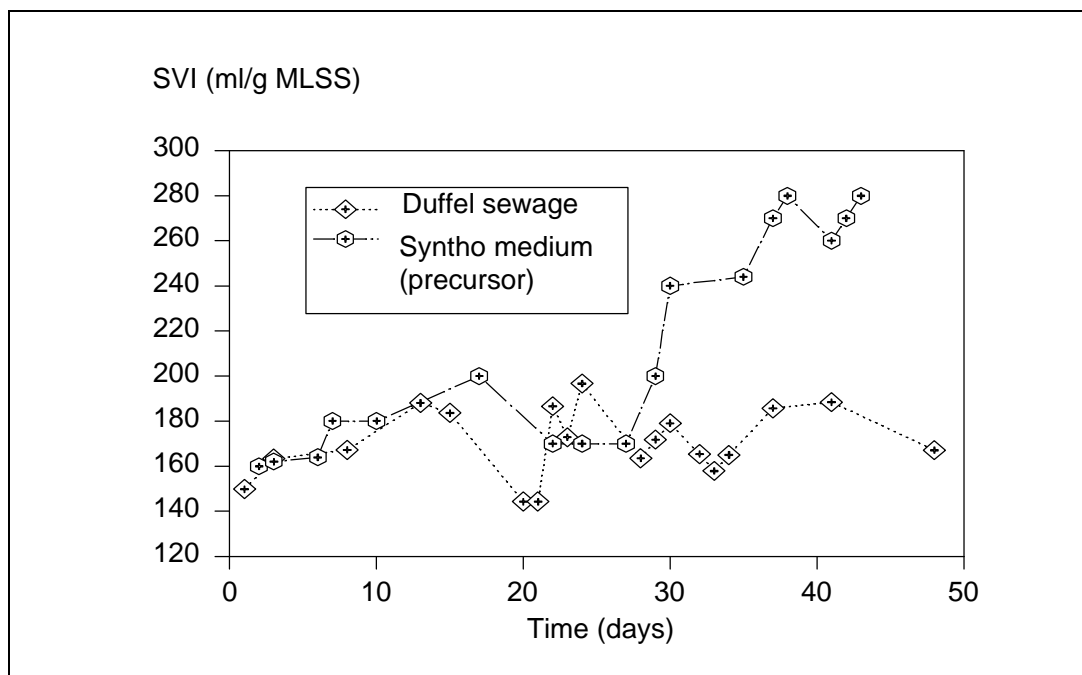


Figure 4.7. SVI - Behr unit Run #2 (Syntho precursor medium and Duffel sewage)

Reformulated Syntho Medium

The above considerations led to the reformulation of the *Syntho* medium to its final composition, described in section 3. The COD:N:P ratio was changed to 100:7:2 (instead of 100:9:2). The acetate level was increased, to drive the BNR processes. Furthermore, to stimulate floc formation and increase floc density, dried yeast was replaced by lyophilized activated sludge, and diatomaceous earth was added.

Later experiments using the *Syntho* medium (which are not described in this thesis) indicated an improvement of P-elimination ($79.6\% \pm 17.5\%$ in a Behr unit, $77.1\% \pm 8.8\%$ in a UCT unit) and sludge settling (SVI in a UCT unit of 173 mL/g on average, over a 40 day test period).

5.2. LAS Removal in the Test Units

Primary removal of LAS was measured in the three units. Experimental conditions are given in Table 4.1 (Run #4 for the Behr unit, using the *Syntho* medium).

A parent LAS removal efficiency of $99.4\% \pm 0.1\%$ was found for the Behr-unit. For the CAS-UCT unit, the primary LAS removal was also found to be 99.4% (single measurement). The OECD 303A CAS unit was observed to have $98.6\% \pm 0.8\%$ parent LAS removal.

The units with BNR performed better than the standard CAS test in terms of LAS removal. This is thought to be caused in first instance by the longer HRT and SRT. It needs to be assessed further whether the presence of different redox environments, and the possibility of additional biochemical pathways, may have contributed in any way to the higher chemical removal efficiencies.

6. Conclusions

Both the CAS-UCT and the Behr-unit are easy to handle laboratory scale BNR simulation systems, which could be included in standard testing, complementary to the CAS system. They can be operated on *Syntho* or on real domestic wastewater (tested for the Behr-unit) in a stable way with minimal extra costs or effort compared to the standard CAS system.

Under the investigated test conditions, a similar degree of COD, N and P removal was achieved with both BNR units. The Behr-unit was observed to be a simple and reliable system, providing all basic BNR functionality; the CAS-UCT unit is in principle a more versatile tool, but it is also more complex. The experimental nutrient removal results corresponded well with ASM2 predictions for both units.

A dissatisfaction with the OECD synthetic sewage and the need for a synthetic medium which supports BNR in lab-scale units resulted in the development of a more realistic synthetic feed for use in standard WWTP simulation tests. Based on a literature review, a new medium (*Syntho*) was developed, consisting of a blackwater (sanitary) and a greywater (household) fraction next to 1/10 real sewage. A respiration test indicated that the new medium is a reasonable approximation of real domestic sewage. Although sludge settling was superior when real sewage was used, the SVI with the synthetic sewage remained sufficiently low to permit a stable test duration of 1 to 3 months.

The longer HRT and SRT applied in the BNR systems led to a reduction in effluent levels of biodegradable chemicals like the surfactant Linear Alkylbenzene Sulphonate (LAS) compared to the CAS test. The role of the system's different redox zones in the overall removal requires further investigation for various types of chemicals.

Chapter 5

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Adaptation of the SimpleTreat Chemical Fate Model to Single-Sludge Biological Nutrient Removal Waste Water Treatment Plants

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Chapter 5

Adaptation of the SimpleTreat Chemical Fate Model to Single-Sludge Biological Nutrient Removal Waste Water Treatment Plants

Many recent developments in municipal waste water treatment technology are directed towards biological nutrient removal (see also chapter 4 of this thesis). Most chemical fate models which are used to predict the behavior of individual chemicals in waste water treatment plants (WWTPs), have until now not incorporated this aspect. In this chapter, two modifications to the steady-state non-equilibrium *SimpleTreat* modeling concept (Struijs *et al.*, 1991a, 1991b; Struijs, 1996) are presented. These focus on an improved description of sludge recycling, and on the presence of different redox zones in the biological reactor (aerobic, anoxic, anaerobic). The updated models were applied to three different WWTP designs, and simulation results were compared to measured values for the surfactant LAS.

1. Introduction

For environmental risk assessment of chemicals, accurate exposure predictions are required (e.g., ECETOC, 1994b). An important factor which determines aquatic exposure to ‘down-the-drain’ chemicals is their degree of elimination in WWTPs. To predict such removal efficiencies, several chemical fate models have been developed during the last decades. Some of these models apply a statistical approach (e.g., Melcer *et al.*, 1989a), but most are mechanistic. The latter can be divided into two groups: steady-state (stationary) models, and dynamic models.

Dynamic models are used to predict the effect of non-steady-state influent concentrations on the plant’s effluent. Some of these models were developed specifically for chemical fate prediction (e.g., Melcer *et al.*, 1994; O’Brien & Teather, 1995; Temmink *et al.*, 1996, Tularak, 1998). Others were adapted from general purpose activated sludge models, such as the IAWPRC (currently IAWQ) Activated Sludge Model N° 1 (Henze *et al.*, 1987). Examples of the latter are given in Siegrist *et al.* (1989) and Jacobsen *et al.* (1996).

The available steady-state models are either black box models (using only the percentage removal for each specific chemical) (e.g., Rapaport, 1988), or conceptual models. The latter differentiate between the different chemical removal processes: volatilization and stripping, sorption to sludge, and (biological) degradation. Two main types of conceptual models can be distinguished:

- One type focuses on the mass-balancing of individual waste water treatment sub-processes. This was applied by e.g. Blackburn & Troxler (1984), Namkung & Rittmann (1987), Melcer *et al.* (1989b), Govind *et al.* (1991), Cowan *et al.*, (1993b), Monteith *et al.* (1993), ECETOC (1994c), Melcer *et al.* (1994), van Wijk *et al.* (1996), McAvoy *et al.*, (1997), Lee *et al.* (1998). In a simplified way, this approach was also used by Birch (1991), only considering chemical removal via biodegradation.
- In a second type, “diffusive” chemical transport is driven by the non-equilibrium between chemical fractions in different phases. Fugacity calculations (after Mackay & Paterson, 1981 and 1982) are used for this purpose. This approach was applied by e.g. Struijs *et al.* (1991a, 1991b), Clark *et al.* (1995), and Struijs (1996).

The existing steady-state WWTP fate models are typically based on ‘standard’ plant configurations, designed in first instance for carbon removal. However, nowadays biological nutrient removal has become an important aspect in municipal waste water treatment and water quality management (e.g., CEC, 1991). Many WWTPs in Europe are upgraded to include nitrogen and phosphorus removal, or will be in the near future. Hence, it is warranted to include the effect of nutrient removal processes on chemical fate.

In this chapter, a modification of the *SimpleTreat* model is presented, which describes chemical fate (as parent removal) in typical single-sludge biological nutrient removal WWTPs. In the modified model, an improved description of sludge recycling is used, and the presence of different redox zones is taken into account. Additionally, the calculation of several plant design and operation parameters was revised.

2. Process Description

2.1. Activated Sludge Plant Configuration

2.1.1. General

In most of the above mentioned steady-state activated sludge models, the modeled plant consists of a primary settler, a completely mixed aeration tank, and a secondary settler. Some models allow to disregard the primary settler (e.g., Struijs, 1996). Others allow to consider several aeration basins in series (e.g., Melcer *et al.*, 1994). In the model presented here, the primary settler is considered a separate module, and was not included as a part of the activated sludge model itself. A scheme of this configuration is given in Figure 5.1.

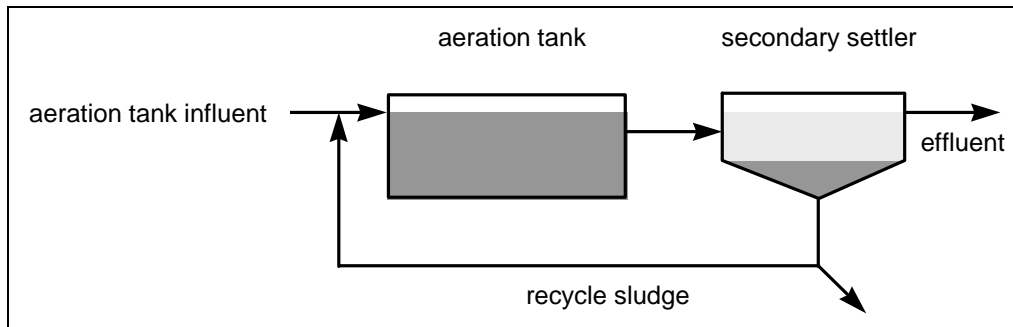


Figure 5.1. Activated sludge WWTP configuration

2.1.2. Nutrient Removal Plants

For development of the fate model, the University of Capetown (UCT) reactor design was chosen as a process template (Ekama *et al.*, 1984). A UCT plant consists of three activated sludge tanks (or zones) in sequence: anaerobic, anoxic and aerobic (Figure 5.2). Sludge is recycled internally between the aerobic and the anoxic tank, and between the anoxic and anaerobic tank. Settled sludge is recycled to the anoxic tank.

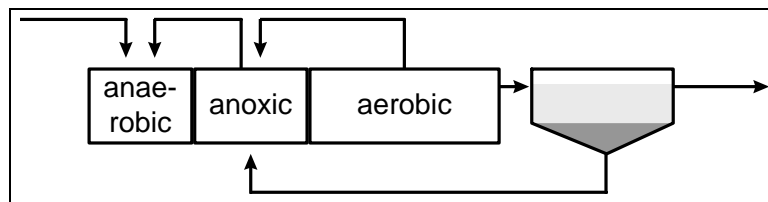


Figure 5.2. UCT process - WWTP configuration

Many other single-sludge biological nutrient removal plant designs are basically identical to this scheme (Henze, 1996), or can be simplified to fit into it. Note that sequential batch reactors (SBR) can also be represented in this framework, using hypothetical volumes derived from the fraction of time taken by the different redox stages.

2.2. Aeration Tank Processes

In the aeration basin, the considered removal processes are volatilization / stripping and degradation. Sorption onto sludge solids is also taken into account. Some models only take into account stripping, while others consider both stripping and volatilization. Stripping is induced by the aeration process and has effect on the entire tank, while volatilization occurs only at the surface of the tank. Different model equations are required for stripping by surface aeration versus stripping by submerged (bubble) aeration. None of the existing models take into account chemical elimination out of the aeration tank through the formation of aerosols. However, as bacteria and viruses from the activated sludge can be found in aerosols above the plants (Carducci *et al.*, 1995; Sawyer *et al.*, 1996), specific chemicals may also be present in them. An overview of the aeration tank processes is shown in Figure 5.3.

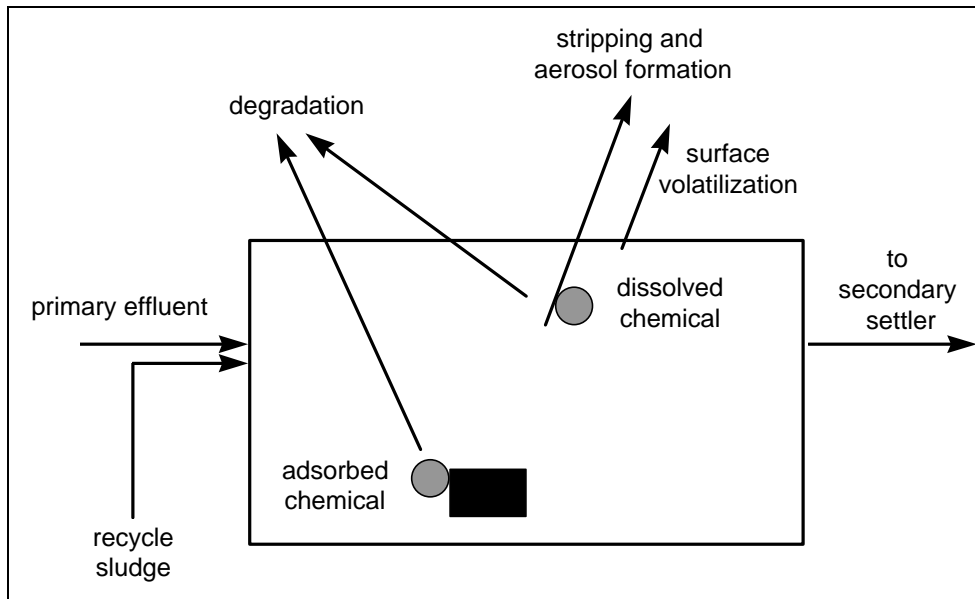


Figure 5.3. Aeration tank chemical fate processes (overview)

2.3. Secondary Settler Processes

In chemical fate models, secondary settlers are typically described by a fixed solids removal percentage. The chemical mass balance includes settling of the adsorbed fraction and surface volatilization of the dissolved fraction (Figure 5.4). Generally, biodegradation processes in the settler are disregarded. It has to be noted that a fraction of the secondary sludge is not recycled but wasted, in order to control the activated sludge solids level and sludge age. Melcer *et al.* (1994) also consider stripping losses at the secondary settler’s weir (after Pincince, 1991).

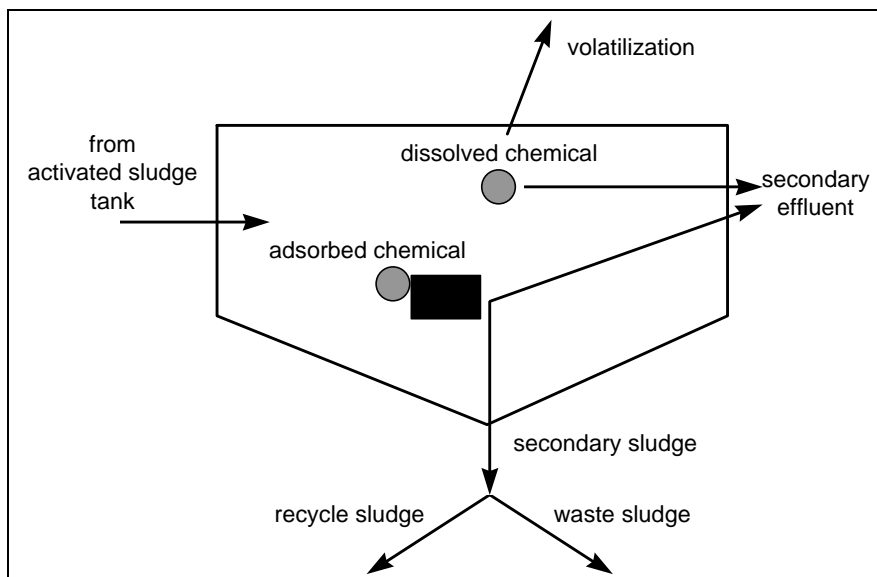


Figure 5.4. Secondary settler chemical fate processes (overview)

3. Modeling Approach

3.1. Model Selection

The current state of the art in steady-state WWTP fate models is mainly represented by *TOXCHEM* (Melcer *et al.*, 1994), *AS-TREAT* (McAvoy *et al.*, 1997) and the model by Lee *et al.* (1998), and *SimpleTreat* (Struijs *et al.*, 1991a, 1991b; Struijs, 1996). The latter was chosen as a starting point for the development of a nutrient removal plant model, because of the inherent flexibility of its fugacity approach, and because of its regulatory acceptance within European Union risk assessment (e.g., Vermeire *et al.*, 1997).

3.2. The *SimpleTreat* Concept

The *SimpleTreat* model was developed by Struijs *et al.* in 1991, mainly for regulatory purposes. Several modifications and improvements to the model and its assumptions were suggested, e.g. by Cowan *et al.* (1993), Mikkelsen *et al.* (1996), Jacobsen *et al.*, (1996). Based on these comments, a revised version was designed by Struijs (1996).

In the *SimpleTreat* approach, a WWTP is represented by a number of compartments (boxes). Each chemical phase (dissolved, sorbed) in each reactor is assigned one box. A standard carbon removal plant (without considering primary settling) consists of 6 boxes: air above the WWTP, dissolved and sorbed chemical in the activated sludge tank, dissolved and sorbed chemical in the settler, and sorbed chemical in the settled sludge. Mass balancing for all boxes is performed using the *SIMPLEBOX* method (van de Meent, 1993). The mass balance for each box *i* is:

mass change = - elimination - outflux to other boxes - outflux out of the system
+ influx from other boxes + influx into the system

or:

$$V_i \cdot \frac{dC_i}{dt} = -k_i \cdot C_i \cdot V_i - \sum_{j=1}^6 (ADV_{i,j} + XCH_{i,j}) \cdot C_i - \Phi_{out}^i + \sum_{j=1}^6 (ADV_{j,i} + XCH_{j,i}) \cdot C_j + \Phi_{in}^i \quad [5.1]$$

At steady state, continuous and constant influxes into and outfluxes out of the system are assumed. The change in concentration dC_i/dt is zero. Hence, the mass balance equation for box *i* can be written as:

$$k_i \cdot C_i \cdot V_i + \sum_{j=1}^6 (ADV_{i,j} + XCH_{i,j}) \cdot C_i + \Phi_{out}^i - \sum_{j=1}^6 (ADV_{j,i} + XCH_{j,i}) \cdot C_j = \Phi_{in}^i \quad [5.2]$$

The chemical fluxes Φ_{in} and Φ_{out} only relate to inputs and outputs at the complete WWTP level. Transport to or exchange with other boxes in the WWTP is described by the advection (*ADV*) and exchange (*XCH*) terms. Both are expressed as media volume flows, where the medium can be air, water or solids. The exchange terms are calculated from chemical diffusion coefficients between boxes ($D_{i,j}$) and the chemical fugacity in each box (Z_i) (after Mackay & Paterson, 1982).

The chemical fluxes out of the system (out of each box i) can be expressed as

$$\Phi_{out}^i = ADV_{i,0} \cdot C_i \quad [5.3]$$

Hence, using matrix notation, the set of all 6 mass balances can be written as:

$$\begin{bmatrix} c_{1,1} & c_{1,2} & \cdots & c_{1,6} \\ c_{2,1} & c_{2,2} & \cdots & c_{2,6} \\ \vdots & \vdots & \ddots & \vdots \\ c_{6,1} & c_{6,2} & \cdots & c_{6,6} \end{bmatrix} \cdot \begin{bmatrix} C_1 \\ C_2 \\ \vdots \\ C_6 \end{bmatrix} = \begin{bmatrix} \Phi_{in}^1 \\ \Phi_{in}^2 \\ \vdots \\ \Phi_{in}^6 \end{bmatrix} \quad \text{where} \quad \begin{cases} c_{i,i} = k_i \cdot V_i + \sum_{j=1}^6 (ADV_{i,j} + XCH_{i,j}) + ADV_{i,0} \\ c_{i,j} = -(ADV_{j,i} + XCH_{j,i}) \end{cases} \quad [5.4]$$

$$\text{or: } \overline{COEF} \cdot \overline{C} = \overline{PHI} \quad [5.5]$$

The concentrations in each box can now be obtained by solving this set of equations through matrix inversion:

$$\overline{C} = (\overline{COEF})^{-1} \cdot \overline{PHI} \quad [5.6]$$

4. Model Description

Two models were developed. The first model is very similar to the original *SimpleTreat* 6-box model. The main modifications are related to sludge recycling and to a correction of the activated sludge tank stripping and degradation rate coefficient, based on the presence of different redox zones. The second model is a direct representation of the UCT process, making use of 3 functionally different activated sludge tanks. Here, a 10-box representation was required.

The model equations were taken from *SimpleTreat* 3.0 (Struijs, 1996), but were modified where needed.

4.1. Model Structure

4.1.1. 6-box Model

The 6-box scheme was derived directly from *SimpleTreat* (Figure 5.5). The boxes were re-numbered, as no primary settler was modeled. Advective flows were added / modified to obtain a better description of sludge recycling. In this model description, internal sludge recycles (i.e. between the different redox zones) can not be taken into account.

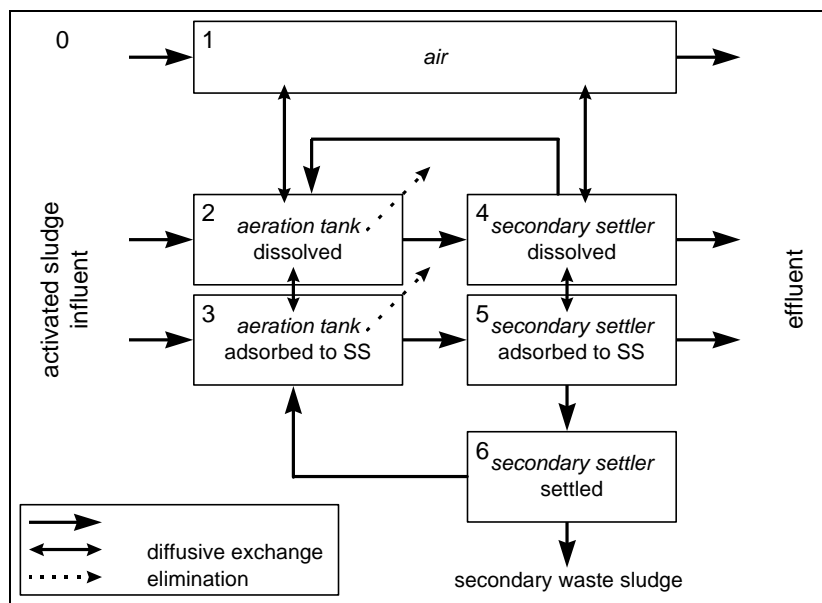


Figure 5.5. Nutrient removal WWTP fate model - 6-box

4.1.2. 10-box Model

The 10-box model scheme is shown in Figure 5.6. Each of the three activated tanks was represented by 2 boxes (dissolved and sorbed phase). All possible sludge recycles (from the settler as well as internal recycles) were implemented. Note that in practice only a limited number of all possible sludge recycles are to be used (as shown in Figure 5.6 for the standard UCT design).

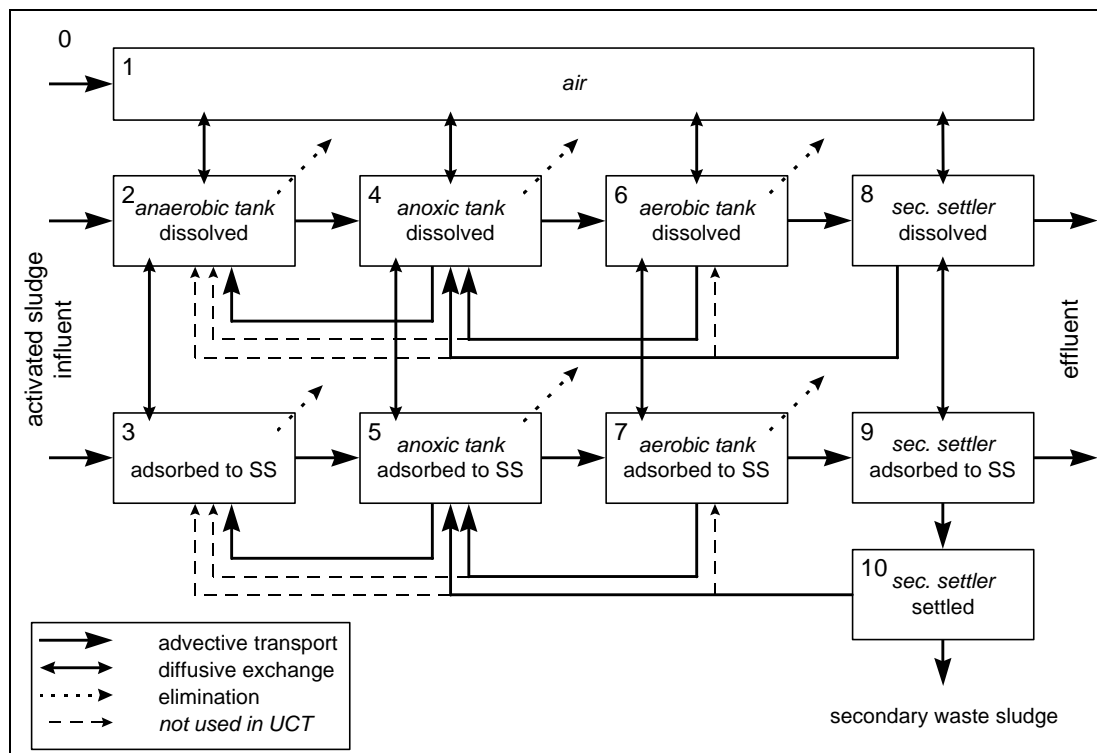


Figure 5.6. Nutrient removal WWTP fate model - 10-box

4.2. Influent Calculation

The influent consist of a dissolved and an adsorbed chemical fraction. The influent enters the treatment system simultaneously into box 2 and box 3 (for both the 6-box and the 10-box model). Other boxes receive no influent flux. If no primary settler is present, the dissolved and sorbed fraction of the influent are assumed to be in complete equilibrium (cf. Struijs, 1996). If a primary settler model is connected in front of the activated sludge model, the dissolved/sorbed fractionation of the settler model is used to calculate the secondary influent partitioning.

4.3. Advective Transport

4.3.1. 6-box Model

In *SimpleTreat*, only the solids phase of the recycled sludge is considered. Moreover, different sludge recycle flows and recycling ratios cannot be taken into account. As in nutrient removal processes sludge recycling is crucial, a more realistic description of these recycles was included into the model. It was assumed that the interstitial water phase of the settled sludge is identical to the main water phase in the settler (box 4). Hence, the water phase of the sludge recycle could be represented by an advective transport of settler water to the activated sludge tank ($ADV_{4,2}$). The activated sludge tank's flow balance was corrected for this additional inflow, by modifying the term $ADV_{2,4}$. To take into account the actual recycle flow of the solids phase, the $ADV_{3,5}$ term was also updated.

Air advection

$$\text{- into / out of area above WWTP: } ADV_{0,1} = ADV_{1,0} = h_{air} \cdot v_{wind} \cdot \sqrt{A_{act.sludge} + A_{sec}} \quad [5.7]$$

Water volume flow rate

$$\text{- WWTP in/outflow: } ADV_{0,2} = ADV_{4,0} = Q \quad [5.8]$$

$$\text{- sludge propagation: } ADV_{2,4} = Q \cdot (1 + R) \quad [5.9]$$

$$\text{- settled sludge recycle: } ADV_{4,2} = Q \cdot R \quad [5.10]$$

An additional advective flow term ($ADV_{2,1}$) may be added to describe the transport of water droplets out of the activated sludge tank through aerosol formation.

Solids volume flow rate

- WWTP in/outflow:
$$ADV_{0,3} = Q \cdot \frac{SS_{sewage}}{10^6 \cdot r_{solids}^{sewage}} \quad [5.11]$$

$$ADV_{5,0} = Q \cdot \frac{SS_{effluent}}{10^6 \cdot r_{solids}^{ML}} \quad [5.12]$$

- settled sludge recycle:
$$ADV_{6,3} = ADV_{5,6} - ADV_{6,0} \quad [5.13]$$

- sludge propagation:
$$ADV_{3,5} = Q \cdot (1 + R) \cdot \frac{SS_{ML}}{10^6 \cdot r_{solids}^{ML}} \quad [5.14]$$

- sludge settling:
$$ADV_{5,6} = ADV_{3,5} - ADV_{5,0} \quad [5.15]$$

- sludge waste:
$$ADV_{6,0} = \frac{\Phi_{surplus}^{SS}}{10^6 \cdot r_{solids}^{ML}} \quad [5.16]$$

4.3.2. 10-box Model

Air advection

- into / out of area above WWTP:
$$ADV_{0,1} = ADV_{1,0} = h_{air} \cdot v_{wind} \cdot \sqrt{A_{act.sludge} + A_{sec}} \quad [5.17]$$

Water volume flow rate

- WWTP in/outflow:
$$ADV_{0,2} = ADV_{8,0} = Q \quad [5.18]$$

- internal sludge recycles:
$$ADV_{4,2} = Q \cdot R_{anox,anaer} \quad [5.19]$$

$$ADV_{6,2} = Q \cdot R_{aer,anaer} \quad [5.20]$$

$$ADV_{6,4} = Q \cdot R_{aer,anox} \quad [5.21]$$

- settled sludge recycles:
$$ADV_{8,2} = Q \cdot R_{S,anaer} \quad [5.22]$$

$$ADV_{8,4} = Q \cdot R_{S,anox} \quad [5.23]$$

$$ADV_{8,6} = Q \cdot R_{S,aer} \quad [5.24]$$

- sludge propagation:
$$ADV_{2,4} = Q \cdot (1 + R_{S,anaer} + R_{aer,anaer} + R_{anox,anaer}) \quad [5.25]$$

$$\begin{aligned} ADV_{4,6} &= Q \cdot (1 + R_{S,anaer} + R_{aer,anaer} + R_{anox,anaer}) \\ &\quad + Q \cdot (R_{S,anox} + R_{aer,anox}) - Q \cdot R_{anox,anaer} \\ &= Q \cdot (1 + R_{S,anaer} + R_{S,anox} + R_{aer,anaer} + R_{aer,anox}) \end{aligned} \quad [5.26]$$

$$\begin{aligned}
 Q_{10,8} &= Q \cdot (R_{S,anaer} + R_{S,anoxic} + R_{S,aer}) + Q \cdot (R_{S,anaer} + R_{S,anoxic}) \\
 &= Q \cdot (1 + R_{S,anaer} + R_{S,anoxic} + R_{S,aer})
 \end{aligned} \quad [5.28]$$

Solids volume flow rate

- WWTP in/outflow:
$$Q_{10,3} = Q \cdot \frac{SS}{10^6 \cdot r_{solids}} \quad [5.29]$$

$$ADV_{9,3} = \frac{SS_{effluent}}{10^6 \cdot r_{solids}} \quad [5.29]$$

- internal sludge recycles:
$$ADV_{5,3} = ADV_{9,2} \cdot \frac{SS_{anoxic}}{10^6 \cdot r_{solids}} \quad [5.30]$$

$$ADV_{7,3} = ADV_{6,2} \cdot \frac{SS_{aerobic}}{10^6 \cdot r_{solids}} \quad [5.31]$$

$$ADV_{7,5} = ADV_{6,4} \cdot \frac{SS_{aerobic}}{10^6 \cdot r_{solids}} \quad [5.32]$$

- settled sludge recycles:
$$ADV_{10,3} = R_{S,anaer} \cdot Z \quad [5.33]$$

$$ADV_{10,5} = R_{S,anoxic} \cdot Z \quad [5.34]$$

$$ADV_{10,7} = R_{S,aer} \cdot Z \quad [5.35]$$

$$\text{with } Z = \frac{ADV_{9,10} - ADV_{10,0}}{R_{S,anaerobic} + R_{S,anoxic} + R_{S,aerobic}}$$

- sludge propagation:
$$ADV_{3,5} = ADV_{2,4} \cdot \frac{SS_{anaerobic}}{10^6 \cdot r_{solids}} \quad [5.36]$$

$$ADV_{5,7} = ADV_{4,6} \cdot \frac{SS_{anoxic}}{10^6 \cdot r_{solids}} \quad [5.37]$$

$$ADV_{7,9} = ADV_{6,8} \cdot \frac{SS_{aerobic}}{10^6 \cdot r_{solids}} \quad [5.38]$$

- sludge settling:
$$ADV_{9,10} = ADV_{7,9} - ADV_{9,0} \quad [5.39]$$

- sludge waste:
$$ADV_{10,0} = \frac{\Phi_{surplus}^{SS}}{10^6 \cdot r_{solids}} \quad [5.40]$$

4.4. Diffusive Exchange

4.4.1. Calculation of Fugacities and Box Volumes

For the calculation of the diffusive exchanges, the fugacity approach is applied. The fugacities of the different media have to be known, as well as the volumes of the different compartments.

Fugacities

Struijs *et al.* (1991a, 1991b) derived expressions for fugacity calculations from Mackay and Paterson (1982):

$$\text{- air:} \quad Z_{air} = \frac{1}{R \cdot (t_{air} + 273)} \quad [5.41]$$

$$\text{- water:} \quad Z_{water} = \frac{1}{H} \quad [5.42]$$

$$\text{- mixed liquor (act. sludge):} \quad Z_{ML} = \frac{K_d^{ML} \cdot r_{solids}^{ML}}{H} \quad [5.43]$$

Box volumes (6-box model)

$$\text{- air above the WWTP:} \quad V_1 = (A_{act.sludge} + A_{sec}) \cdot h_{air} \quad [5.44]$$

$$\text{- activated sludge tank (water phase):} \quad V_2 = V_{act.sludge} \quad [5.45]$$

$$\text{- activated sludge tank (solids phase):} \quad V_3 = V_{act.sludge} \cdot \frac{SS_{ML}}{10^6 \cdot r_{solids}^{ML}} \quad [5.46]$$

$$\text{- secondary settler (water phase):} \quad V_4 = V_{sec} \quad [5.47]$$

$$\text{- secondary settler (solids phase):} \quad V_5 = V_{sec} \cdot \frac{(1 - R_{sec}^{SS}) \cdot SS_{ML}}{10^6 \cdot r_{solids}^{ML}} \quad [5.48]$$

The volume of compartment 6 (secondary sludge thickening layer) need not be known by the model.

Box volumes (10-box model)

Similar calculations as in the 6-box model are used for the 10-box model volumes. Obviously the box numbering is different.

$$\text{- air above the WWTP:} \quad V_1 = (A_{act.sludge} + A_{sec}) \cdot h_{air} \quad [5.49]$$

- activated sludge tank (water phase): $V_2 = V_{act.sludge} \cdot f_{anaerobic}$ [5.50]

$$V_4 = V_{act.sludge} \cdot f_{anoxic} \quad [5.51]$$

$$V_6 = V_{act.sludge} \cdot f_{aerobic} \quad [5.52]$$

- activated sludge tank (solids phase): $V_3 = V_{act.sludge} \cdot f_{anaerobic} \cdot \frac{SS_{anaerobic}}{10^6 \cdot r_{solids}^{ML}}$ [5.53]

$$V_5 = V_{act.sludge} \cdot f_{anoxic} \cdot \frac{SS_{anoxic}}{10^6 \cdot r_{solids}^{ML}} \quad [5.54]$$

$$V_7 = V_{act.sludge} \cdot f_{aerobic} \cdot \frac{SS_{aerobic}}{10^6 \cdot r_{solids}^{ML}} \quad [5.55]$$

- secondary settler (water phase): $V_8 = V_{sec}$ [5.56]

- secondary settler (solids phase): $V_9 = V_{sec} \cdot \frac{(1 - R_{sec}^{SS}) \cdot SS_{aerobic}}{10^6 \cdot r_{solids}^{ML}}$ [5.57]

As in the 6-box model, the volume of the secondary sludge thickening layer (compartment 10) is not required.

4.4.2. Diffusive Chemical Exchange

The diffusion coefficient for chemical exchange between two boxes i and j is expressed in terms of first order kinetics, after Mackay and Paterson (1982):

$$D_{i,j} = D_{j,i} = \frac{k_{diff}}{\frac{1}{V_i \cdot Z_i} + \frac{1}{V_j \cdot Z_j}} \quad [5.58]$$

Then, the exchange from box i to j , expressed as medium volume flow rate, is calculated as:

$$XCH_{i,j} = \frac{D_{i,j}}{Z_i} \quad [5.59]$$

Sludge / water exchange

Between the dissolved and the adsorbed phases in the activated sludge tank and in the secondary settler, non-equilibrium partitioning is described, in terms of first order (de-)sorption kinetics (cf. [5.58]):

- activated sludge tank (mixed liquor): [5.60]
 (additional terms for 10-box model between square brackets)

$$D_{2,3}[D_{4,5}, D_{6,7}] = D_{3,2}[D_{5,4}, D_{7,6}] = \frac{k_{act.sludge}^{sorb}}{\frac{1}{V_2[V_4, V_6] \cdot Z_{water}} + \frac{1}{V_3[V_5, V_7] \cdot Z_{ML}}}$$

and $XCH_{2,3}[XCH_{4,5}, XCH_{6,7}] = \frac{D_{2,3}[D_{4,5}, D_{6,7}]}{Z_{water}}$

$$XCH_{3,2}[XCH_{5,4}, XCH_{7,6}] = \frac{D_{3,2}[D_{5,4}, D_{7,6}]}{Z_{ML}}$$

- secondary settler: [5.61]
 (alternative terms for 10-box model between brackets)

$$D_{4,5}(D_{8,9}) = D_{5,4}(D_{9,8}) = \frac{k_{sec}^{sorb}}{\frac{1}{V_4(V_8) \cdot Z_{water}} + \frac{1}{V_5(V_9) \cdot Z_{ML}}}$$

and $XCH_{4,5}(XCH_{8,9}) = \frac{D_{4,5}(D_{8,9})}{Z_{water}}$

$$XCH_{5,4}(XCH_{9,8}) = \frac{D_{5,4}(D_{9,8})}{Z_{ML}}$$

The applied kinetic rate coefficients for sorption / desorption are given in Table 5.1 (taken from Struijs, 1996).

Table 5.1. Sorption/desorption kinetic rate coefficients

		Half-life (s)	1 st order rate coefficient (s ⁻¹)
Activated sludge tank	$k_{act.sludge}^{sorb}$	360	$1.925 \cdot 10^{-3}$
Secondary settler	k_{sec}^{sorb}	3600	$192.5 \cdot 10^{-6}$

Air / water exchange

Activated sludge tank

For the activated sludge tank(s), two types of air-water exchange are considered: surface volatilization (without the impact of aeration) and stripping (due to aeration). Stripping can be due to either surface aeration (surface impellers) or (submerged) bubble aeration. The modeling approach is based on the two-layer model (Liss and Slater, 1974; Mackay and Leinonen, 1975).

6-box model

Only the aerobic (fraction of the) activated sludge tank is aerated. Hence a correction factor for the tank volume which undergoes stripping is taken into account. The diffusion coefficients and exchange terms for air / water exchange in the activated sludge tank are calculated as shown below in [5.62]. The surface volatilization term (right) was not changed compared to *SimpleTreat*. In the stripping term (left), both the tank volume and the tank surface area were corrected for the aerobic fraction, finally leading to the aerobic fraction term in the numerator.

$$\begin{aligned}
 D_{1,2} = D_{2,1} &= \frac{k_{str}}{\frac{1}{V_1 \cdot \frac{(f_{aerobic} \cdot A_{act.sludge})}{A_{total}} \cdot Z_{air}} + \frac{1}{(f_{aerobic} \cdot V_2) \cdot Z_{water}}} + \frac{k_v}{\frac{1}{V_1 \cdot \frac{A_{act.sludge}}{A_{total}} \cdot Z_{air}} + \frac{1}{V_2 \cdot Z_{water}}} \\
 &= \frac{f_{aerobic} \cdot k_{str} + k_v}{\frac{1}{V_1 \cdot \frac{A_{act.sludge}}{A_{total}} \cdot Z_{air}} + \frac{1}{V_2 \cdot Z_{water}}}
 \end{aligned} \tag{5.62}$$

and

$$\begin{aligned}
 XCH_{1,2} &= \frac{D_{1,2}}{Z_{air}} \\
 XCH_{2,1} &= \frac{D_{2,1}}{Z_{water}}
 \end{aligned}$$

Like in Struijs (1996), the surface volatilization rate coefficient k_v is estimated as:

$$k_v = \frac{\frac{1}{h_{air}} + \frac{K_H}{h_{act.sludge}}}{\frac{1}{K_{air}} + \frac{K_H}{K_{water}}} \tag{5.63}$$

Compared to Struijs (1996), two modifications were made to the calculation of the stripping rate coefficient k_{str} . First, the total activated sludge tank volume was replaced by the aerobic volume. Second, the calculation of oxygen requirement was adjusted (see below, section 4.6).

The calculation of the stripping rate coefficient depends on the type of aeration: surface aeration versus bubble aeration:

- surface aeration (after Roberts *et al.*, 1984; Munz & Roberts, 1989):

$$k_{str}^{surface} = \Psi \cdot GPC \cdot \frac{OxReq}{3600 \cdot (f_{aerobic} \cdot HRT_{act.sludge}) \cdot (DO_{sat} - DO)} \quad [5.64]$$

$$\left\{ \begin{array}{l} H \geq 250 \frac{Pa}{m^3 mol} \Rightarrow GPC = 1 \\ H < 250 \frac{Pa}{m^3 mol} \Rightarrow GPC = \frac{\frac{k_G a}{k_L a} \cdot K_H}{\frac{k_G a}{k_L a} \cdot K_H + 1} \cong \frac{40 \cdot K_H}{40 \cdot K_H + 1} \end{array} \right.$$

- bubble aeration (after Hsieh *et al.*, 1993):

$$k_{str}^{bubble} = 0.89 \cdot 10^{-3} \cdot \frac{OxReq}{f_{aerobic} \cdot V_{act.sludge}} \cdot H^{1.04} \quad [5.65]$$

It has to be noted that the Oxygen Requirement (*OxReq*) concept (as for surface aeration) is used in the bubble aeration stripping model, rather than the per capita bubble aeration rate (G^{cap}) which is used in *SimpleTreat*.

10-box model

The calculation of the diffusion coefficients and exchange terms for air / water exchange in the different activated sludge tanks are given below. Surface volatilization is assumed to occur in all tanks, while stripping is assumed to occur only in the aerobic tank (equation [5.66]). The volatilization rate coefficients are calculated by the standard *SimpleTreat* method (as shown in equation [5.63]). The calculation of the stripping rate coefficient in the aerobic tank is identical to that in the 6-box model (equations [5.64] and [5.65]), also taking into account the adjusted oxygen requirement (see below, section 4.6).

$$D_{1,2/1,4} = D_{2,1/4,1} = \frac{k_v^{2/4}}{\frac{1}{V_1 \cdot \frac{f_{anaerobic / anoxic} \cdot A_{act.sludge}}{A_{total}} \cdot Z_{air}} + \frac{1}{V_{2/4} \cdot Z_{water}}} \quad [5.66]$$

$$D_{1,6} = D_{6,1} = \frac{k_{str} + k_v^6}{\frac{1}{V_1 \cdot \frac{f_{aerobic} \cdot A_{act.sludge}}{A_{total}} \cdot Z_{air}} + \frac{1}{V_6 \cdot Z_{water}}}$$

$$\text{and } XCH_{1,2/1,4/1,6} = \frac{D_{1,2/1,4/1,6}}{Z_{air}} \quad XCH_{2,1/4,1/6,1} = \frac{D_{2,1/4,1/6,1}}{Z_{water}}$$

Secondary settler

For the secondary settler, only surface volatilization was taken into account - stripping at the weir was not considered. The expressions for the transfer coefficients $D_{i,j}$ were taken from Mackay *et al.* (1985). It can be shown that these expressions are equivalent to the 'standard' diffusive exchange equations (based on [5.58]), which are applied for the solids/water exchange, and for volatilization and stripping from the aerator. Note that in equation [5.67] below, alternative terms for the 10-box model are given between brackets.

$$D_{1,4}(D_{1,8}) = D_{4,1}(D_{8,1}) = \frac{A_{sec}}{\frac{1}{K_{air} \cdot Z_{air}} + \frac{1}{K_{water} \cdot Z_{water}}} \quad [5.67]$$

$$\text{and} \quad XCH_{1,4}(XCH_{1,8}) = \frac{D_{1,4}(D_{1,8})}{Z_{air}} \quad XCH_{4,1}(XCH_{8,1}) = \frac{D_{4,1}(D_{8,1})}{Z_{water}}$$

4.5. Chemical Degradation in the Activated Sludge Tank

4.5.1. (Bio)degradation Models

For the description of chemical degradation, several fundamentally different approaches have been proposed. At this moment, a wide scientific consensus has not yet been reached on this topic. The major approaches are given below.

(Pseudo) First-order degradation - dissolved phase only

This method assumes that only the freely dissolved chemical is subject to degradation. The chemical fraction which is sorbed to (or otherwise associated with) mixed liquor suspended solids, is assumed to be not bio-available and inert. Kinetics are assumed to be 1st order. This approach is e.g. applied in Struijs *et al.* (1991a, 1991b).

$$\frac{dC_d}{dt} = -k_1^d \cdot C_d \quad \frac{dC_s}{dt} = 0 \quad [5.68]$$

In Melcer *et al.* (1994), a "double" first-order biodegradation approach is followed. Here, decay is first-order in both the chemical and the biomass concentration. As the biomass level is assumed to be constant, this is reduced to pseudo 1st order. Note that this approach is only relevant for biological degradation.

$$\frac{dC_d}{dt} = -k_2^d \cdot X \cdot C_d = -k_1^d \cdot C_d \quad \frac{dC_s}{dt} = 0 \quad [5.69]$$

By McAvoy *et al.* (1997) and Lee *et al.* (1998), it is assumed that for chemicals which are degraded by primary utilization (in contrast with cometabolism), the competent biomass level at steady-state is adapted to the chemical influent concentration. This approach can be used to explain the independence of effluent concentrations on influent concentrations for these substances.

(Pseudo) First-order degradation - dissolved and sorbed phase

In this method it is assumed that both the freely dissolved chemical and the sorbed chemical can be degraded. Kinetics are assumed to be (pseudo) 1st order (Cowan *et al.*, 1993; Struijs, 1996). This method was used in the model corroboration described below (section 6 in this chapter).

$$\frac{dC_d}{dt} = -k_1^d \cdot C_d \qquad \frac{dC_s}{dt} = -k_1^s \cdot C_s \qquad [5.70]$$

Monod kinetics with steady-state competent biomass

Monod kinetics have been applied by e.g. Pirt (1985), Birch (1991), Struijs (1996), van Wijk *et al.* (1996). They take into account the saturation of the biodegradation rate coefficient at high substrate levels:

$$\frac{dC}{dt} = -\frac{k_{max}}{K_s + C} \cdot C \qquad [5.71]$$

Growth of specific competent biomass (i.e., biomass which only degrades the considered chemical) is also described according to Monod kinetics:

$$m_{growth} = \frac{m_{max}}{K_s + C} \cdot C = \frac{Y \cdot k_{max}}{K_s + C} \cdot C \qquad [5.72]$$

Specific competent biomass decay (microbial cell death) and biomass wasting (via waste sludge) is expressed as:

$$m_{decay/waste} = \left(\frac{1}{SRT} + b \right) \cdot (24 \cdot 3600)^{-1} \qquad [5.73]$$

Note that in Pirt (1985) and van Wijk *et al.* (1996), biomass decay (*b*) is not considered.

At steady-state plant operation, the specific competent biomass level is constant. Growth and decay/waste rates are equal. From this, the steady-state chemical concentration can be derived:

$$m_{growth} = m_{decay/waste}$$

$$\begin{aligned} \Rightarrow \frac{Y \cdot k_{max} \cdot (24 \cdot 3600)^{-1}}{K_s + C_{st.st.}} \cdot C_{st.st.} &= \frac{1}{SRT} + b \\ \Rightarrow C_{st.st.} &= \frac{\left(\frac{1}{SRT} + b\right) \cdot K_s}{Y \cdot k_{max} \cdot (24 \cdot 3600)^{-1} - \left(\frac{1}{SRT} + b\right)} = \frac{(1 + b \cdot SRT) \cdot K_s}{SRT \cdot (Y \cdot k_{max} \cdot (24 \cdot 3600)^{-1} - b) - 1} \end{aligned} \quad [5.74]$$

Using this approach, the predicted steady-state concentration is independent of the influent concentration. Hence, it can be used to explain the independence of effluent chemical levels on their concentration in the influent.

From the steady-state and the influent concentration, a first-order rate coefficient can be derived (assuming that biodegradation is the only removal mechanism), which can be used in a more general 1st order framework (e.g. in Struijs, 1996):

$$\begin{aligned} C_{st.st.} &= C_{influent} \cdot e^{-k_{monod} \cdot (HRT_{act.sludge} \cdot 3600)} \\ \Rightarrow \ln\left(\frac{C_{st.st.}}{C_{influent}}\right) &= -k_{monod} \cdot (HRT_{act.sludge} \cdot 3600) \\ \Rightarrow k_{monod} &= \ln\left(\frac{C_{influent}}{C_{st.st.}}\right) \cdot \frac{1}{HRT_{act.sludge} \cdot 3600} \end{aligned} \quad [5.75]$$

The critical sludge retention time, below which all specific competent organisms are washed out, was derived by Birch (1991):

$$SRT_{crit} = \left(\frac{(Y \cdot k_{max} \cdot (24 \cdot 3600)^{-1}) \cdot C_{influent}}{K_s + C_{influent}} - b \right)^{-1} \quad [5.76]$$

$$SRT < SRT_{crit} \Rightarrow k_{monod} = 0$$

A comparison between steady-state Monod kinetics and first-order kinetics was made by Boeije & Feijtel (1995).

4.5.2. Oxygen Correction

6-box model

The chemical degradation rate coefficient in the hypothetical single (completely mixed) activated sludge tank is calculated as the average of 3 degradation rate coefficients, weighted by the residence time in the 3 redox zones. This average rate coefficient is derived from the standard aerobic degradation rate coefficient, by applying the following correction factor:

$$a_{redox} = f_{aerobic} \cdot 1 + f_{anoxic} \cdot a_{anoxic} + f_{anaerobic} \cdot a_{anaerobic} \quad [5.77]$$

10-box model

In the 10-box model, separate degradation rate coefficients are used for the three different tanks (anaerobic, anoxic and aerobic). These rate coefficients are derived from the standard aerobic rate coefficient, using the same correction factors as described above for the 6-box model ($a_{anaerobic}$ and a_{anoxic}).

4.6. Estimation of Design and Operation Parameters

Several design and operation parameters are required for the mechanistic simulation of chemical fate in a WWTP. These include a.o. tank volumes or hydraulic residence times, sludge loading rate or SRT, information about aeration, etc. It can be expected that many of these parameters are not readily available for a majority of treatment plants. To deal with the lack of WWTP-specific data, an estimation procedure can be applied, based on standard rules of thumb. In *SimpleTreat* 3.0 (Struijs, 1996), a number of straightforward calculations are presented. In this chapter, modifications are proposed for the estimation of oxygen requirement and of the secondary settler's dimensions.

The calculation of the oxygen requirement was adjusted. In *SimpleTreat*, it is assumed that the need for oxygen input into the activated sludge tank is equal to the biological oxygen demand (BOD) of the influent. This does not take into account the oxygen requirement for endogenous respiration of the biomass, nor the oxygen balance of nitrification / denitrification. Hence, an alternative calculation of *OxReq* is proposed. For nitrification, an additional oxygen input into the aerobic tank is required (4.33 mgO₂ per mgN, after Metcalf & Eddy, 1991). On the other hand, oxygen is recuperated thanks to denitrification (2.86 mgO₂ per mgN, after Klapwijk, 1978). Nitrogen uptake into biomass was also accounted for (assuming a 5% N-content in biomass). Note that in the calculation below, the effect of biological phosphorus removal on the oxygen balance was assumed to be negligible.

$$\begin{aligned}
OxReq = & \\
& \frac{\Phi_{BOD} \cdot (1 - 1.33 \cdot Y)}{Q} \quad \text{(organics oxidation)} \\
& + \frac{V_{act.sludge} \cdot SS_{ML} \cdot \left(r_{end} \cdot \frac{1}{3600 \cdot 24} \right)}{Q} \quad \text{(endogenous respiration)} \\
& + \frac{(\Phi_N - Y \cdot \Phi_{BOD} \cdot 5\%) \cdot (4.33 \cdot e_N - 2.86 \cdot e_N \cdot e_{DN})}{Q} \quad \text{(nitrification / denitrification)}
\end{aligned} \tag{5.78}$$

In *SimpleTreat* 3.0, the main settler parameter is the hydraulic residence time. However, the key parameter in settler design is the overflow rate (Metcalf & Eddy, 1991; Verstraete, 1992). For the secondary settler of an activated sludge system, an overflow rate of 0.7 - 1.4 $m^3 \cdot m^{-2} \cdot h^{-1}$ is recommended (Metcalf & Eddy, 1991). The settler's volume and surface area are estimated from the dry weather overflow velocity and dry weather flow. Note that the waste sludge flow is considered negligible compared to the effluent flow.

$$v_{sec}^{overflow} = \frac{Q^{sec} - Q_{waste}}{A_{sec}} \cong \frac{Q^{sec}}{A_{sec}} \quad \Rightarrow \quad A_{sec} = \frac{Q^{sec}}{v_{sec}^{overflow}} \tag{5.79}$$

The suspended solids removal efficiency of settlers generally decreases with increasing hydraulic load (e.g. Pflanz, 1969). Lessard and Beck (1993) used the following equation to relate the effluent suspended solids concentration (of a secondary clarifier) to flow:

$$SS_{effluent} = a_1 + a_2 \cdot Q^{sec} \tag{5.80}$$

The general applicability of this equation has not been proven. Hence, it is recommended to apply it only when a plant-specific calibration is possible.

5. Effect of Recycle Ratio on Predicted Chemical Removal

One of the modifications of *SimpleTreat* described higher in this chapter, is the use of a more realistic description of sludge recycle ratios (both settled sludge and internal recycles). In this section, it was investigated which is the effect of the settled sludge recycle ratio on predicted chemical removal efficiencies .

5.1. Theoretical Considerations

The chemical concentration entering the settler is equal to the completely mixed activated sludge tank concentration. Surface volatilization in the settler causes further elimination of the dissolved chemical. Hence, for volatile chemicals, the dissolved concentration in the settler is expected to be lower than that in the activated sludge tank. As a result, recycling of the settler's water phase will have a (relatively small) diluting effect on the latter.

The hydraulic residence time in the activated sludge tank is decreased by including a water recycle flow, as more water has to pass through the same volume. However, the average total residence time is not affected, as the recycling causes multiple passes through the tank instead of a single-pass when no recycle is considered.

Non-volatile chemicals

For chemicals with a low volatility, it is expected that the predicted dissolved phase concentration in the settler and in the activated sludge tank are very similar. Hence, the water phase recycle will have a negligible effect on the concentration in the activated sludge tank. As the net residence time in the tank is also not affected, it is expected that including the water phase recycle will have a negligible effect on predicted chemical elimination.

Volatile chemicals

Volatile chemicals are expected to have a lower predicted dissolved concentration in the settler than in the activated sludge tank. Hence, recycling the settler's water phase will cause a dilution of the activated sludge tank's dissolved phase. This is expected to affect several fate processes. There will be desorption from the activated sludge tank's solids phase, due to the increased concentration gradient (stronger non-equilibrium). Consequently, a larger chemical fraction will be available for volatilization and dissolved phase degradation. Based on these considerations, it is expected that chemical elimination will be increased.

5.2. Simulation Experiment

To illustrate the above theoretical points, the fate of four hypothetical chemicals in the default *SimpleTreat* WWTP configuration (Struijs, 1996) was simulated, using different sludge recycle ratios. These simulations were performed with the 6-box model.

The four simulated chemicals are Hypotheticum (the default *SimpleTreat* substance), Chemical A (sorbing, degradable in the dissolved phase and non-volatile), Chemical B (similar to Chemical A, but also degradable in the sorbed phase), and Chemical C (sorbing, non-degradable and highly volatile). The properties of these chemicals are given in Table 5.2.

Table 5.2. Chemical properties of hypothetical substances

	K_d^{sewage} (L/kg)	K_d^{ML} (L/kg)	$k_{degradation}$ (h ⁻¹)	degradation phase	H (Pa.m ³ .mol ⁻¹)
Hypotheticum	300	370	0.1	dissolved	1
Chemical A	2000	2000	0.69	dissolved	10 ⁻⁶
Chemical B	2000	2000	0.69	diss. + sorbed	10 ⁻⁶
Chemical C	2000	2000	0	n.a.	10 ⁴

Sludge recycle ratios were varied between 0 and 3. This interval represents a realistic range of recycles used in nutrient removal practice. Note that the case with recycle ratio 0 is equivalent to the original *SimpleTreat* model. In Figure 5.7, removal efficiencies of the different chemicals are plotted as a function of recycle ratio.

For the low- or non-volatile chemicals Hypotheticum, Chemical A and Chemical B, the influence of the sludge recycle ratio on chemical elimination was negligible; the absolute difference in predicted removal efficiency was less than 0.1% in all three cases.

For the highly volatile Chemical C, the impact of the recycle ratio was significant. The absolute increase in predicted removal efficiency was approximately 3% when the recycle ratio was varied from 0 to 3. As the predicted removal for this substance was very high (> 96%), the corresponding decrease in the predicted effluent concentration was by a factor 4. This result confirms what was expected from the theoretical considerations above.

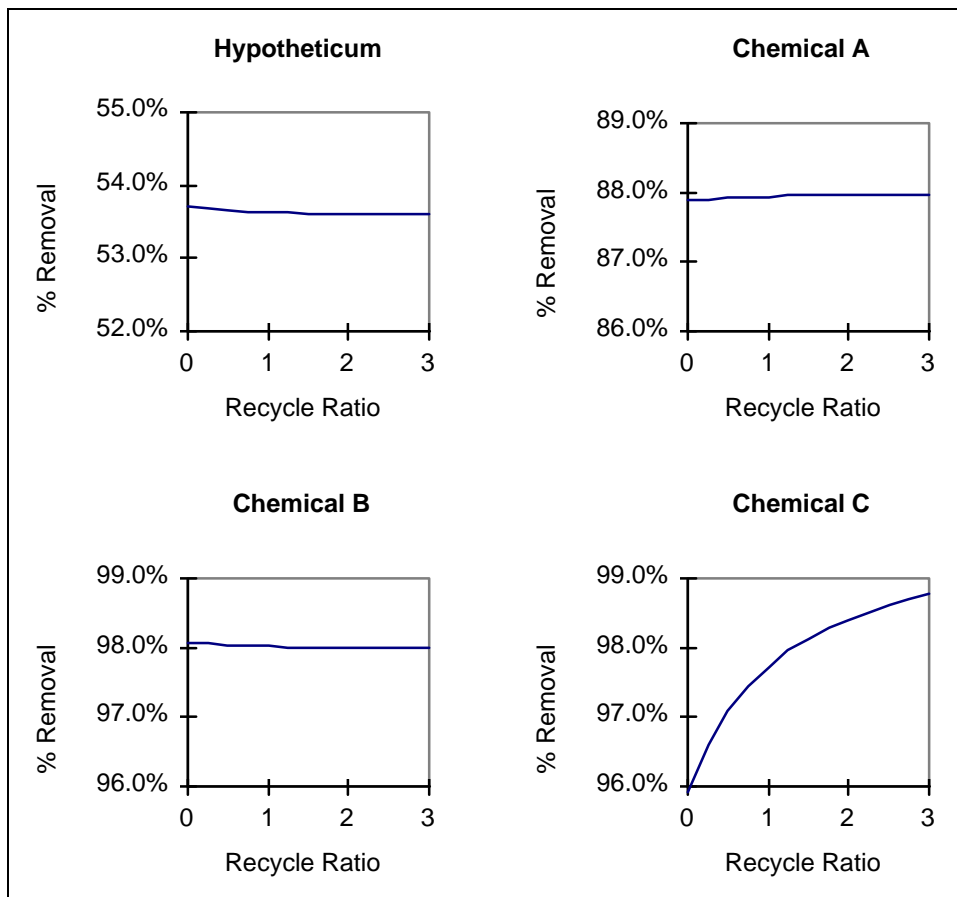


Figure 5.7. Predicted removal efficiencies as a function of sludge recycle ratio

6. Model Application and Corroboration

Both the 6-box model and the 10-box model were applied to simulate the fate of Linear Alkylbenzene Sulphonate (LAS), a common surfactant, in three laboratory-scale activated sludge plants. Next to LAS, the fate of Hypotheticum (*SimpleTreat*'s default substance) was also simulated. The LAS removal predictions were compared to measured values.

6.1. Description of the Experiments

6.1.1. Treatment Plants

Three laboratory-scale activated sludge waste water treatment plants were investigated. These were a standard OECD Continuous Activated Sludge (CAS) unit (OECD, 1993), the Behr KLD-4 unit (Behr Labor-Technik, Düsseldorf-Reisholz), and an expanded nutrient removal CAS unit based on the UCT process (see above in Figure 5.2).

The standard OECD CAS unit consists of a single activated sludge aeration tank and a settler. It is routinely used for regulatory testing of chemicals. The Behr unit consists of two activated sludge reactors (one anoxic and one aerated tank) and a settler. This approach was described and tested in detail by Gronenberg & Schöberl (1994). The UCT CAS unit was developed by Boeije (1996). The reactor design was based on an OECD CAS unit, with 2 additional reactors (anaerobic and anoxic). Reactor dimensions and sludge recycle ratios were optimized by means of simulations with the IAWQ Activated Sludge Model N° 2 (Henze *et al.*, 1995b). A brief description of the three units is given in Table 5.3. The building, testing and comparison of the units is given Rottiers *et al.* (1998) and in chapter 4 of this thesis.

Table 5.3. WWTP design and operation conditions

	OECD CAS unit	Behr unit	UCT CAS unit
anaerobic volume (L)	-	-	1.5
anoxic volume (L)	-	4.2	1.5
aerobic volume (L)	3.5	4.5	3.0
influent flow (L/h)	0.58	0.75	0.50
B_x (mgCOD/mgSS.d)	0.25	0.20	0.25
settler recycle ratio (-)	0.85	2.5 (to anoxic)	2 (to anoxic)
internal recycle ratio (-)	-	none	2 (aer. to anoxic) 2 (anoxic to anaer.)

6.1.2. Test Chemicals

For the model calibration and corroboration, LAS measurements in the three test units were used. The LAS influent levels were: OECD CAS unit: 1.2 mg/L; Behr unit: 2.6 mg/L; UCT CAS unit: 3.6 mg/L. The relevant physical/(bio)chemical properties of LAS are listed in Table 5.4. The sorption and volatilization properties were taken from Cowan *et al.* (1993b). The 1st order degradation rate coefficient was obtained by fitting the 6-box model to the standard OECD CAS test results (see below, section 6.2.1). The physical / chemical properties of Hypotheticum can be found in Table 5.2. Note that it was assumed that Hypotheticum degradation goes on at the same rate in all three redox zones (hence the correction factors a_{anoxic} and $a_{anaerobic}$ are both equal to 1).

Table 5.4. Properties of the test chemicals LAS and hypotheticum

K_d (sewage & mixed liquor)	(L/kg)	2000
H	(Pa.mol ⁻¹ .m ³)	10 ⁻⁶
k_1^d, k_1^s	(h ⁻¹)	4*
a_{anoxic}	(-)	0
$a_{anaerobic}$	(-)	0

* obtained by fitting the 6-box model to the OECD CAS standard test measurements (see below)

6.2. Results and Discussion

Laboratory measurements of the (parent) removal efficiencies of LAS in the three studied WWTPs are described in detail in Rottiers & Decraene (1996). The results are shown in Figure 5.8.

6.2.1. Calibration for LAS

The LAS degradation rate coefficient was calibrated by fitting the 6-box model to the standard OECD CAS test measurements. The observed LAS removal in the CAS test (98.6 %) could be obtained as a 6-box model prediction by setting the degradation rate coefficient to 4 h⁻¹ (degradation in both sorbed and dissolved phase). Note that in this study, only the disappearance of the parent compound was considered. Hence, the calibrated rate coefficient of 4 h⁻¹ only applies to the primary degradation process of LAS. This rate coefficient is slightly higher (but in the same order of magnitude) than the standard value for readily biodegradable chemicals (3 h⁻¹) which is suggested in Struijs *et al.* (1991b).

6.2.2. Corroboration for LAS

In Figure 5.8, simulated and measured LAS removal efficiencies are compared. For the OECD CAS unit, the 6-box model's prediction perfectly matched the measurements, as this case was used for calibration. Also the 10-box model resulted in a perfect fit for the CAS. This is obvious, as the CAS test unit consists of a single reactor, and hence a 10-box model of the CAS is reduced to only 6 boxes, equivalent to the 6-box model used for calibration.

For the multiple reactor Behr and UCT units, the predictive power of the 10-box model was superior to that of the 6-box approach. The 6-box model typically under-predicted the LAS removal efficiency by 0.5% (absolute difference). As removal was very high (> 98%), this resulted in an over-prediction of the effluent concentrations with a factor 2. The 10-box model removal prediction was within 0.1% (absolute difference) of the measurements. Hence, this model allowed to make more accurate predictions of LAS removal in both nutrient removal plants, using a calibration which was only based on the results of a standard OECD CAS test.

Both models predicted a slightly higher LAS removal efficiency in the UCT unit compared to the Behr unit. However, this was not confirmed by the measurements.

6.2.3. Simulations for Hypotheticum

Simulation results for Hypotheticum are given in Figure 5.9. For this substance, the 6-box and 10-box model predictions for the CAS unit were identical, as both models are equivalent in this case (see above). For the Behr and UCT units, the 10-box model predicted a higher removal than the 6-box model (an absolute difference of more than 3.5%). This trend is similar to what was observed with the predictions for LAS.

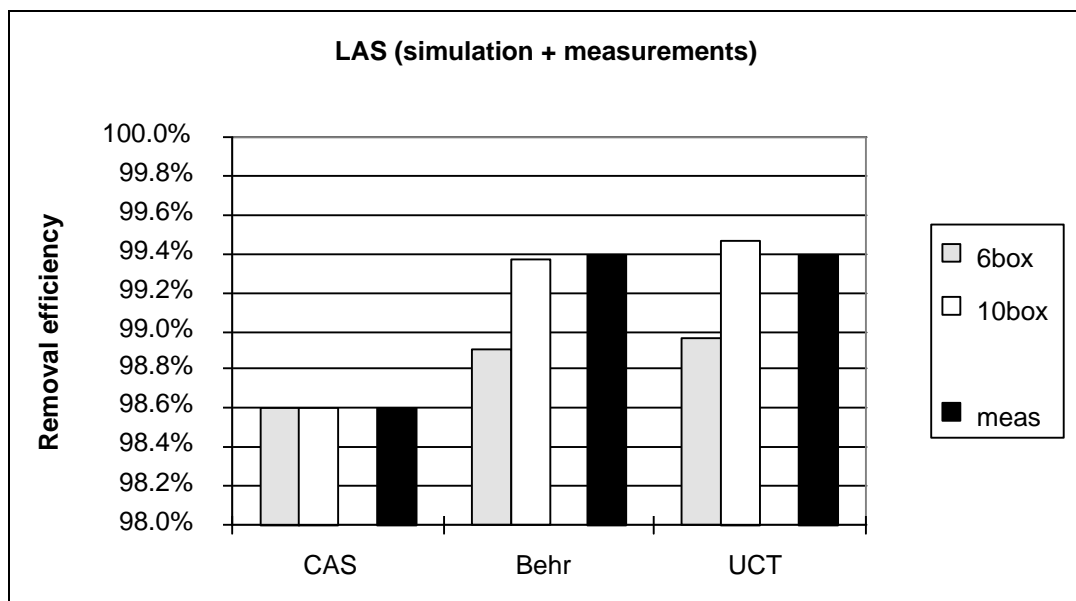


Figure 5.8. Measured and predicted LAS removal in the three considered test units

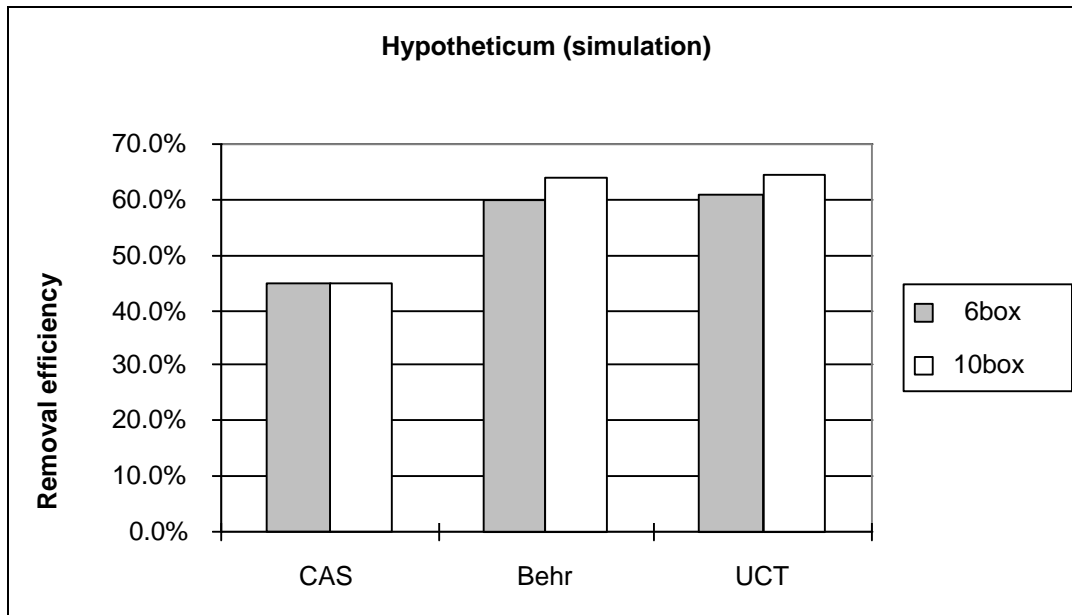


Figure 5.9. Predicted Hypotheticum removal in the three considered test units

7. Conclusions

In this chapter it was shown that by a number of simple modifications, the *SimpleTreat* concept could be adapted to single-sludge nutrient removal WWTPs. A more realistic description of sludge recycling, taking into account the water phase of these recycles and the actual recycling ratios, is proposed. This may improve the fate prediction of highly volatile chemicals.

Two modeling approaches for nutrient removal plants were presented, both based on the UCT design: a 6-box model derived directly from *SimpleTreat*, and a more detailed 10-box model. Simulation results of both models were compared to measured removals for LAS in three lab-scale plants. The LAS degradation rate coefficient was calibrated only using standard OECD CAS test data, and was subsequently used to predict the fate of LAS in two biological nutrient removal plants. The 10-box model was more accurate than the 6-box model, which (slightly) underestimated removal. Lower removal predictions by the latter were also found for the default substance hypotheticum.

It is recommended to focus further research on the corroboration of these models for different chemical types. Especially simulation and laboratory measurements of volatile and / or less easily degradable substances would allow to further test the underlying assumptions. This should also give more conclusive evidence on the relative performance of the 6-box versus the 10-box model.

Chapter 6

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Measuring the Fate of LAS in a Pilot-Scale Trickling Filter

a condensed version of this chapter, together with chapter 7, was submitted for publication as:

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Chapter 6

Measuring the Fate of LAS in a Pilot-Scale Trickling Filter

1. Introduction

To test the chemical fate model for trickling filters which is presented in chapter 7 of this thesis, LAS removal experiments were conducted in a pilot-scale trickling filter unit. The design of the unit allowed a characterization of all relevant model parameters, and an easy monitoring of the system's performance. Using this lab setup, steady-state removal of LAS was measured under different well-characterized operating conditions. This laboratory study was complementary to a full scale trickling filter sewage treatment plant monitoring study, which was conducted within the GREAT-ER project by Holt *et al.* (1998).

2. Development and Characterization of the Trickling Filter

2.1. Design and Development

As the pilot-scale trickling filter unit was to be used for several purposes, outside of the work described in this thesis, it was not aimed to mimic a typical domestic 'low rate' filter plant. Instead, its design was focused on practical feasibility and on the possibility to easily quantify and control all relevant operating parameters and conditions.

2.1.1. Dimensioning

In Table 6.1, a number of general design criteria for trickling filter waste water treatment plants is given. No consensus exists for the terminology 'high rate', 'low rate', etc. In this text, the nomenclature of Metcalf & Eddy (1991) was used.

The filter unit's dimensions were chosen to represent a cylindrical core taken from a full-scale unit. In contrast to completely mixed pilot or bench scale activated sludge units, the reactor's depth can not be scaled down without fundamentally affecting the system's behavior. Practical considerations limited the depth to 1.8 m, which is within the range given in Metcalf & Eddy (1991) for both intermediate rate [1.8 m - 2.4 m] and high rate [0.9 m - 1.8 m] filters. Contrary to the depth, it is possible to downscale the diameter, provided wall effects (hydraulic shortcuts) remain negligible. Based on the availability of standard PVC sewer pipe components, an internal diameter of 0.388 m was chosen. Hence, the filter's cross-sectional area was 0.118 m², and its volume was 0.213 m³.

Table 6.1. Typical trickling filter design criteria mentioned in the literature

	Carrier medium	B_A ($m^3/m^2.d$) { m/h }	B_V ($kgBOD/m^3.d$)	R (-)	h_f (m)
Metcalf & Eddy (1991)					
Low Rate	rock	1.2 - 3.5 {0.05 - 0.15}	0.08 - 0.4	none	1.8 - 2.4
Intermediate Rate	rock	3.5 - 9.4 {0.15 - 0.40}	0.24 - 0.48	0 - 1	1.8 - 2.4
High Rate	rock	9.4 - 37.5 {0.40 - 1.60}	0.48 - 0.96	1 - 2	0.9 - 1.8
Super High Rate	plastic	12 - 70 {0.50 - 2.9}	0.48 - 1.6	1 - 2	3 - 12
Roughing	plastic (or redwood)	47 - 188 {1.96 - 7.8}	1.6 - 8	1 - 4	4.6 - 12
Henze <i>et al.</i> (1995a)					
Low Rate		4.8 {0.2}	0.2	*	
Moderate Rate		9.6 - 19.2 {0.4 - 0.8}	0.2 - 0.45		
Normal Rate		14.4 - 28.8 {0.6 - 1.2}	0.45 - 0.75		
High Rate		> 28.8 {> 1.2}	> 0.75		
ATV (1989)					
No nitrification	rock	11.8 - 23.5 {0.5 - 1.0}	0.4	≤ 1	2.8 - 4.2
	plastic	18.8 - 42.3 {0.8 - 1.8}	0.4 - 0.8	≤ 1	2.8 - 4.2
With Nitrification	rock	9.4 - 18.8 {0.4 - 0.8}	0.2	≤ 1	2.8 - 4.2
	plastic	23.5 - 35.3 {1.0 - 1.5}	0.2 - 0.4	≤ 1	2.8 - 4.2

* on the one hand it is recommended in this book to use $R < 1$; on the other hand a recycle ratio of > 8 was calculated for a high rate example

For the settler design calculations, it was assumed that the entire flow through the trickling filter (1.3 L/min) also passes through the settler ('worst-case' hydraulics). For practical and cost reasons, the settler diameter was fixed at 0.25 m , hence its surface area was 0.049 m^2 . The corresponding overflow velocity (at maximal flow) is 1.5 m/h , which is within the safety range for poorly settling sludge ($SVI = 200 mL/g$) (after Verstraete, 1992). Based on Grijspeerdt *et al.* (1996), the downscaled settler's height was fixed at 0.75 m .

2.1.2. Carrier Material

To ensure uniform conditions throughout the filter, to allow quantification of specific surface area and biofilm parameters, and to ensure a low weight, a plastic carrier medium was used. The selected medium was obtained from the company Filtermat (Temse, Belgium). Its specific surface area was 220 m^2/m^3 , its density 61 kg/m^3 , and it had 96 % voids. The volume of plastic contained in one piece of carrier material (excluding voids) was measured to be 0.005 L (using a submersion technique). The surface area of a carrier material unit (0.0225 $m^2/carrier$) was calculated based on its actual geometry (Figure 6.1).

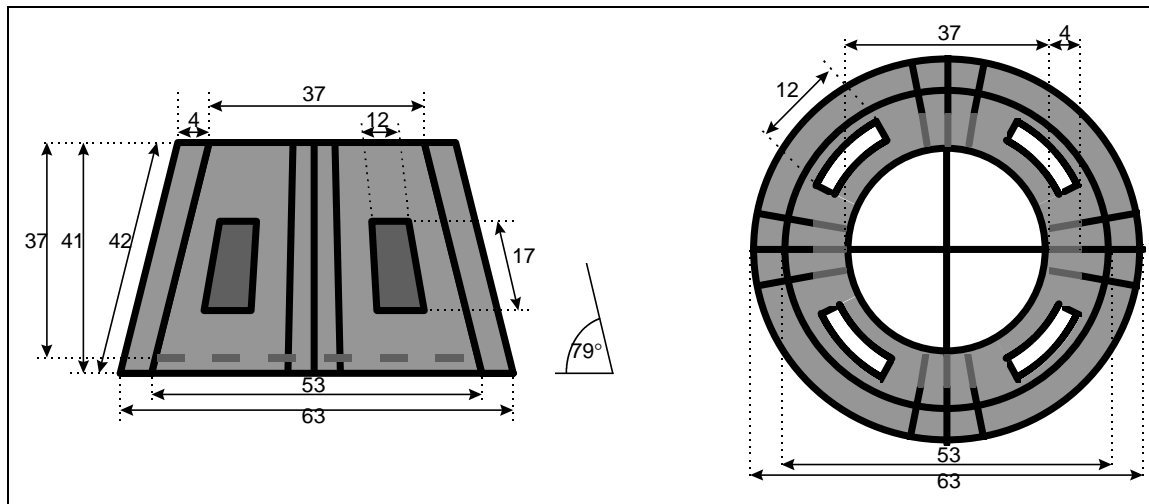


Figure 6.1. Schematic drawing of the carrier material used in the pilot-scale trickling filter

2.1.3. Loading and Flows

Metcalf & Eddy (1991) advise to apply a high rate loading with a plastic filter medium. A volumetric loading rate $B_V = 0.6 \text{ kgBOD}/\text{m}^3 \cdot \text{d}$ was selected. The hydraulic surface loading rate B_A was set at $15 \text{ m}^3/\text{m}^2 \cdot \text{d}$ ($= 0.625 \text{ m/h}$). These values are within the range for high and super high rate trickling filters (Metcalf & Eddy, 1991), or for normal rate filters as mentioned by Henze *et al.* (1995a). A B_V of $0.2 \text{ kgBOD}/\text{m}^3 \cdot \text{d}$ is recommended for nitrifying filters by ATV (1989), hence a high degree of nitrification is not expected in this case. The total flow through the filter (influent + recycle flow) is equal to B_A multiplied by the surface area = 1.3 L/min . Assuming an influent BOD level of 300 mg/L (typical for domestic sewage, after Verstraete, 1992), the influent flow (= the product of B_V and volume divided by BOD) is 0.29 L/min .

From the total and the influent flow, it can be derived that the recycle ratio is to be 3.5. This is higher than mentioned in Metcalf & Eddy (1991) for super high rate filters, but within the range for roughing filters. It is also higher than recommended in Henze *et al.* (1995a) for typical cases, but on the other hand much lower than the factor 8 from their calculation example. It was decided to retain this relatively high recycle ratio (and wetting rate) as a default for the experiments, to ensure proper wetting of the filter material and a uniform spatial distribution of the influent over the filter's surface. The recycle rate was assumed to have no effect on sloughing, as this is generally quite unpredictable and often related to atmospheric conditions (van Loosdrecht, 1998).

2.1.4. Construction

The influent was pumped into the pumping reservoir of the treatment plant, where it was mixed with the recycle water. This mixture was pumped up into the filter unit itself. The water trickled down the filter and was then split into two fractions: the short recycle which flowed directly to the pumping reservoir, and the long recycle which flowed into the settler. Of the latter, one part (equal

in flow rate to the influent) was the plant's effluent; the other part - the long recycle - flowed to the pumping reservoir. An overview is given in Figure 6.2.

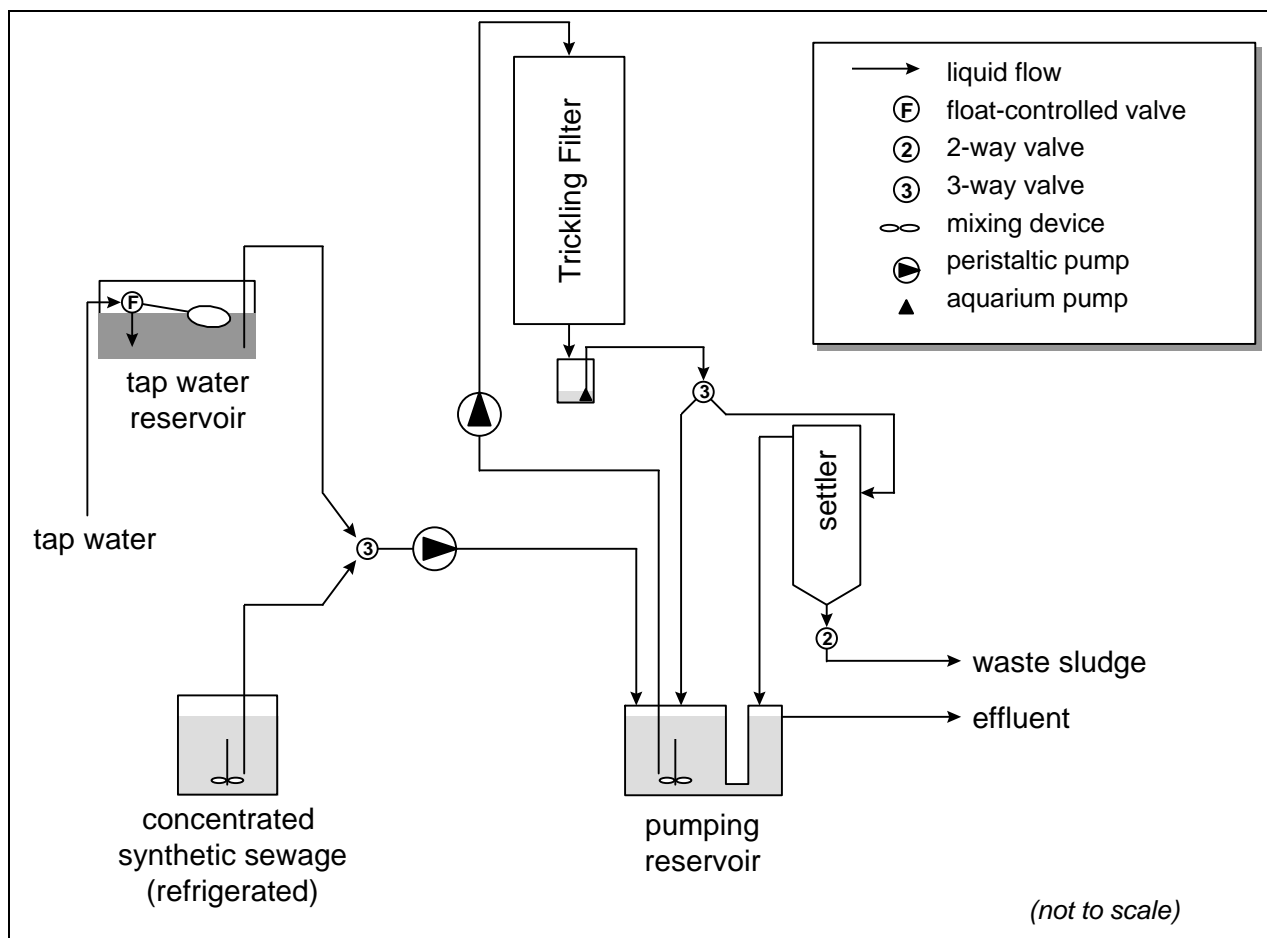


Figure 6.2. Schematic overview of the pilot-scale trickling filter hydraulics

Filter unit

The filter was constructed using a PVC tube (ext. diameter = 0.4 m, wall thickness = 6.2 mm). The filter length was 1.8 m; the total length of the tube was 2.1 m. Five sampling ports were foreseen. To counteract hydraulic wall effects (short circuiting), four horizontal rings (width of 5 cm) were placed in the filter. At the bottom of the filter, a perforated disc was used to support the carrier material. At the top of the filter unit, the inflow was split into 16 subflows, and each subflow tube was attached to a horizontal perforated disc to ensure a uniform partitioning over the filter's surface. The top of the filter was closed by a polyethylene funnel, which was connected to an air pump (KNF-Verder). In domestic trickling filters, air flow typically is by natural ventilation (chimney effect), and is poorly quantified. Based on an example of a pilot scale TF plant (Melcer *et al.*, 1995), an upward air flow through the filter of 10 L/min was chosen (upward air flow velocity of 5 m/h). At the bottom of the filter body, a polyethylene funnel was used to direct the filter's outflow to a small collection vessel, from which it was pumped to a timer-controlled three-way pinch valve (Sirai S307-01, silicone tubing of 4.8/7.9 mm int./ext. diameter) switching between the short and the

long recycle (by means of an aquarium pump: Rena C40 Turbo, max. capacity 1000 L/h). By an electronic balance (modified Mettler-Toledo Spider 1S-150, max. capacity 150 kg, accuracy 10 g) connected to a PC, the filter unit's mass was continuously monitored. This information could be used to determine hydraulic and biofilm characteristics. A schematic overview of the filter unit is shown in Figure 6.3.

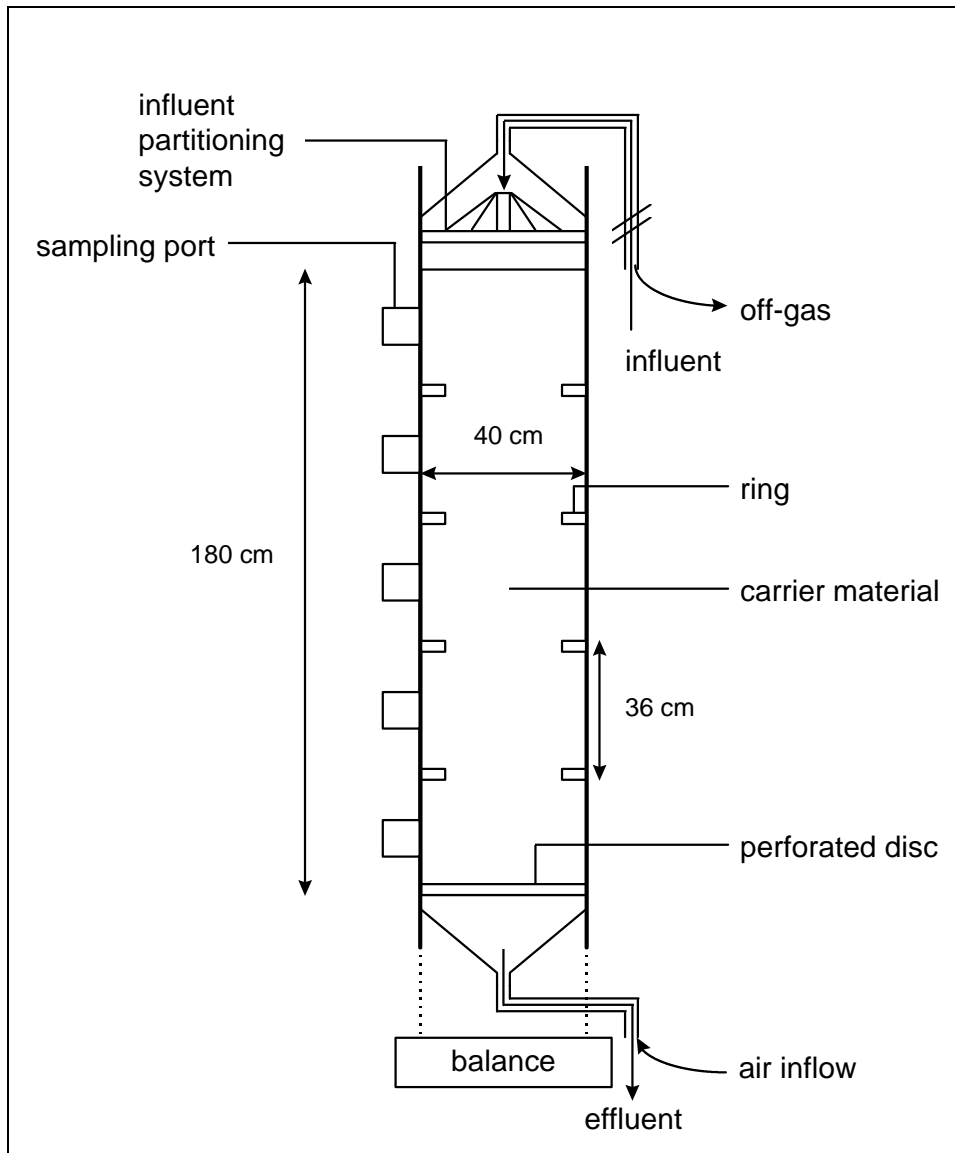


Figure 6.3. Schematic drawing of the pilot-scale trickling filter body

Settler

The settler was constructed from transparent plexi-glass. The settler was located below the filter unit, but hydraulic headlosses in the tubing made gravitational flow unreliable. Hence, a small pump was required (see higher). The waste sludge flow was periodically switched on by means of a timer-controlled two-way pinch valve (Sirai S106-03, with silicone tubing of 6.4/9.5 mm internal/external diameter).

Pumping Reservoir

The influent and the short recycle flows were mixed in the pumping reservoir. Through hydraulic contact with the effluent reservoir (which received the settler's outflow), the long recycle flow could also enter the pumping reservoir. To avoid settling of solids, the pumping reservoir was continuously mixed by means of a small aquarium pump (Rena C10, max. capacity 240 L/h).

Influent

As influent to the trickling filter plant, a synthetic sewage was used which aimed to mimic real domestic waste water. A synthetic medium was preferred over actual sewage, because (1) its composition is constant; (2) its composition is well-characterized; (3) its composition can be controlled; and (4) for practical reasons: a synthetic sewage can be prepared as a concentrate which is only to be diluted when it enters the plant. The composition of the sewage was based on the *Syntho* medium (Boeije *et al.*, 1998a) which is also described in chapter 4 of this thesis. For cost reduction, this medium was slightly simplified: urea: 55, NH₄Cl: 13 Na-acetate.3H₂O: 148, peptone: 17, MgHPO₄.3H₂O: 29, K₃PO₄: 20, CaCl₂: 2.3, FeSO₄.7H₂O: 5.8, NaHCO₃: 29, starch: 122, milk powder: 116, yeast: 52, soy oil: 29, Na-LAS paste (60%): 14, Alkyl Ethoxylate (Neodol) (100%): 9, Cr(NO₃)₃.9H₂O: 0.770, CuCl₂.2H₂O: 0.536, MnSO₄.H₂O: 0.108, NiSO₄.6H₂O: 0.336, PbCl₂: 0.100, ZnCl₂: 0.208 (in mg/L). The calculated COD:N:P ratio of the synthetic sewage is 462:43:9 or 100:9.3:2. The theoretical BOD (assuming a COD to BOD conversion factor of 0.65) is 300 mg/L.

In practice, the influent was prepared as a concentrated liquid (20x or 30x), and was diluted with tap water when it was pumped into the filter setup. One pump was used for this purpose, which alternated between concentrate and tap water by means of a timer-controlled three-way pinch valve (Sirai S307-01, with silicone tubing of 4.8/7.9 mm internal/external diameter) (time intervals for 20x concentrated influent: 2 seconds / 38 seconds). A constant supply of tap water was provided in a reservoir which was continuously filled by means of a float-controlled valve (cf. toilet system). To keep its quality constant, the concentrated sewage was stored in a refrigerator, and was continuously mixed by means of 2 aquarium pumps (Rena C40 Turbo, 1000 L/h).

2.2. Hydraulic Characterization

2.2.1. Without Biofilm

A NaCl tracer test was conducted on the filter without biofilm (i.e., before the startup of the biological experiments). NaCl was injected into the filter as a pulse, and subsequently the NaCl was detected in the filter's outflow using conductivity measurements (Yokogawa sensor). The filter was operated 'single-pass' (no effluent recycle was applied). After the injection of the tracer, pure tap water was pumped over the filter. The test was conducted with two flow rates (1.66 and 0.81 L/min). Based on the tracer response, the mean and mode tracer residence times (*TRT*) were

obtained (Table 6.2). For a flow of 1.3 *L/min*, linear interpolation resulted in an estimated mean and mode *TRT* of 6.35 and 1.89 minutes.

The tracer response curves are presented in Figure 6.4. Note that the raw conductivity data (in *mS/cm*) were transformed to E-curves (for which the surface under the curve equals 1).

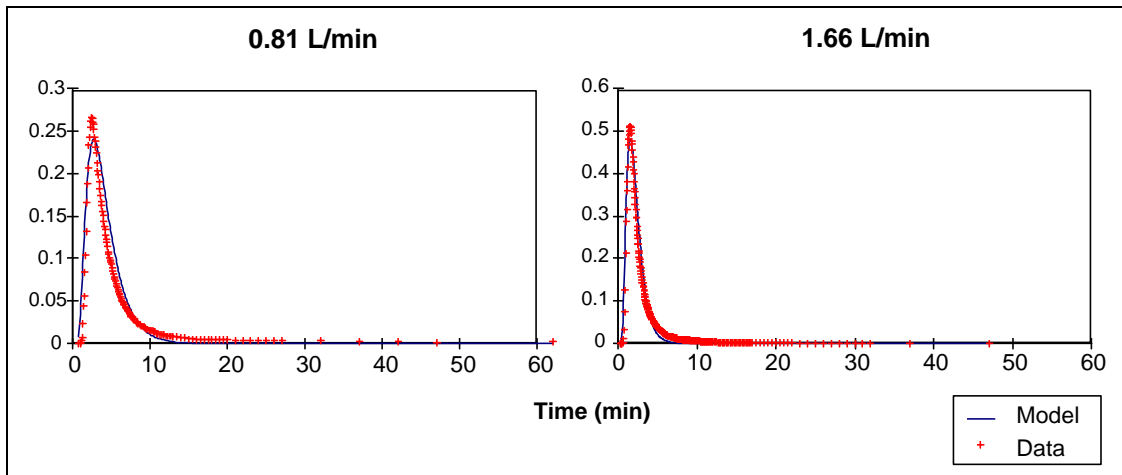


Figure 6.4. Tracer test without biofilm (*E*-curves)

The open vessel advection-dispersion model (Levenspiel, 1972) was fitted to the experimental tracer data (v and D fitted, l fixed at 1.8 *m*):

$$E = \frac{v}{\sqrt{4p \cdot D \cdot t}} \cdot \exp\left(-\frac{(l - v \cdot t)^2}{4 \cdot D \cdot t}\right) \quad [6.1]$$

The fitted parameter values (sum of squared errors (SSE) minimization, SPSS software, version 7.5, SPSS Inc.) are given in Table 6.2. Although the determination coefficients R^2 indicate an acceptable fit, Figure 6.4 shows that the measured tracer response was heavier in the tail region compared to the model, and the model also underpredicted the importance of the mode.

Table 6.2. Tracer test without biofilm - results

		0.81 <i>L/min</i>	1.66 <i>L/min</i>
from tracer data			
<i>TRT mean</i>	(<i>min</i>)	8.75	3.28
<i>TRT mode</i>	(<i>min</i>)	2.42	1.50
from advection-dispersion model fitting			
v	(<i>m/s</i>)	0.009491	0.017159
D	(<i>m</i> ² / <i>s</i>)	0.002533	0.003685
R^2	(-)	0.9075	0.9676

2.2.2. With Biofilm

As high NaCl concentrations may disrupt biological activity, the fluorescent agent Thioflavine-S was used as a tracer when biofilm was present. This tracer was injected into the filter as a pulse, and its fluorescence was measured in the filter's outflow (Ingold fluorescence detector, excitation wavelength 360 nm, measurement wavelength 450 nm). The filter was operated 'single-pass'. After the tracer injection, tap water was pumped over the filter. The test was conducted with 3 flow rates (0.42, 0.83 and 1.3 L/min). The tracer response (E-curves) is shown in Figure 6.5.

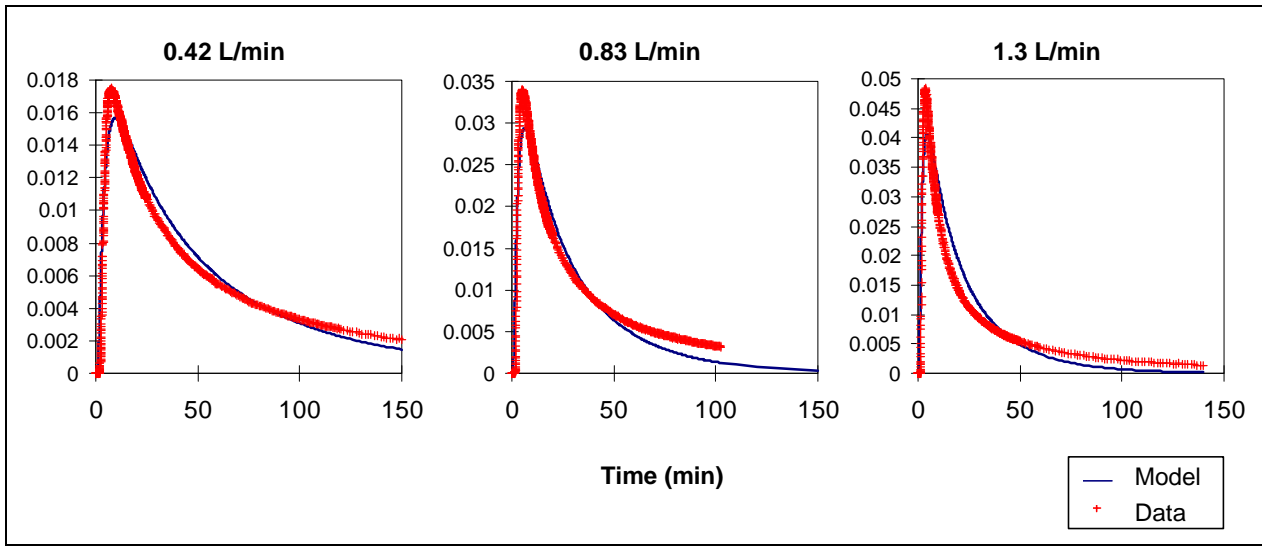


Figure 6.5. Tracer test with biofilm (E-curves)

As the tails were especially heavy, the tracer experiments could not be conducted until complete disappearance of the tracer. To complete the curves, a tail extrapolation was performed. The mean and mode TRTs are given in Table 6.3.

Table 6.3. Tracer test with biofilm - results

		0.42 L/min	0.83 L/min	1.3 L/min
from tracer data				
TRT mean	(min)	84.0	40.0	38.6
TRT mode	(min)	7.8	5.1	3.7
from advection-dispersion model fitting				
u	(m/s)	0.001312	0.002288	0.003207
D	(m ² /s)	0.002319	0.003179	0.004682
R^2	(-)	0.9330	0.9150	0.8947

The advection-dispersion model was fitted to the experimental tracer data (Table 6.3) (SSE minimization, SPSS software, version 7.5, SPSS Inc.). The quality of the fit was similar to that in the 'no biofilm' case. As for the tracer test without biofilm, the measured tracer response data were heavier in the tail region compared to the model, and the model also underpredicted the importance of the mode *TRT* (Figure 6.5). However, the large discrepancy between the modeled and real tracer tail is not fully reflected in the R^2 values, as the measurements used to fit model were not continued until complete disappearance of the tracer. Hence, it is expected that the presented coefficients of determination are too optimistic.

2.2.3. Amount of water in the filter

The mass of the filter unit was monitored on-line. The dry mass was determined prior to the experiments: 62.93 kg. The total mass of water present in the filter (in the absence of biofilm) was measured at a filter inflow rate of 1.3 L/min: 6.66 kg. At this flow, the 'dynamic' amount of water present in the filter was measured by stopping the inflow: 1.45 kg. Hence, the 'static' amount of water (which remains in the filter even if there is no inflow) was found to be 5.21 kg.

In the presence of biofilm, the 'dynamic' water layer mass was 3.06 kg with a flow of 1.3 L/min and 2.38 kg at 0.5 L/min. Assuming that the 'static' water mass was not affected by the presence of biofilm or by the flow, the total water mass in the presence of biofilm was 8.27 kg (at 1.3 L/min) and 7.59 kg (at 0.5 L/min). From this information, the mean hydraulic residence time in the presence of biofilm was estimated to be 6.36 min (with a flow of 1.3 L/min) or 15.18 min (at 0.5 L/min). In the absence of biofilm, this was estimated to be 5.12 min at a flow of 1.3 L/min. Based on the water volume, the total filter volume (213 L) and the porosity (96 %), the fraction of water in the filter pores (in the presence of biofilm) was calculated to be 4 % at 1.3 L/min and 3.7 % at 0.5 L/min.

2.2.4. Discussion

As expected, in all examined cases the hydraulic residence time in the filter was inversely proportional to the water flow rate. It was not possible to perfectly describe the tracer response by means of the open vessel advection-dispersion model: the model underpredicted the importance of the tail (especially in the presence of biofilm) and of the peak height. Still, the coefficients of determination indicated an acceptable fit (R^2 around 90 % or higher).

A large difference between the mean tracer residence time in the case with and without biofilm was detected. With a flow of 0.8 ; 1.3 L/min, this was by a factor 4.6 ; 6.1. For the mode (peak), the difference was more limited (a factor 1.3 ; 2.0).

For 1.3 L/min, the mean *TRT* in the absence of biofilm deviated less than 25 % from the *HRT* estimated from the mass of water present in the filter. In the presence of biofilm, this deviation was more than 600 %. The tracer residence time in the presence of biofilm is expected to be an overestimation of the hydraulic residence time. The heavy tails of the E-curves can be explained by

diffusion of the tracer substance into the biofilm, later followed by diffusion back into the water phase (e.g. Rozzi & Massone, 1995). Because of this, the tracer retention in the filter is expected to be much longer than the hydraulic retention as such. This explains the discrepancy between the *HRT* estimated from the amount of water in the filter and the measured *TRT* in the presence of biofilm.

2.3. Biofilm and Suspended Solids Characterization

2.3.1. Biofilm Density

Biofilm density was determined by measuring the dry weight (24 hours at 100 °C) of a known volume (2 mL) of biofilm, which was scraped off the trickling filter's carriers. Three replicates were performed, for which the biofilm was sampled from three different carriers, taken from different locations in the filter. The biofilm density was found to be 38.8 ± 0.8 g/L. This corresponds well with the typical value of 40 g/L which is e.g. mentioned in Melcer *et al.* (1995).

2.3.2. Biofilm Thickness

Total biofilm thickness was determined using two different methods: (1) based on the wet and dry biofilm mass attached to individual carriers, and (2) based on the mass of the entire filter unit.

Based on mass of individual carriers

The wet biofilm mass attached to one carrier was calculated as the difference of the wet (but leaked out) mass of a carrier taken out of the filter, and the dry mass of a 'clean' carrier. The associated dry biofilm mass is obtained as the difference of the dried mass (24 hours at 100 °C) of the carrier, and the dry mass of a 'clean' carrier. The wet biofilm volume was derived from its wet mass by assuming a density of 1 kg/L. The dry biofilm mass was calculated back to wet biofilm volume by means of the measured biofilm density of 38.8 g/L (see above). Biofilm thickness was obtained by dividing the wet biofilm volume by the surface area of one carrier material (Table 6.4).

Table 6.4. Total biofilm thickness based on mass of individual carriers

	May 18	June 11
Based on wet biofilm mass	$430 \pm 64 \mu m$	$526 \pm 205 \mu m$
Based on dry biofilm mass	$428 \pm 86 \mu m$	$687 \pm 354 \mu m$
Number of measurements	4	3

Based on the entire filter unit mass

The wet biofilm mass present in the filter could be determined by subtracting the total (static + dynamic) water mass and the dry filter mass (see higher) from the total filter mass. This was converted to volume using a density of 1 kg/L. By dividing this volume by the total carrier surface area within the filter (46.86 m^2), an average biofilm thickness (over the entire filter) was obtained.

The on-line mass measurements during the experiments, together with the calculated biofilm thickness, are illustrated in Figure 6.6. During the first month of operation, the calculated biofilm thickness evolved from 50 to $100 \mu\text{m}$. The next month it quickly evolved to more than $900 \mu\text{m}$. Because of the balance's limited capacity, it was necessary to reduce the filter's mass by feeding with only tap water for 1 week. This reduced biofilm thickness, which varied between 500 and $750 \mu\text{m}$ during the next 2 months. The average calculated biofilm thickness over the entire period was $410 (\pm 260) \mu\text{m}$.

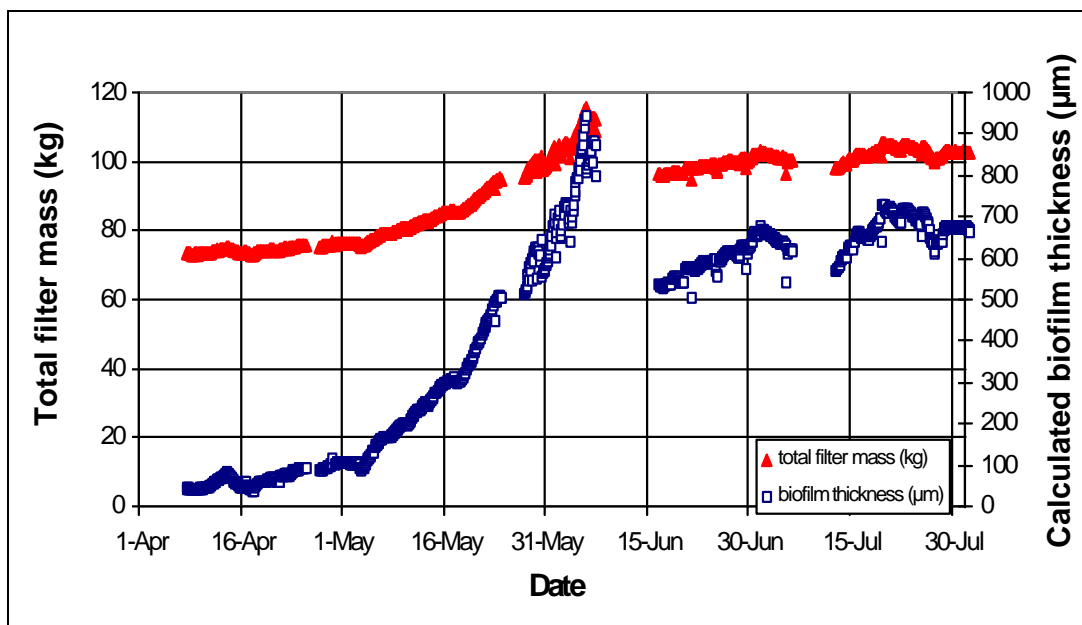


Figure 6.6. Filter mass and calculated total biofilm thickness

Interpretation and discussion

The average total biofilm thickness measurements obtained using the different presented methods are in the same order of magnitude, which shows the reliability of the on-line results.

In biofilm modeling after Melcer *et al.* (1995), the active biofilm thickness is required rather than the total thickness. In the case of LAS biodegradation, presence of oxygen is needed for activity (e.g. Jimenez *et al.*, 1991). However, it may be that only the upper layer of a biofilm is aerobic (e.g. Horn & Hempel, 1997). In the measurements presented here, the total biofilm thickness was determined, thus including both active and inactive biomass. Hence, these measurements can not be used as such to describe the active biofilm thickness.

Ramsing *et al.* (1993) analyzed the O₂ profiles in a 4500 μm thick trickling filter biofilm. They found a maximal O₂ penetration depth of 400 μm ; O₂ levels dropped below 1 mg/L at a depth of 200 μm . This biofilm was incubated using a medium with a COD of 90 mg/L. In the trickling filter described in this chapter, the biofilm was in contact with higher COD levels (between \sim 200 mg/L at the filter's top and \sim 100 mg/L at its bottom) which are expected to have caused a faster O₂ depletion in the biofilm, and hence a lower penetration depth. In Verstraete (1992), it is mentioned that - in general - a biofilm using organics is only functional to a depth of 50 - 100 μm . In a calculation example for a trickling filter, Henze *et al.* (1995) derived an O₂ penetration depth of 117 μm .

Based on these different considerations, it is a realistic assumption that from May onwards, the biofilm thickness which was active in LAS degradation was in the order of 100-200 μm .

2.3.3. Suspended Solids

Suspended solids were determined in the influent, the pumping reservoir, the filter outflow, and the final effluent. Duplicate measurements were made at four different dates, resulting in the following values: influent: 124 ± 51 mg/L, pumping reservoir: 22 ± 14 mg/L, filter outflow: 33 ± 31 mg/L, effluent: 15 ± 8 mg/L. The variability was especially high for the filter outflow. This is most probably due to the irregularity of the biomass sloughing process. Based on the SS measurements in the filter outflow and in the final effluent, a solids removal efficiency in the settler of (36.5 ± 7.5) % could be calculated.

2.3.4. LAS and COD Removal Experiments

Four different experimental series were conducted. In series (A) and (B), only the short recycle (i.e., bypassing the settler) was used. In series (A), the operating conditions were typically high-rate, while in series (B), conditions were closer to low-rate as the recycle flow was much lower. Series (C) was conducted to determine the influence of the long recycle (i.e., over the settler). Except for the recycle regime, it was identical to series (A). In series (D), the influent LAS concentration was 3-4 times higher than in the other experimental series. Due to a malfunctioning valve there was no short recycle, hence the recycle regime was also different. The experimental conditions in the different series are given in Table 6.5 below. LAS and COD concentrations were measured at four locations: (1) influent (total); (2) pumping reservoir (total); (3) filter outflow (total); (4) final effluent (total + dissolved). The average total biofilm thickness is also given in Table 6.5. As mentioned higher, the active biofilm thickness was expected to be lower (100-200 μm in all series).

Table 6.5. Experimental conditions in the pilot-scale trickling filter
(for LAS and COD removal experiments)

	Series A	Series B	Series C	Series D
Date (from - to)	28-Apr 28-May	28-May 4-Jun	11-Jun 2-Jul	2-Jul 3-Aug
Influent flow rate (mL/min)	290	290	290	290
Recycle ratio (-)	3.5	0.5	3.5	3.5
- Short recycle ratio (-)	3.5	0.5	1.75	0
- Long recycle ratio (-)	0	0	1.75	3.5
Influent COD (mg/L) (measured)	414	360 ± 8	397 ± 94	387 ± 17
Influent LAS (mg/L) (measured)	5.3 ± 2.1	3.5 ± 0.5	4.2 ± 0.9	15.2 ± 4.5
Total biofilm thickness (µm)	100 - 500	500 - 700	500 - 700	550 - 750

3. Analytical Methods

LAS was measured by means of an aspecific analytical method for anionic surfactants based on the Azure-A dye reaction, after Den Tonkelaar & Bergshoeff (1969). This method was applicable because no other anionic surfactants than LAS were present in the filter's synthetic influent. The LAS samples were preserved by adding 3% formaline solution (1% formaldehyde). COD was determined by means of Dr. Lange test kits (Dr. Bruno Lange GmbH). Dissolved effluent samples were obtained after filtration using an Schleicher & Schuell filter (S&S 597½). Suspended solids were determined after Standard Methods (APHA *et al.*, 1995).

4. Results & Discussion

4.1. Trickling Filter - LAS and COD Removal Experiments

4.1.1. Results

An overview of the LAS measurements and removal efficiencies is given in Table 6.6. The measurements in the pumping reservoir were considered unreliable, as sampling (in this vessel as well as at all other locations) disrupted the hydraulic balance in this tank. Instead, concentrations for the pumping vessel were calculated from the mass balance of the measured concentrations in the influent and the recycle flows (assuming complete mixing of these flows). To derive the single pass LAS removal in the filter unit as such (i.e., filter outflow vs. pumping reservoir), these calculated concentrations were used.

The average COD removal efficiency which was measured in the trickling filter was 85 ± 6 %, with no significant difference between the different experimental series (Tukey test, $\alpha = 0.05$).

On average, LAS removal in the settler (i.e., between final effluent and filter unit's outflow) was negligible. The average calculated removal was close to zero, sometimes negative, and variability was very high. For COD, the average removal over the settler was $(16 \pm 21) \%$. The high variability can be explained by the poor settling properties of the filter's sludge, and by the very irregular sloughing behavior.

By means of a Tukey test ($\alpha = 0.05$) (SPSS software version 7.5, SPSS Inc.), no statistically significant difference was found between LAS removal in the first three experimental series. However, removal in Series D (with higher influent LAS levels) was significantly higher than in the other series. A Tukey test ($\alpha = 0.05$) for LAS effluent levels showed no significant difference between the LAS effluent concentration in all four experimental series.

Table 6.6. Overview of LAS measurements and removals in the pilot-scale trickling filter

	Series A	Series B	Series C	Series D
	Short Recycle	Short Recycle, Low rec. ratio	Short + Long Recycle	Long Recycle High LAS conc.
LAS influent (mg/L)	5.3 ± 2.1	3.5 ± 0.5	4.2 ± 0.9	15.2 ± 4.5
# measurements	9	4	7	5
LAS measurements (% relative to influent concentrations)				
Influent (total)	100	100	100	100
Pumping reservoir				
- measured (total)	74 ± 20	77 ± 20	61 ± 14	38 ± 14
- calculated (total)	$64 - 17$	$83 - 6$	$56 - 14$	$34 - 8$
Filter outflow (total)	54 ± 22	50 ± 17	44 ± 18	15 ± 11
Effluent				
- total	51 ± 17	52 ± 24	44 ± 17	15 ± 10
- dissolved	45 ± 16	41 ± 18	36 ± 14	7 ± 5
LAS removal (%)				
- complete WWTP	49 ± 17	48 ± 24	56 ± 17	90 ± 3
- single pass *	19 ± 14	41 ± 16	25 ± 15	58 ± 19

* based on *calculated* concentrations in the pumping reservoir

4.1.2. Discussion

Filter COD removal performance

The COD removal experiments showed that the trickling filter had a normal treatment efficiency. The measured COD removal of $85 \pm 6 \%$ corresponds well with ATV (1985), whose rule of thumb predicts a treatment efficiency of $(93 - 17 * B_V) \% = 82.8 \%$ in this case. There was no significant effect of the different experimental operating conditions on COD elimination.

Comparison of experimental series (LAS removal)

No significant difference in LAS removal was found between the first three experimental series. When the lower recycle ratio was applied (series B) the single pass removal was much higher than with the high recycle (series A), but this effect was neutralized by the smaller number of passes through the filter. Hence, no difference could be seen in the total LAS removal. Applying a long recycle (series C) next to the short one also had no detectable effect on LAS removal. This can be explained by the high similarity between the concentrations in the filter outflow and the settler outflow (both were identical in series C).

There was a clear effect of the influent LAS concentration on the removal efficiency. This effect was seen in the overall removal efficiency as well as in the single pass removal. LAS effluent levels in the different experimental series were not significantly different from each other. Hence, the LAS influent levels did not influence the LAS concentrations in the effluent. This could suggest that the amount of active biomass, which is capable of biodegrading LAS, may adapt itself to the higher LAS influent concentrations. Similar observations have been described for activated sludge by Birch (1991) and by Lee *et al.* (1998). On the other hand, this effect might also be due to the occurrence of different kinetics at higher LAS concentrations.

Effect of biofilm thickness

There are a number of reasons to assume that the total biofilm thickness had no effect on LAS removal. (1) LAS removal in series A, B, and C was not significantly different. On the other hand, the total biofilm thickness in series B and C was much higher than the biofilm thickness in series A. (2) In series D, LAS removal was significantly higher than in B and C. However, the biofilm thickness was similar in these three series. (3) The variability of LAS removal efficiency in series A (relative standard deviation = 35%) was similar to that in series B (rel. std. dev. = 50%) and C (rel. std. dev. = 30%). Hence, there was no detectable effect of the 5-fold increase in biofilm thickness during Series A. On the other hand, the variability in series D was very low (rel. std. dev. = 3%), even though the variation in biofilm thickness was similar to that found in series B and C.

Based on these considerations, it can be concluded that the active biomass thickness was identical in all four experimental series. A plausible value for the active biofilm thickness can be estimated as the minimal total biofilm thickness which occurred: between 100 and 200 μm . This confirms the considerations mentioned higher in 2.3.2.

5. Conclusions

The removal of LAS in a pilot-scale trickling filter waste water treatment plant was measured as a function of different operating conditions, and at high and normal LAS influent levels. The effect of the operating conditions (short versus long recycle, high versus low recycle ratio) was not significant. At normal LAS influent levels (4 mg/L), LAS removal in this high-rate filter was in the order of 50 %. On the other hand, a COD removal efficiency between 70 % and 90 % was monitored. When a 3-4 times higher LAS level was present in the influent (15 mg/L) (with an unchanged COD concentration), the LAS elimination increased to 90 %.

The higher LAS removal efficiency related to the increased influent concentration may have been due to biological adaptation to the higher concentrations. On the other hand, it may also indicate a different kinetic behavior at high concentrations. Further research (preferably dynamic experiments) is required to study the effect of biological adaptation to different LAS influent concentrations on removal efficiency.

Chapter 7

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A Steady-State Non-Equilibrium Chemical Fate Model for Trickling Filters

a condensed version of this chapter, together with chapter 6, was submitted for publication as:

Boeije, G., Vanhooren, H. & Vanrolleghem, P.A. (submitted) *Development of a steady-state chemical fate model for trickling filters supported by measurements in a pilot-scale plant.* Submitted to Environmental Science and Technology.

Chapter 7

A Steady-State Non-Equilibrium Chemical Fate Model for Trickling Filters

1. Introduction

Over the last 20 years, several models which describe the fate and behavior of individual organic compounds in biofilms have been formulated (e.g. Harremoës, 1978; Rittmann & McCarty, 1980; Namkung *et al.*, 1983; Stratton *et al.*, 1983; Namkung & Rittmann, 1986a and 1986b; Golla & Overcamp, 1990; Melcer *et al.*, 1995). Specific applications to trickling filter systems are given in e.g. Duncan *et al.* (1995), Melcer *et al.* (1995) and Snape *et al.* (1995). In this chapter, the development of a chemical fate model for trickling filters is presented, based on the *SIMPLEBOX* approach (van de Meent, 1993) combined with the biofilm diffusion / biodegradation model of Melcer *et al.* (1995). The *SIMPLEBOX* approach calculates chemical fate under steady-state non-equilibrium conditions, using a mass balance between several completely mixed boxes. This method was also used for activated sludge modeling in *SimpleTreat* (Struijs *et al.*, 1991b), of which an adapted version was selected for use within the GREAT-ER project (described in chapter 5 of this thesis).

The biodegradation and sorption aspects of the newly developed fate model were tested by experimental data for the surfactant LAS (Linear Alkylbenzene Sulphonate) obtained in a pilot-scale trickling filter setup (see chapter 6 of this thesis). The model was also applied to predict the fate of LAS in two full-scale trickling filter plants in Yorkshire (UK), for which a detailed LAS removal study was performed in the scope of the GREAT-ER project (Holt *et al.*, 1998).

2. Model Formulation

2.1. Process Description

The modeled configuration was limited to the trickling filter process as such, i.e. a filtration unit coupled with a secondary settler (Figure 7.1). Primary settling was not taken into account. Short and long effluent recycles were considered (i.e. both before and after the secondary settler). The secondary settling process in a trickling filter plant is similar to that in activated sludge, the main difference being that sludge is not recycled.

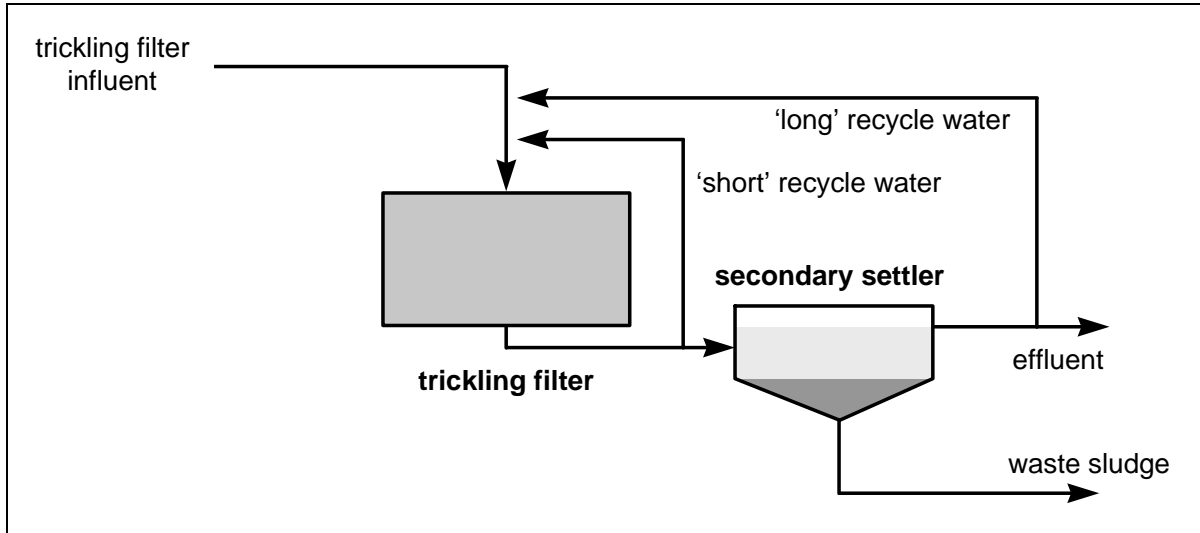


Figure 7.1. Trickling filter model - plant configuration

An overview of biological and chemical processes which may occur in a trickling filter is given in Figure 7.2. Chemicals are present in the dissolved phase and sorbed to suspended solids. Through ad-/desorption there may be an interchange between these two phases. The dissolved chemical can diffuse into the biofilm. Suspended solids with sorbed chemicals may be filtered out of the water; on the other hand chemicals associated with biofilm solids may be released to the water phase in the sloughing process. (Biological) degradation may take place both inside the biofilm and in the water, both in the adsorbed and the dissolved phases. Finally, the dissolved chemical may be subject to volatilization, and be removed with the ventilation air.

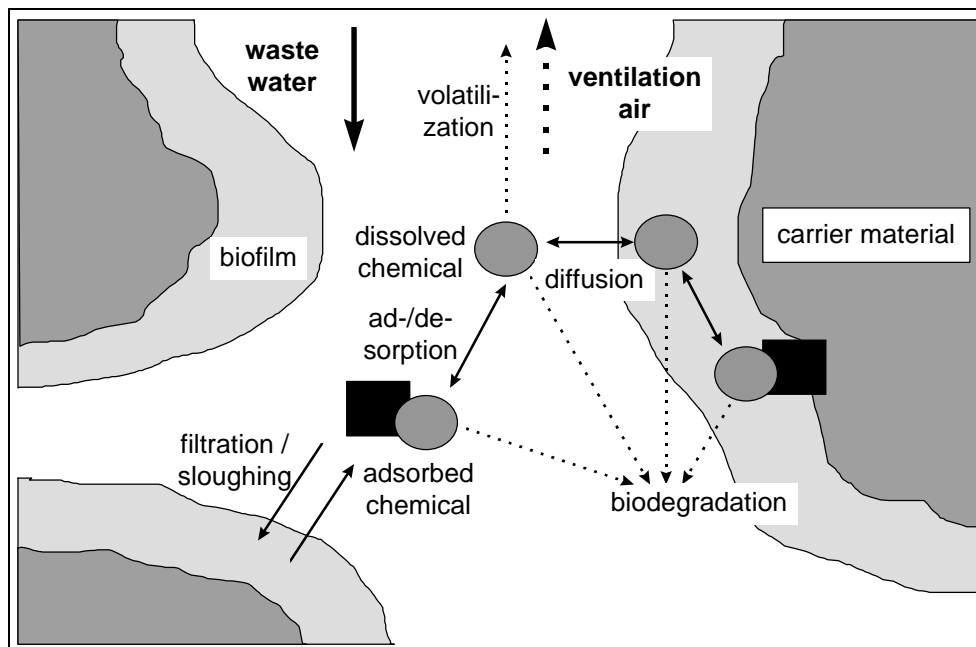


Figure 7.2. Chemical fate processes in a trickling filter (overview)

2.2. Systems Analysis and Segmentation

To apply the *SIMPLEBOX* approach, the trickling filter system was split up into a number of completely mixed boxes (Figure 7.3). The first segmentation was between the air above the plant, the filter unit, and the settler. The settler was further divided into a dissolved (water) and a sorbed (solids) phase. A settled sludge box (cf. *SimpleTreat*) was not needed, as sludge is not recycled. The filter itself was split up into several horizontal layers, connected in series (cf. tanks-in-series model to model imperfect plug flow hydraulics). The actual number of layers is determined by the hydraulics of the modeled filter unit, by the required accuracy and by the desired computation speed of the model.

Each horizontal layer of the filter was subdivided into three compartments (Figure 7.3, Figure 7.4): pore air, pore water (dissolved phase) and pore water (sorbed phase). Downward transport of chemicals through the filter unit is between the pore water phase of the different layers. By ventilation, pore air is transported upward between the layers. Within a layer, exchange processes take place between air and water (volatilization) and between the sorbed and dissolved phases. Biodegradation mainly occurs by biofilm activity. Continuous chemical diffusion from the pore water into the biofilm is only possible if a concentration gradient is maintained by biodegradation in the biofilm. These coupled processes are dealt with by the steady-state biofilm model of Melcer *et al.* (1995). In this model the calculated diffusion flux from the pore water (dissolved phase) into the biofilm is expressed as removal out of the water phase. In this approach, the biofilm compartment need not be represented as an extra box (Figure 7.4). To simplify the model, it was assumed that filtration and release (by sloughing) of the sorbed chemical balance each other, resulting in a zero net effect. Furthermore, chemical sorption equilibria within the biofilm were not considered in the biodegradation model.

Next to the between-layer transport, there is transport of air from the top layer of the filter to the air above the plant, and volatilization from the settler surface. There is water and solids transport by means of the long and short effluent recycles to the first filter layer. Influent (dissolved and sorbed phase) enters the plant into the top filter layer, and effluent (dissolved and sorbed phase) leaves the plant via the settler, as well as waste sludge (sorbed phase only). Finally, the air above the plant is refreshed by the wind and ambient air flows counter-current through the filter unit (either by the chimney effect or by forced aeration).

As the number of layers n used to describe the filter unit is not necessarily fixed, the following flexible box numbering approach was followed in this text (Figure 7.3). The 'outside world' is box 0; the air compartment above the WWTP is box 1. Each horizontal layer i has the box numbers L_i+1 until L_i+3 (dissolved, sorbed, air), with $L_i = 1+3*(i-1)$. The settler has box numbers $S+1$ and $S+2$ (dissolved, sorbed), with $S = 1+3*n$.

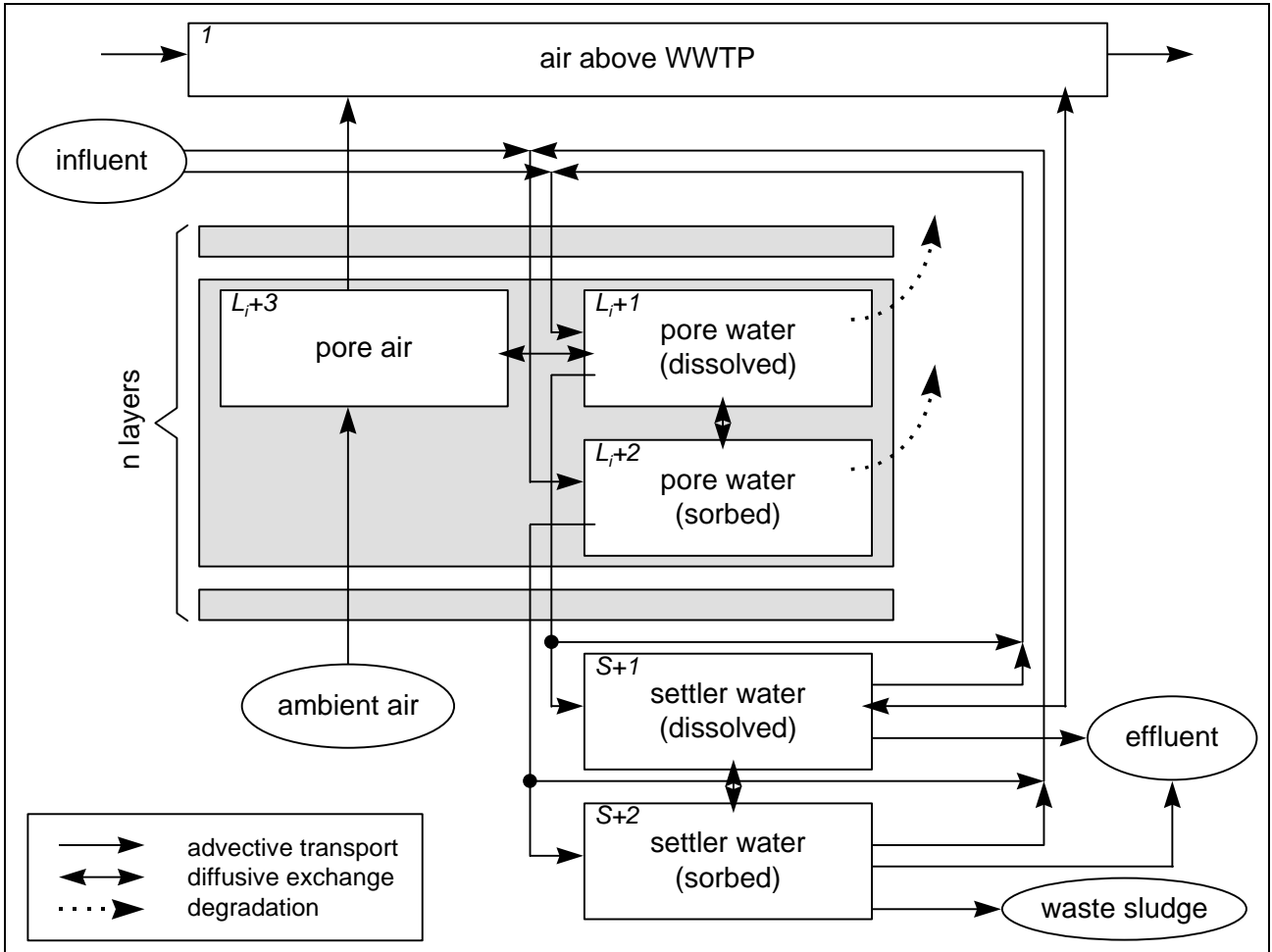


Figure 7.3. Entire trickling filter plant: model scheme

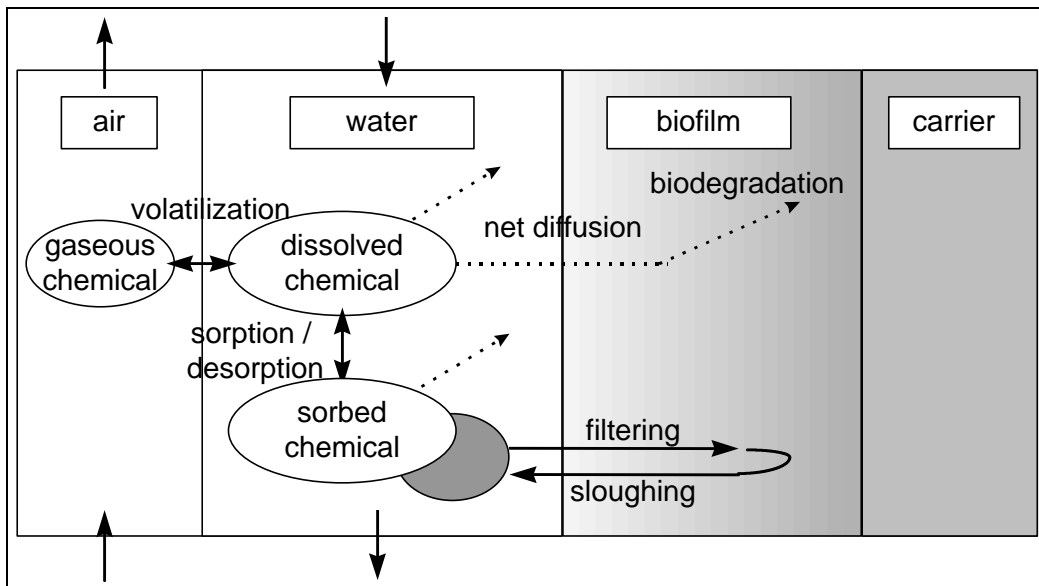


Figure 7.4. Processes in one horizontal trickling filter layer: model scheme

2.3. Calculations

2.3.1. Influent

The influent (dissolved and sorbed chemical fraction) enters the treatment system simultaneously into box 2 and box 3. Without a primary settler, the dissolved and sorbed influent fractions are assumed to be in complete equilibrium:

$$\text{- into filtration unit (dissolved):} \quad \Phi_{in}^2 = \Phi_{in}^{tf} \cdot \frac{1}{1 + 10^{-6} \cdot SS_{sewage} \cdot K_d^{sewage}} \quad [7.1]$$

$$\text{- into filtration unit (sorbed):} \quad \Phi_{in}^3 = \Phi_{in}^{tf} \cdot \frac{10^{-6} \cdot SS_{sewage} \cdot K_d^{sewage}}{1 + 10^{-6} \cdot SS_{sewage} \cdot K_d^{sewage}} \quad [7.2]$$

If a primary settler model is connected in front of the trickling filter model, the dissolved/sorbed fractionation obtained in the former is used to calculate the influent partitioning:

$$\text{- into filtration unit (dissolved):} \quad \Phi_{in}^2 = \Phi_{in}^{tf} \cdot f_d^{primary} \quad [7.3]$$

$$\text{- into filtration unit (sorbed):} \quad \Phi_{in}^3 = \Phi_{in}^{tf} \cdot f_s^{primary} \quad [7.4]$$

2.3.2. Advective Transport Fluxes

The advective transport between layers is described for a generic layer with number i . Non trickling filter specific equations were taken from Struijs (1996).

Air advection

$$\text{- into / out of area above WWTP:} \quad ADV_{0,1} = ADV_{1,0} = h_{air} \cdot v_{wind} \cdot \sqrt{A_{filter} + A_{sec}} \quad [7.5]$$

$$\text{- air into / out of / between pores:} \quad ADV_{0,L_n+3} = ADV_{L_n+3,L_{n-1}+3} = Q^{air} \quad [7.6]$$

Water volume flow rates

$$\text{- into / out of WWTP:} \quad ADV_{0,L_n+1} = ADV_{S+1,0} = Q \quad [7.7]$$

$$\text{- propagation through filter:} \quad ADV_{L_i+1,L_{i+1}+1} = Q \cdot (1 + f_{rec}^1 + f_{rec}^2) \quad [7.8]$$

$$\text{- filter to secondary settler:} \quad ADV_{L_n+1,S+1} = Q \cdot (1 + f_{rec}^2) \quad [7.9]$$

$$\text{- effluent recycles:} \quad \text{- before settler:} \quad ADV_{L_n+1,2} = Q \cdot f_{rec}^1 \quad [7.10]$$

$$\text{- after settler:} \quad ADV_{S+1,2} = Q \cdot f_{rec}^2 \quad [7.11]$$

Solids volume flow rates

In the *SIMPLEBOX* approach, all flow rates are expressed as volume flows. Hence, solids mass fluxes were recalculated to volumetric fluxes, using the solids' density.

$$\text{- influent into WWTP: } ADV_{0,3} = \frac{SS_{sewage}}{10^6 \cdot r_{solids}^{sewage}} \cdot Q \quad [7.12]$$

$$\text{- propagation through filter: } ADV_{L_i+2, L_{i+1}+2} = \frac{SS_{tf}}{10^6 \cdot r_{solids}^{tf}} \cdot Q \cdot (1 + f_{rec}^1 + f_{rec}^2) \quad [7.13]$$

$$\text{- filter to secondary settler: } ADV_{L_n+2, S+2} = \frac{SS_{tf}}{10^6 \cdot r_{solids}^{tf}} \cdot Q \cdot (1 + f_{rec}^2) \quad [7.14]$$

$$\text{- effluent recycles: } \quad \text{- before settler: } ADV_{L_n+2,3} = \frac{SS_{tf}}{10^6 \cdot r_{solids}^{tf}} \cdot Q \cdot f_{rec}^1 \quad [7.15]$$

$$\quad \quad \quad \text{- after settler: } ADV_{S+2,3} = (1 - R_{sec}^{SS}) \cdot \frac{SS_{tf}}{10^6 \cdot r_{solids}^{tf}} \cdot Q \cdot f_{rec}^2 \quad [7.16]$$

$$\text{- effluent + waste sludge out of WWTP: } ADV_{S+2,0} = \frac{SS_{tf}}{10^6 \cdot r_{solids}^{tf}} \cdot Q \quad [7.17]$$

2.3.3. Diffusive Exchange

For the calculation of the diffusive exchanges, the fugacity approach is applied. Expressions for fugacities, diffusion coefficients and kinetics were taken from Struijs (1996), after Mackay and Paterson (1982).

Fugacities

$$\text{- air: } Z_{air} = \frac{1}{R \cdot (t_{air} + 273)} \quad [7.18]$$

$$\text{- water: } Z_{water} = \frac{1}{H} \quad [7.19]$$

$$\text{- filter unit solids: } Z_{tf} = \frac{K_d^{tf} \cdot r_{solids}^{tf}}{H} \quad [7.20]$$

Box volumes

$$\text{- air above the WWTP: } V_1 = (A_{tf} + A_{sec}) \cdot h_{air} \quad [7.21]$$

$$\text{- filter unit (water): } V_{L_i+1} = \frac{V_{tf} \cdot e_{tf} \cdot f_{water}^e}{n} \quad [7.22]$$

- filter unit (suspended solids):
$$V_{L_i+2} = \frac{V_{tf} \cdot e_{tf} \cdot f_{water}^e}{n} \cdot \frac{SS_{tf}}{10^6 \cdot r_{solids}^{tf}} \quad [7.23]$$

- filter unit (air):
$$V_{L_i+3} = \frac{V_{tf} \cdot e_{tf} \cdot f_{air}^e}{n} \quad [7.24]$$

- secondary settler (water):
$$V_{S+1} = V_{sec} \quad [7.25]$$

- secondary settler (solids):
$$V_{S+2} = V_{sec} \cdot \frac{(1 - R_{sec}^{SS}) \cdot SS_{tf}}{10^6 \cdot r_{solids}^{tf}} \quad [7.26]$$

The sum of pore fractions $f_{water}^e + f_{air}^e + f_{biofilm}^e = 1$. These fractions may depend on the type and size of carrier material, on the biofilm age, and on hydrodynamic conditions.

Media volume flow rates

$$D_{i,j} = D_{j,i} = \frac{k_{diff}}{\frac{1}{V_i \cdot Z_i} + \frac{1}{V_j \cdot Z_j}} \quad [7.27]$$

Next, the exchange from box i to j (expressed as a volume flow rate) is calculated as:

$$XCH_{i,j} = \frac{D_{i,j}}{Z_i} \quad [7.28]$$

Suspended solids / water exchange

- filter unit:

$$D_{L_i+1,L_i+2} = D_{L_i+2,L_i+1} = \frac{k_{tf}^{sorb}}{\frac{1}{V_{L_i+1} \cdot Z_{water}} + \frac{1}{V_{L_i+2} \cdot Z_{tf}}} \quad [7.29]$$

$$\rightarrow XCH_{L_i+1,L_i+2} = \frac{D_{L_i+1,L_i+2}}{Z_{water}} \quad XCH_{L_i+2,L_i+1} = \frac{D_{L_i+2,L_i+1}}{Z_{tf}}$$

- secondary settler:

$$D_{S+1,S+2} = D_{S+2,S+1} = \frac{k_{sec}^{sorb}}{\frac{1}{V_{S+1} \cdot Z_{water}} + \frac{1}{V_{S+2} \cdot Z_{tf}}} \quad [7.30]$$

$$\rightarrow XCH_{S+1,S+2} = \frac{D_{S+1,S+2}}{Z_{water}} \quad XCH_{S+2,S+1} = \frac{D_{S+2,S+1}}{Z_{tf}}$$

The kinetic rates for sorption / desorption are given in Table 5.1 (chapter 5). For trickling filter solids, the same sorption kinetics were assumed as for activated sludge (after Struijs, 1996).

Air / water exchange

Volatilization was modeled using the two-layer approach (Liss and Slater, 1974; Mackay and Leinonen, 1975), based on Struijs (1996).

- filter unit:

Surface volatilization was assumed to occur at the air / water interface between pore air and pore water. It was assumed that the aeration rate (either natural or forced) does not influence the volatilization process directly (only indirectly by transporting air out of the filter). Hence, the approach of Mackay *et al.* (1985) could be used to describe this process.

$$D_{L_i+3, L_i+1} = D_{L_i+1, L_i+3} = \frac{A_{a/w}^{L_i}}{\frac{1}{K_{air} \cdot Z_{air}} + \frac{1}{K_{water} \cdot Z_{water}}} \quad [7.31]$$

$$\rightarrow \quad XCH_{L_i+3, L_i+1} = \frac{D_{L_i+3, L_i+1}}{Z_{air}} \quad XCH_{L_i+1, L_i+3} = \frac{D_{L_i+1, L_i+3}}{Z_{water}}$$

$A_{a/w}^{L_i}$ is the interfacial area between pore air and pore water within one horizontal layer of the trickling filter unit. This can be calculated from the filter's specific air / water interfacial area, $a_{a/w}$.

$$A_{a/w}^{L_n} = a_{a/w} \cdot \frac{V_{tf}}{n}$$

- secondary settler:

For the secondary settler, the expressions for the transfer coefficients $D_{i,j}$ were taken directly from Struijs (1996), after Mackay *et al.* (1985).

$$D_{1, S+1} = D_{S+1, 1} = \frac{A_{sec}}{\frac{1}{K_{air} \cdot Z_{air}} + \frac{1}{K_{water} \cdot Z_{water}}} \quad [7.32]$$

$$\rightarrow \quad XCH_{1, S+1} = \frac{D_{1, S+1}}{Z_{air}} \quad XCH_{S+1, 1} = \frac{D_{S+1, 1}}{Z_{water}}$$

Pore water / biofilm exchange

By diffusion, chemicals are exchanged between the pore water's dissolved phase and the biofilm. This process was not described as such, but was considered together with biodegradation as a lumped chemical elimination from the pore water.

2.3.4. Biodegradation

Biodegradation in the dissolved phase of the water compartment consists of biodegradation by suspended biomass and disappearance of the chemical into the biofilm. This can be expressed as the sum of two first-order rates. In the sorbed phase of the water compartment, only the suspended biomass activity is taken into account.

Suspended biomass

“Double” first-order kinetics (both in active biomass and in chemical concentration) can be used to describe biodegradation. A correction factor can be applied for the sorbed phase, to take into account the lower bio-availability (e.g. Lee *et al.*, 1998).

$$k = K_b \cdot SS_{act} \quad [7.33]$$

Biofilm

Melcer *et al.* (1995) developed a biofilm model which predicts the mass flux of a chemical substance from the bulk water phase into the biofilm phase per unit of interfacial area. This process is driven by diffusion and by biodegradation (which is needed to maintain a concentration gradient to allow diffusion into the biofilm). An analytical solution for the per area mass flux N_b into the biofilm is:

$$N_b = K_L \cdot \frac{D_e \cdot r_1 \cdot \tanh(r_1 \cdot L_f)}{D_e \cdot r_1 \cdot \tanh(r_1 \cdot L_f) + K_L} \cdot C$$

$$r_1 = \sqrt{\frac{X_f \cdot K_b}{D_e}} \quad [7.34]$$

$$K_L = \frac{D_l}{L}$$

The corresponding chemical mass flux calculation to express chemical elimination via degradation in the *SIMPLEBOX* approach is:

$$\Phi_{degradation} = -k \cdot C \cdot V \quad [7.35]$$

The flux per unit surface area N_b can be related to the total degradation flux as follows:

$$N_b = \frac{-\Phi_{degradation}}{A} = \frac{k \cdot C \cdot V}{A} \quad [7.36]$$

From this, the first-order elimination rate for combined diffusion and biodegradation $k_{biofilm}$ can be obtained as:

$$k_{biofilm} = \frac{A}{V} \cdot \frac{N_b}{C} = a_{b/w} \cdot K_L \cdot \frac{D_e \cdot r_1 \cdot \tanh(r_1 \cdot L_f)}{D_e \cdot r_1 \cdot \tanh(r_1 \cdot L_f) + K_L} \quad [7.37]$$

Biofilm related parameters

A typical value for the biofilm density X_f is 40 kg/m^3 (Melcer *et al.*, 1995). Chemical diffusivity in the biofilm D_e can be estimated as a fraction (typically 80 %) of the diffusivity in pure water D_l (Verstraete, 1992; Melcer *et al.*, 1995). Biofilm thickness L_f is a.o. related to organic loading, to flow and flow velocity, and to hydraulic shear stress. As estimations of L_f (e.g. Rittmann and McCarty, 1980 and 1981) require intensive calculations and specific data, this was considered inappropriate for use in a simple model. As an alternative, a default value for biofilm thickness can be used. A value in the range of $100\text{-}200 \mu\text{m}$ is appropriate, as substrate and/or oxygen limitation will typically reduce the active biofilm thickness to this order of magnitude. A default value for the stagnant water layer thickness L (i.e., the laminar water layer directly in contact with the biofilm) is $100 \mu\text{m}$ (after Melcer *et al.*, 1995).

In the presented model, the biofilm / water interfacial area has to be known to estimate diffusion into the biofilm. A biofilm consists of two different structures: a base film, in which the particulate components form a solid matrix, and a surface film, which has a discontinuous structure (Figure 7.5) (e.g. Wanner & Gujer, 1986; Suschka, 1987; Characklis & Marshall, 1990). It can be assumed that the surface area of the base film is equal to that of the carrier material. However, the actual biofilm / water interfacial area is determined by the (higher) surface area of the irregular surface film. No simple or universal estimation methods for the biofilm / water interfacial area exist. In this thesis, a correction factor $Z_{biofilm} = 2$ was used to convert carrier surface to biofilm surface.



Figure 7.5. Biofilm morphology (schematic)

3. Sensitivity Analysis

A sensitivity analysis of the trickling filter model was performed using three hypothetical substances: the standard *SimpleTreat* benchmark chemical Hypotheticum (Struijs, 1996), which is affected by all relevant fate processes in the model (volatilization, sorption and biodegradation), a Chemical A (volatile), and a Chemical B (sorbing and degradable) (Table 7.1). Contrary to Struijs (1996), Hypotheticum was assumed to be also degraded in the sorbed phase. For the diffusion coefficient D an average value from Melcer *et al.* (1995) was taken. Further, a hypothetical but realistic trickling filter plant was defined (Table 7.2). The applied environmental conditions and physical / chemical defaults were taken from Struijs (1996).

Table 7.1. Sensitivity analysis: hypothetical chemical properties

		Hypotheticum	Chemical A	Chemical B
K_d^{tf}	(L/kg)	370	10^{-6}	2000
K_d^{sewage}	(L/kg)	300	10^{-6}	2000
H	(-)	1	100	10^{-6}
K_b	$((g/m^3)^{-1} \cdot s^{-1})$	$9.26 \cdot 10^{-9}$	0	$2.78 \cdot 10^{-7}$
a_{sorbed}	(-)	0.5	-	0.5
D_l	(m^2/s)	$5.55 \cdot 10^{-5}$	$5.55 \cdot 10^{-5}$	$5.55 \cdot 10^{-5}$

Table 7.2. Sensitivity analysis: plant parameters and default values

Dimensions		Flows	
A_{ff}	300 m^2	Q	0.017361 m^3/s
V_{ff}	1125 m^3	f_{rec}^1	0 -
A_{sec}	62.5 m^2	f_{rec}^2	1 -
V_{sec}	125 m^3	Q^{air}	1.7 m^3/s
Biofilm and Carrier		Suspended Solids	
e	0.5 -	SS_{ff}	200 g/m^3
f_{water}	0.05 -	SS_{sewage}	200 g/m^3
f_{air}	0.90 -	R_{sec}^{SS}	0.95 -
$a_{a/w}$	100 m^2/m^3		
$a_{b/w}$	200 m^2/m^3		
L	10^{-4} m		
L_f	$1.5 \cdot 10^{-4}$ m		
X_f	40000 g/m^3		
Default Values			
h_{air}	10 m	k_{tf}^{sorb}	$1.925 \cdot 10^{-3}$ s^{-1}
v_{wind}	1 m/s	k_{sec}^{sorb}	$1.925 \cdot 10^{-4}$ s^{-1}
r_{solids}^{tf}	1.4 kg/L	K_{air}	$2.78 \cdot 10^{-3}$ m/s
r_{solids}^{sewage}	1.4 kg/L	K_{water}	$2.78 \cdot 10^{-5}$ m/s
t_{air}	20 °C		

Sensitivities were calculated for all parameters, for the three test substances. The number of layers n was fixed at 5. Relative sensitivities were obtained numerically, by increasing the value of each parameter with 1%, and then applying the following calculation:

$$S_R = \frac{\Delta R^*/R^*}{\Delta P/P} = \frac{\Delta R^*/R^*}{0.01 \cdot P/P} = 100 \cdot \Delta R^*/R^* \quad [7.38]$$

Note that in this analysis, the effluent recycle was always after the settler (i.e. only long recycle: $f_{rec}^1 = 0$). The resulting relative sensitivities are shown below in Table 7.3. On average, the highest sensitivities were found for R_{sec}^{SS} (solids removal in the settler), Q (influent flow), SS_{tf} (suspended solids in the trickling filter water phase), K_d^{tf} (chemical sorption equilibrium constant), V_{tf} (filter unit volume), ϵ (carrier material's porosity), f_{water} (fraction of water in the filter pores) and K_b (chemical biodegradation rate constant).

It is stressed that this is a local linear sensitivity analysis of a non-linear model. Because the local analysis was conducted at three different points (3 completely different chemicals), a tentative interpretation could be made about which parameters are generally most sensitive and which are not. A full sensitivity analysis, on the other hand, was outside the scope of this work.

Chemical specific interpretation

The most sensitive parameters for Hypotheticum are related to sorption and settling, volatilization and (via the hydraulics) to biological contact time. This could be expected as the chemical undergoes the three associated elimination processes. For Chemical A, the most sensitive parameters all have an impact on volatilization, as this is the only active fate process. Note that for this substance, no parameters have a relative sensitivity higher than 5 %, and only 4 parameters have a sensitivity above 1 %. The removal prediction of Chemical B was mainly influenced by parameters related to biodegradation and sorption / settling. This was again expected as Chemical B is highly sorbing and degradable.

Implications for data collection

Except for the diffusion coefficient D_l and the sorbed phase biodegradation correction, all chemical properties may have high sensitivities, depending on the nature of the chemical. Hence the accuracy of these (relevant) parameters should be maximized. D_l has a very low sensitivity (rounded to 0% in all three examined cases); using a default value for this parameter will not significantly affect the model's output.

The only important treatment plant dimension is the volume of the filter unit. The flow Q is always very important; the recycle ratio somewhat less. The air flow Q^{air} only has a high sensitivity for volatile chemicals.

The porosity and the water fraction in the pores had a high sensitivity for 2 substances, while the fraction of air in the pores had no importance. The interfacial areas air/water and biofilm/water are important if this interface is limiting for mass transfer or biodegradation - hence, this is chemical-dependent. The biofilm-related parameters L_f and X_f are sensitive ones for biodegradable compounds. The stagnant water layer thickness L always has a low sensitivity. The parameters related to suspended solids and settling are sensitive for highly sorbing chemicals. SS_{sewage} has a much lower importance than SS_{tf} .

Most of the default values have a low sensitivity in all cases. However, the sorption kinetics constant in the trickling filter k_{tf}^{sorb} is important for sorbing chemicals, and the mass transfer coefficients K_{air} and K_{water} may be important for volatile substances.

Table 7.3. Sensitivity analysis: relative sensitivities to trickling filter model parameters

Parameter	S_R (%)			
	Hypotheticum	Chemical A	Chemical B	Average
Chemical Properties				
K_d^{tf}	<u>47</u>	0	<u>17.1</u>	<u>22</u>
K_d^{sewage}	6.7	0	3.3	3.3
H	<u>22</u>	3.7	0	8.5
K_b	<u>10</u>	0	<u>24</u>	<u>11.5</u>
a_{sorbed}	0.02	0	0.32	0.11
D_l	0	0	0	0
Plant Parameters				
A_{tf}	0.01	0	0	0
V_{tf}	<u>20</u>	0.31	<u>25</u>	<u>15.2</u>
A_{sec}	1.88	0.03	0	0.64
V_{sec}	0.28	0	-0.04	0.08
Q	<u>-42</u>	<u>-4.4</u>	<u>-25</u>	<u>-24</u>
f_{rec}^2	<u>17.9</u>	<u>-1.53</u>	<u>6.6</u>	<u>7.7</u>
Q^{air}	<u>20</u>	3.7	0	7.9
e	<u>20</u>	0	<u>25</u>	<u>15.1</u>
f_{water}	<u>20</u>	0	<u>25</u>	<u>15.1</u>
f_{air}	0	0	0	0
$a_{a/w}$	0.01	0.31	0	0.11
$a_{b/w}$	8.6	0	<u>21</u>	9.7
L	0	0	0	0
L_f	8.6	0	<u>21</u>	9.7
X_f	8.6	0	<u>21</u>	9.7
SS_{tf}	<u>49</u>	0	<u>21</u>	<u>23</u>
SS_{sewage}	6.7	0	3.3	3.3
R_{sec}^{SS}	<u>48</u>	0	<u>35</u>	<u>28</u>
h_{air}	0.02	0.01	0	0.01
Default Values				
v_{wind}	0.02	0.01	0	0.01
r_{solids}^{tf}	0	0	0	0
r_{solids}^{sewage}	0	0	0	0
t_{air}	<u>-1.49</u>	-0.26	0	-0.58
k_{tf}^{sorb}	<u>10.2</u>	0	0.76	3.7
k_{sec}^{sorb}	0.28	0	-0.04	0.08
K_{air}	1.82	0.07	0	0.63
K_{water}	0.07	0.27	0	0.12

Notation: **$S_R > 10\%$** , $1\% < S_R < 10\%$, $S_R < 1\%$

4. Model Testing for LAS

The biodegradation and sorption aspects of the presented fate model were tested by applying it to a pilot-scale trickling filter plant (chapter 6 of this thesis) and to two full-scale plants for which an LAS monitoring campaign was performed in the framework of the GREAT-ER project (Holt *et al.*, 1998).

The same environmental and default values as in the sensitivity analysis were applied (Table 7.2, bottom section). Air temperature was approximately 20 °C, both in the lab and in the field study. The parameters Q^{air} , f_{air} and h_{air} were not required to model the fate of the non-volatile LAS, as they are only related to volatilization.

The chemical properties used to model LAS are given below in Table 7.4. The K_d (for sewage and trickling filter solids) and H coefficients were taken from Cowan *et al.* (1993b). For the value of D_b , an average from Melcer *et al.* (1995) was taken (not specifically for LAS), as the sensitivity for this parameter is very low. The sorbed phase biodegradation correction factor a_{sorbed} was set to 1 (cf. Cowan *et al.*, 1993b; Boeije *et al.*, 1998b).

The double first-order biodegradation rate coefficient (K_b) of LAS was calculated from the first-order rate coefficient typically used for biodegradation by suspended biomass in activated sludge ($3 h^{-1}$, with mixed liquor $SS = 3000 g_{dwt}/m^3$) (e.g. Struijs *et al.*, 1991b).

Table 7.4. LAS chemical properties

K_d	2000 L/kg
H	$1 * 10^{-6} Pa.m^3.mol^{-1}$
K_b	$0.278 * 10^{-6} (g/m^3)^{-1}.s^{-1}$
a_{sorbed}	1 (-)
D_l	$55 * 10^{-6} m^2/s$

4.1. Pilot-scale Trickling Filter

Trickling filter plant

LAS removal measurements in a pilot-scale trickling filter plant (chapter 6 of this thesis) were used to test the presented fate model. Plant operating parameters were known; hydraulics and biofilm characteristics were measured or estimated (Table 7.5). Four experimental series were conducted, with different recycles (Table 7.5) and with a normal (4 mg/L) (series A, B and C) versus high (15 mg/L) LAS influent level (series D).

With a total flow of 1.3 L/min (series A, C and D), the *HRT* for a single pass through the filter was estimated to be 6.4 minutes (estimated $f_{water} = 4\%$). At 0.5 L/min (~ series B), the estimated *HRT* was 15.2 minutes (estimated $f_{water} = 3.7\%$) (see also chapter 6 of this thesis).

Measured LAS elimination efficiencies, both ‘single-pass’ and total, are given in Table 7.6 (see also chapter 6 of this thesis).

Table 7.5. Pilot-scale TF plant - model parameters

Known		
A_f	(m^2)	0.118
V_f	(m^3)	0.213
A_{sec}	(m^2)	0.049
V_{sec}	(m^3)	0.034
Q	(m^3/s)	$4.83 \cdot 10^{-6}$
f_{rec}^1, f_{rec}^2	(-)	Series A: 3.5, 0 Series B: 0.5, 0 Series C: 1.75, 1.75 Series D: 0, 3.5
e_f	-	96 %
Measured		
SS_f	(mg/L)	27.5
SS_{sewage}	(mg/L)	124
R_{sec}^{SS}	(-)	36.5 %
X_f	(g/m^3)	38800
Estimated		
$a_{a/w}$	(m^2/m^3)	100
$a_{b/w}$	(m^2/m^3)	200
L_f	(m)	0.000150
Default		
L	(m)	0.000100

Table 7.6. Pilot-scale TF plant - measured LAS removal efficiencies

Series	Total removal (%)	Single-pass removal (%)
A	49 ± 17	19 ± 14
B	48 ± 24	41 ± 16
C	56 ± 17	25 ± 15
D	90 ± 3	58 ± 19

Model testing

As all required model parameters were known, it was possible to apply the model to the pilot-scale trickling filter without any calibration based on the measured LAS elimination data. The resulting total and single-pass removal predictions for the 4 experimental series, next to their relative deviation from the measurements, are given in Table 7.7.

Table 7.7. Pilot-scale TF plant - uncalibrated predictions for LAS

Series	Total removal		Single-pass removal	
	Predicted	Relative deviation	Predicted	Relative deviation
A	55.2 %	+ 12.6 %	20.4 %	+ 7.5 %
B	57.2 %	+ 19.1 %	45.7 %	+ 11.5 %
C	57.0 %	+ 1.8 %	20.8 %	- 17.0 %
D	58.3 %	- 35.2 %	21.0 %	- 63.8 %

Next to the uncalibrated simulations, the single-pass removal predictions for the different experimental series were fitted to the measurements by tuning the parameter related to the amount of water in the filter (f_{water}). For series D, with a higher LAS influent concentration, the calibration of series C was used next to the calibration of f_{water} and a calibration of K_b . The calibrated f_{water} values (together with the corresponding HRT) are given in Table 7.8, next to the predicted total removal efficiencies and the relative deviation from the measurements.

Table 7.8. Pilot-scale TF plant - model calibration for LAS

	Calibration		Total removal	
	f_{water} (-)	HRT (min)	Predicted	Relative deviation
Series A	3.7 %	5.8	53.0 %	+ 8.1 %
Series B	3.2 %	15.0	52.6 %	+ 9.6 %
Series C	5.0 %	7.8	62.3 %	+ 11.2 %
Series D ⁽¹⁾	15.8 %	24.8	86.8 %	- 3.6 %
Series D ⁽²⁾	5.0 %	7.8	63.3 %	- 29.6 %
Series D ⁽³⁾	5.0 %	7.8	87.6 %	- 2.7 %

(1) calibrated f_{water}

(2) using the f_{water} calibration of series C (predicted single-pass removal = 25.1 %)

(3) calibrated $K_b = 0.991 \cdot 10^{-6} \text{ (g/m}^3\text{)}^{-1} \cdot \text{s}^{-1}$ - f_{water} from series C

Discussion

The uncalibrated predictions for series A, B and C were within one standard deviation of the measurements' means, both for total and single-pass removal. The relative deviation from the means was at the most 20 %. For series D, however, a much larger deviation was found: over 30 % underestimation for the total removal and over 60 % underestimation for the single-pass.

The calibrated f_{water} values for series A, B and C are in line with the measured values. Similarly, the corresponding HRT s in series A, B and C correspond very well with the measured HRT s. The calibrated f_{water} for series D and the corresponding HRT are unrealistic: they are a factor 3 higher than what was expected based on the measurements and on the other series' calibrations. Alternatively, the f_{water} value from the calibration of series C was applied to series D, because both experimental series were conducted close to each other and were hydraulically very similar. However, this caused an underprediction of the single-pass removal in series D by 56 %, and of the total removal by 28 %. To fit the model to series D using realistic hydraulics and biofilm parameters (which were similar to the other experimental series, see chapter 6 of this thesis), it was necessary to modify the biodegradation constant K_b . To calibrate the single-pass removal, a K_b of $0.0035 (g/m^3)^{-1}.h^{-1}$ or $0.979 \cdot 10^{-6} (g/m^3)^{-1}.s^{-1}$ was required, which is 3.5 times higher than the K_b used for the other experimental series (derived from activated sludge data). This observation indicates that LAS removal kinetics may be different at higher influent concentrations (possibly because of adaptation of the competent biomass to these higher concentrations).

The model calibration focused on fitting the predicted single-pass removal to the data. This resulted in an overprediction of total removal by ca. 10 % in series A, B and C, and in a small underestimation of total removal in series D (by ca. 3 %). Except for possible inaccuracies in the measurements of both total and single-pass removal, no other plausible explanation for this phenomenon could be found.

4.2. Full-scale Sewage Treatment Plants

Trickling filter plants

In the sewage treatment plants of Gargrave and Dowley Gap (Yorkshire, UK), LAS removal over the trickling filter as such (including secondary settling but excluding primary treatment) was measured by Holt *et al.* (1998). Gargrave is a very small plant, treating the sewage of 1450 people, while the Dowley Gap plant serves a community of 30150 people. For the latter, the volumetric organic loading B_V was $0.07 kgBOD/m^3.d$ (very low loading according to the range given in Metcalf & Eddy, 1991). BOD removal in this plant was on average 91 %.

Measured flow data and LAS elimination percentages in both treatment plants are given in Table 7.9. Plant dimensions are given in Table 7.10. In these systems, no effluent recycles were applied. Data on suspended solids were not available; a default value of $200 mg/L$ (for SS_{tf} and SS_{sewage}) was assumed, together with a secondary settler solids removal efficiency of 90 %. The applied biofilm and carrier material related data are given in the bottom section of Table 7.10. For both plants, the bed material consisted of lava rock, with a specific surface area of $100 m^2/m^3$ and a porosity of 50 %. The air/water interfacial area was assumed equal to the carrier material's specific surface area, while the biofilm/water area was assumed to be twice that area (i.e. $Z_{biofilm}=2$). For the stagnant

water zone thickness and the biofilm density, defaults from Melcer *et al.* (1995) were used. An active biofilm thickness of 150 μm was selected (cf. considerations in chapter 6).

Table 7.9. Full-scale domestic TF plants - flow data and LAS elimination (August/September '96)

Gargrave						
Date		19-20 / 8	20-21 / 8		Average	
Mean Q	(m^3/s)	0.0057	0.0078		0.00675	
TF influent LAS	(mg/L)	2.64	2.28			
TF effluent LAS	(mg/L)	0.20	0.40			
LAS Removal	(%)	92.42	82.46		87.44	
Dowley Gap						
Date		20-21 / 8	21-22 / 8	3-4 / 9	4-5 / 9	Average
Mean Q	(m^3/s)	0.136	0.104	0.143	0.129	0.128
TF influent LAS	(mg/L)	2.60	2.72	1.74	1.69	
TF effluent LAS	(mg/L)	0.43	0.35	0.35	0.31	
LAS Removal	(%)	83.46	87.13	79.90	81.66	83.04

Table 7.10. Full-scale domestic TF plants - model parameters

		Gargrave	Dowley Gap
Known			
A_{tf}	(m^2)	538	13130
V_{tf}	(m^3)	1236.5	25130
A_{sec}	(m^2)	112.5	1016
V_{sec}	(m^3)	360	2830
f_{rec}^1, f_{rec}^2	(-)	0	0
Defaults			
SS_{tf}	(mg/L)	200	
SS_{sewage}	(mg/L)	200	
R_{sec}^{SS}	(-)	90 %	
Biofilm and carrier material			
e_{tf}	(-)	50 %	
$a_{a/w}$	(m^2/m^3)	100	
$a_{b/w}$	(m^2/m^3)	200	
L	(m)	0.000100	
L_f	(m)	0.000150	
X_f	(g/m^3)	40000	

Model testing

The parameter f_{water} was used for calibration. Two calibrations were performed: one based on the measurements in Gargrave on 19-20 / 8 and one based on the measurements in Dowley Gap on 20-21 / 8. For Gargrave, the calibrated f_{water} value was 9.355 %; for Dowley Gap it was 6.552 %. In both cases, the order of magnitude of the calibrated f_{water} values was realistic. They corresponded with a total water layer thickness of 300 - 500 μm and a mean *HRT* of 5.6 hours in Gargrave or 3.4 hours in Dowley Gap.

Subsequently, these calibrations were applied to all other monitored situations. The predicted and measured removal efficiencies, as well as the relative deviation of the predictions from the measurements, is given in Table 7.11.

Table 7.11. Full-scale domestic TF plants - model calibration for LAS

	Predicted LAS removal	Relative deviation
Calibration based on Gargrave, 19-20 / 8		
Gargrave		
19-20 / 8	92.4 %	calibrated
20-21 / 8	87.4 %	+ 5.9 %
Dowley Gap		
20-21 / 8	90.1 %	+ 8.0 %
21-22 / 8	93.9 %	+ 7.7 %
3-4 / 9	89.3 %	+ 11.8 %
4-5 / 9	91.0 %	+ 11.4 %
Calibration based on Dowley Gap, 20-21 / 8		
Gargrave		
19-20 / 8	86.5 %	- 6.4 %
20-21 / 8	79.9 %	- 3.1 %
Dowley Gap		
20-21 / 8	83.5 %	calibrated
21-22 / 8	88.6 %	+ 1.7 %
3-4 / 9	82.4 %	+ 3.1 %
4-5 / 9	84.6 %	+ 3.5 %

Discussion

When the model calibration was based on one day's measurement in Gargrave, LAS removal in the same plant during the next day was overpredicted by 6 %. This could be due to the very high removal found in the calibration case, which may have been exceptional and possibly not steady-

state. For Dowley Gap, the calibration based on one day could be extrapolated more reliably to the other three measurement days: the deviation of predicted removal was at the most 3.5 %.

Extrapolating the Gargrave calibration to Dowley Gap resulted in an overestimation of LAS removal by 8 to 12 %. The Dowley Gap calibration caused a (smaller) underestimation of removal in Gargrave by 3 to 6 %. As mentioned above, the higher predictive error with the Gargrave calibration could be due to the non-typical high removal found in the calibration case.

5. Conclusions

Based on the *SimpleTreat* / *SIMPLEBOX* methodology, together with the biofilm diffusion / biodegradation model of Melcer *et al.* (1995), a chemical fate model for trickling filter waste water treatment plants was conceived. A sensitivity analysis showed that chemical properties determine which model parameters are important. Flow, volume and suspended solids data are needed for the specific plant that is modeled. For biodegradable substances, biofilm thickness is a crucial parameter which is generally not measured; hence, this value has to be estimated. For volatile chemicals it is required to estimate the air flow through the filter, which may be difficult. Finally, the fraction of water in the filter's pores is also an important parameter. This may be derived from measured *HRTs*.

The model was able to predict LAS removal in a pilot-scale high rate trickling filter, using measured, estimated or realistic default parameter values. The same biodegradation rate constant K_b (derived from activated sludge data) could be used in 3 different experimental series with a normal LAS influent concentration. However, for one series with 3-4 times more LAS in the influent, a 3.5 times higher K_b value was needed. This may indicate that LAS biodegradation follows different kinetics at these high concentrations, possibly due to biological adaptation (increase of the competent biomass level at higher substrate concentrations, e.g. Lee *et al.*, 1998; Magbanua *et al.*, 1998). This is a shortcoming of the trickling filter fate model as it is presented here: the model can only deal with this situation by recalibration of the biodegradation rate coefficient. It is recommended to focus further research on the effect of influent concentrations on LAS biodegradation rates, and on the effect of adaptation to different concentrations on these rates.

Finally, the model was also successfully applied to predict the fate of LAS in two full-scale low rate domestic trickling filter plants. Again, measured, estimated or realistic default parameter values were applied. A plant-specific calibration produced more accurate predictions than the extrapolation of another plant's calibration. However, if a relative deviation in the order of 10 % is deemed acceptable, such a plant-specific calibration appeared to be not strictly required.

In this work, only the biodegradation (and partly sorption) aspects of the model were confronted with measurement data. To test the relevance and validity of the volatilization aspects, further research is needed.

Chapter 8

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Modeling Chemical Fate in Rivers

a condensed version of this chapter was submitted for publication as:

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Chapter 8

Modeling Chemical Fate in Rivers

The GREAT-ER project aims to refine aquatic exposure assessments, by modeling the fate pathway of ‘down-the-drain’ chemicals from the household to the river, and by applying specific river fate models to predict concentrations downstream of pollution sources. In this chapter, a suitable river fate modeling approach is selected from existing models. Next, an in-stream biodegradation model is presented, which considers biofilm activity next to the activity of suspended biomass. The biodegradation model was calibrated using artificial river experiments, and was tested by comparing its results to a field in-stream removal study.

1. Selection of a River Fate Modeling Approach

1.1. Literature Review

In this section, an overview is given of several existing steady-state river fate models. Dynamic flow or chemical load models were not included. Examples of the latter are TOXIWASP (Ambrose *et al.*, 1983; Kuo & Hu, 1989), SeauS (Bildstein & Vançon, 1994), or EXDISP (Brüggemann *et al.*, 1991). Furthermore, this overview is limited to one-dimensional models.

Chemical transport can be described by advection only (i.e. transport together with the bulk fluid transport), or by advection and dispersion (i.e. also dilution of the chemical due to concentration gradients along the river’s length).

The ‘advection only’ approach is applied in e.g. SIMCAT (NRA, 1995), EXWAT (Trapp *et al.*, 1990 and 1991), SAMS RIVER (Matthies *et al.*, 1992), the non-dispersive mode of ROUT (Cowan *et al.*, 1993a), RIVMODEL (ECETOC, 1994c), SMPTOX4 mode 1+2 (US-EPA, 1995), CemoS WATER (Trapp & Matthies, 1996), TOXIROUTE (Lahlou *et al.*, 1996). In these models, chemical in-stream removal is assumed to be first-order in chemical concentration. Chemical fate and advective transport, assuming steady-state emissions, is described by:

$$\begin{cases} \frac{dC}{dt} = -k \cdot C \\ dt = \frac{ds}{v} \end{cases} \Rightarrow \frac{dC}{ds} = -\frac{k}{v} \cdot C \quad \text{hence} \quad C_x = C_0 \cdot e^{-k \cdot \frac{x}{v}} \quad [8.1]$$

Advection and longitudinal dispersion are considered by the dispersive mode of ROUT (Cowan *et al.*, 1993a) and SMPTOX4 mode 3 (US-EPA, 1995). First-order chemical fate and advective + dispersive transport can be described by:

$$\frac{\partial C}{\partial t} = -v \cdot \frac{\partial C}{\partial s} + D \cdot \frac{\partial^2 C}{\partial s^2} - k \cdot C \quad [8.2]$$

Assuming steady-state conditions, the following analytical solution is applicable:

$$C_x = \frac{C_0}{\sqrt{1 + \frac{4 \cdot k \cdot D}{v^2}}} \cdot e^{-\frac{x(v - \sqrt{v^2 + 4 \cdot k \cdot D})}{2 \cdot D}} \quad [8.3]$$

In general, models which predict in-stream removal kinetics can be subdivided into the following classes: non physically based models, physically based models, and conceptual models.

Non physically based models describe chemical decay kinetics using a very simple model structure requiring a limited number of parameters. These parameters depend on chemical properties and local environmental conditions, hence such models require re-calibrations (using monitoring data) when they are to be applied for different chemicals or for different river types. Examples are SIMCAT (NRA, 1995), TOXIROUTE (Lahlou *et al.*, 1996), SMPTOX4 mode 1 (US-EPA, 1995).

Physically based models describe each process in a detailed, mechanistic way. For example, biological conversions would be modeled using knowledge about the involved metabolic pathways. Such models tend to be very complex and require a high number of parameters. As all parameters are physically-based, it should be possible to derive these from knowledge or from laboratory analyses, rather than from calibrations.

Conceptual ‘gray box’ models are situated in between both the above approaches. Different fate processes and sub-processes are separated, and described in a more or less physically relevant way. However, at a certain level of detail, empirical or non physically based descriptions are applied for the description of specific sub-processes. In practice, most “mechanistic” river fate models belong to this category, e.g. QWASI (Mackay *et al.*, 1983), EXWAT (Trapp *et al.*, 1990 and 1991), SAMS RIVER (Matthies *et al.*, 1992), ROUT (Cowan *et al.*, 1993a), RIVMODEL (ECETOC, 1994c), SMPTOX4 mode 2 and 3 (US-EPA, 1995), EXAMS (Burns, 1996), TOXSWA (Adriaanse, 1996), CemoS WATER (Trapp & Matthies, 1996).

The main fate processes which are dealt with in these models are: degradation (= destruction of the chemical), consisting of biodegradation (= microbial process), hydrolysis (= strictly chemical process) and photolysis (= light-induced photochemical process); sedimentation (= transport of the chemical to the river’s bed sediment); and volatilization (= transport of the chemical out of the water column, into the air). Typically, separate sub-models are used to predict a first-order chemical removal rate coefficient for each individual fate process. Afterwards, the overall first-order rate coefficient is obtained as the sum of these individual rate coefficients.

1.2. Model Selection

1.2.1. General

Depending on the objectives of the application, on the required accuracy and on data availability, different levels of model complexity can be appropriate. This chapter only deals with the highest complexity level used in GREAT-ER: a mechanistic model, in which (partly) physically-based descriptions are used to describe fate, provided available data and process understanding allow this. The following general model specifications were selected a priori:

Steady state. Only steady-state models are used, as it is not the objective to analyze the effect of transient events or process dynamics. Moreover, it is assumed that the emission dynamics of down-the-drain consumer chemicals are very limited.

One-dimensional. Rivers are considered as one-dimensional systems. Hence, horizontal and vertical transport / dispersion are not considered. Immediate and complete mixing is assumed after waste water inputs or after confluences with tributaries,

Negligible dispersion. In steady-state problems, longitudinal dispersion is only expected to have a significant impact when chemical decay rates are very large (De Smedt, 1989) or when important concentration gradients can occur. In the first case, the environmental concern of the studied chemical will be limited. In the second, the main environmental concern will be on the local level, immediately after a large waste water discharge point. As the work described in this thesis ultimately focuses on a larger regional scale, and is not directed towards acute predictions on a small-scale local level, dispersion can be neglected.

River sediment. Chemical sedimentation is considered to be a sink process. Accumulation of chemicals in the sediment and their release of out of the sediment are not taken into account because these processes are typically of a dynamic nature.

In-stream removal kinetics. First-order decay kinetics (in chemical concentration) are used to describe the in-stream removal of chemicals in rivers. An overview of the chemical partitioning and fate processes which are considered in the prediction of in-stream removal is given in Figure 8.1.

1.2.2. In-stream Removal Calculations

The lumped 1st-order in-stream removal rate coefficient k is calculated as the sum of the different fate processes' rate coefficients:

$$k = k_{deg} + f_s \cdot k_{sed} + f_d \cdot k_{vol} \quad \text{with} \quad k_{deg} = k_{hydrolysis} + k_{photolysis} + k_{biodeg} \quad [8.4]$$

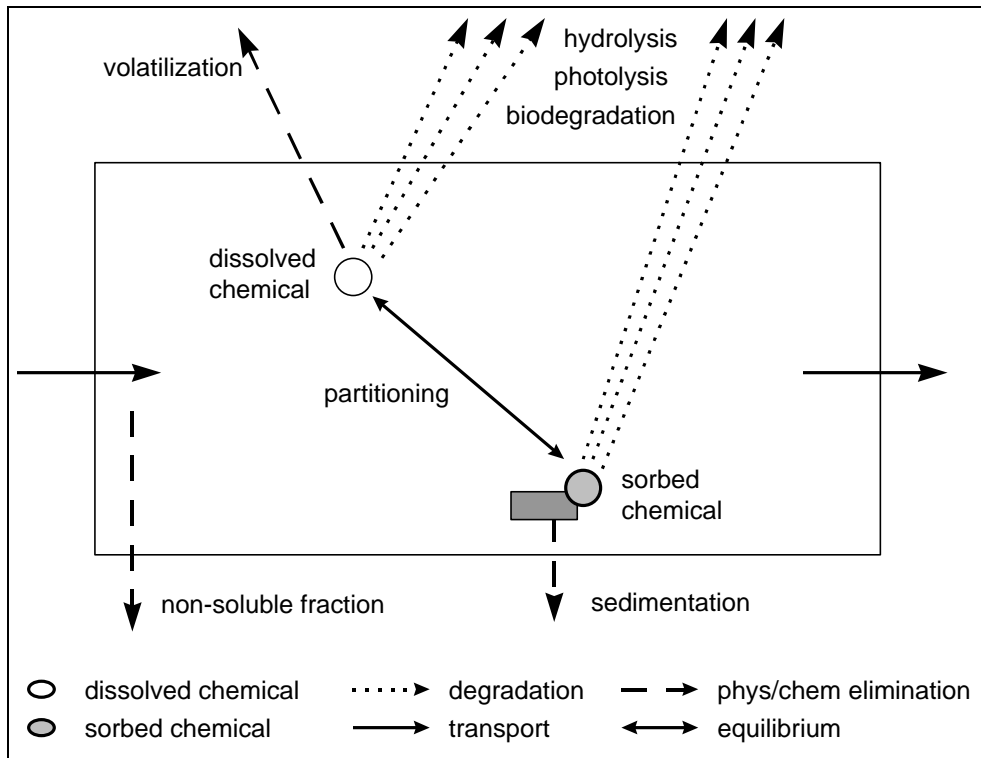


Figure 8.1. Overview of considered chemical fate processes in rivers

In equation [8.4], it is assumed that sedimentation only occurs with the sorbed chemical fraction, and that only the dissolved fraction can volatilize. The dissolved and sorbed chemical fractions are calculated as:

$$f_d = \frac{C_d}{C_s + C_d} = \frac{1}{1 + C_s/C_d} = \frac{1}{1 + 10^{-6} \cdot K_d \cdot SS} \quad [8.5]$$

$$f_s = \frac{C_s}{C_s + C_d} = 1 - f_d$$

The theoretical initial concentration is calculated assuming complete and instantaneous mixing, and is compared to the chemical's solubility limit. If the latter is exceeded, the initial concentration is set equal to the solubility limit.

Chemical Degradation

The hydrolysis model can be taken from SMPTOX4 mode 3 (US-EPA, 1995), which differentiates between neutral, acid and basic conditions.

As photolysis depends on the irradiation of sunlight, it only occurs during the daylight hours. Hence, it is an intrinsically dynamic process, which is not functional during the night and which reaches its maximum at noon. Taking these limitations into account, a simple photolysis model can be taken from SMPTOX4 mode 3 (US-EPA, 1995), in which a chemical-specific near-surface photolysis rate coefficient is corrected for light extinction in the water column.

This photolysis model is a very rough approximation of reality. It does not consider short-term temporal variations: day versus night and varying light intensity during the day. It also ignores long-term temporal variations: different light intensity depending on the season, different light extinction rate coefficients during algal bloom periods. Neither does it take into account spatial variability: different extinction rate coefficients in different rivers, dependence on geographical latitude of sunlight intensity and daylight duration. It can be concluded that this model can only be used in a regional exposure assessment context if river-specific estimations of the extinction coefficient are provided, and if the near-surface photolysis rate coefficient is corrected for geographic latitude. The model is not suitable when photodegradation is the main fate process, as it fails to describe the strong diurnal dynamics of in-stream removal in these cases.

In most chemical fate models, biodegradation is modeled as a non-physically based process, using a first-order chemical biodegradation rate coefficient as the only parameter. Temperature effects and the influence of dissolved oxygen levels in the river are typically not considered, and the activity of biofilms is ignored. Consequently, the existing river fate models require a site- and situation-specific calibration of the chemical in-stream biodegradation rate coefficient. As this is not always feasible or desirable, an alternative approach is presented later in this chapter. A site-specific prediction of in-stream biodegradation kinetics was developed, based on chemical properties and river characteristics.

Chemical Sedimentation

Chemical elimination through sedimentation is directly related to settling of suspended solids. The SS settling rate coefficient can be derived from the settling velocity and the river's depth. In its turn, the settling velocity can be estimated from annual sediment growth and sediment porosity and density (Trapp & Matthies, 1996). However, the calculation of suspended solids settling rate coefficients - or of sediment bed growth - is a problem which can typically not be solved on a regional scale. Hence, the accuracy of settling rate coefficients will generally be very low.

Chemical Volatilization

River volatilization models are typically based on the two-film theory (Whitman, 1923). Complete mixing (due to turbulence) of on the one hand the river water column and on the other hand the atmospheric compartment above it is assumed. The two boundary layers are assumed to be laminar and to control the exchange rate coefficient between water and air. This exchange rate coefficient is calculated from the chemical's Henry's law constant, the conductance of the gaseous and liquid films, and the river's depth.

For the estimation of these conductances, two different approaches are required. For lakes, the method described by Mackay & Yeun (1983) can be used. For rivers, the approach of Southworth (1979) can be applied. Both approaches are described and compared in Trapp & Harland (1995). A similar approach was used in SAMS (Matthies *et al.*, 1992), RIVMODEL (ECETOC, 1994c), SMPTOX4 (US-EPA, 1995), and CemoS (Trapp & Matthies, 1996). It was successfully applied to modeling the fate of chemical intermediates in the river Rhine by Koormann *et al.* (1998).

2. In-stream Biodegradation Modeling - Case Study for LAS

Chemical biodegradation in rivers is typically described by 1st-order kinetics in chemical concentration, requiring a chemical-specific 1st-order in-stream biodegradation rate coefficient. However, in-stream removal kinetics of biodegradable substances are highly variable between different river systems and between different locations within a single river. For example for BOD US-EPA (1985) reports half-lives between 3h and 170d (rate coefficient between 0.23 h⁻¹ and 0.00017 h⁻¹).

To apply river fate models in a regional exposure assessment context, it is desirable to be able to predict chemical in-stream biodegradation for different river types. A mathematical model is presented which estimates in-stream biodegradation as a function of available biomass, both biofilms and suspended microorganisms. Biofilm presence is linked with the surface area available for attached growth in the river. Hence, it is related to river geometry, to bed characteristics and to the presence of aquatic vegetation. A calibration of this model for the chemical LAS (Linear Alkylbenzene Sulphonate) is presented, based on experimental data collected in an artificial river. A tentative corroboration was performed by applying the model to field study data.

2.1. LAS In-stream Removal: Literature Review

An overview was made of studies which analyzed parent in-stream removal of LAS, considering both in-situ and mesocosm experiments (Table 8.1).

A range of LAS in-stream removal rate coefficients between 0.006 h⁻¹ and 1.71 h⁻¹ was found in the literature. This corresponds with a half-life range of 0.40 h - 116 h. The measured in-stream removal rate coefficients comprise both biodegradation and sorption / sedimentation. However, since SS levels in rivers are relatively low, biodegradation can be assumed the predominant fate process. The mesocosm studies showed that biological adaptation was an important factor (which suggests that biodegradation was more important than abiotic processes). Temperature effects were shown in several studies, but can not be used to explain the entire range of variability. Takada *et al.* (1994) showed that the microbial population density (e.g. the presence of biofilms) had a major influence on the river's biodegradation potential. Biofilms have the highest relative importance in small rivers, as these have a higher surface area to volume ratio (A/V).

Table 8.1. LAS in-stream removal rates in the literature

Reference	Rate coefficient (h ⁻¹)	River	Notes
Waters & Garrigan (1983)	0.13 - 0.90 *	Avon, Tean	temperature: Q10 = 1.5 - 2
Schröder (1995)	0.08 - 0.46	mesocosm	no vs. 17d adaptation
Steber (1996)	0.15 - 0.31	mesocosm	LAS conc. 0.1 - 5 mg/L
Hennes & Rapaport (1989)	0.02 - 0.12	Rapid Creek	5 °C
Amano <i>et al.</i> (1991)	0.07	Oohori,	25 °C, large river + lake
	0.006 - 0.009	Teganuma	5 °C, large river + lake
Schöberl <i>et al.</i> (1994)	1.09	Isar	below WWTP outfall
Takada <i>et al.</i> (1994)	0.43 - 1.73	Nogawa	small river, 7 - 27 °C
Schröder (1996)	0.21 - 0.63	Anger, Rur	small rivers
Grob (1996)	0.03 - 0.77	Itter	river source to mouth
Fox <i>et al.</i> (submitted)	0.26 - 0.31	Red Beck	small river, 9 °C

* assuming flow velocity of 1 m/s

Next to the in-situ and mesocosm studies, a review was made of laboratory river water die-away tests (Larson & Payne, 1981; Kawasaki *et al.*, 1983; Yediler *et al.*, 1989; Amano *et al.*, 1991; Terzic *et al.*, 1992; Larson *et al.*, 1993; Takada *et al.*, 1994; Nuck, 1996; Cassani *et al.*, 1996). This showed 1st-order removal rate coefficients ranging between 0.0044 h⁻¹ and 0.048 h⁻¹. These are much lower than those found in reality, which could be due to unrealistic test conditions (e.g. absence of biofilms).

2.2. Biodegradation Model

2.2.1. Model Formulation

Both 'bulk water' biodegradation by suspended organisms, and biodegradation in biofilms are considered. The latter depends on the geometry of the river and on the river bed characteristics. The more biofilm surface is present per volume of water, the higher the degradation rate coefficient will be. This way, the large variation of decay rate coefficients between different river types can be represented. The concept is illustrated below in Figure 8.2.

'Bulk water' and biofilm degradation are considered to be independent processes. In the 'bulk water', micro-organisms are present as suspended solids, assumed to be uniformly distributed over the volume of a river stretch. At the 'edges' of the river (its bed and banks), a biofilm is present. Biodegradation processes in this bacterial film are controlled by the amount of biofilm (surface area and film thickness), by diffusion limitation (into and within the film), and by biodegradation kinetics. The implemented biofilm diffusion / biodegradation model was taken from an existing trickling filter fate model (Melcer *et al.*, 1995).

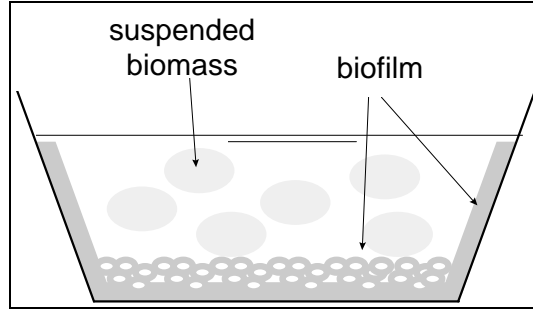


Figure 8.2. In-stream biodegradation processes (schematic)

The total biodegradation rate coefficient is calculated as the sum of both independent rate coefficients:

$$k_{biodeg} = k_{biodeg}^{bulk} + k_{biodeg}^{biofilm} \quad [8.6]$$

Biodegradation is assumed to follow first-order kinetics to both chemical and biomass concentration. Note that the standard “double” first-order biodegradation rate coefficient can be corrected for dissolved oxygen and temperature.

Bulk water (suspended biomass)

From the standard “double”-first-order rate coefficient K_b , a pseudo-first-order rate coefficient is derived by multiplying the former with the biomass level (i.e. biologically active SS). Further, a distinction can be made between sorbed and dissolved processes.

$$k_{biodeg}^{bulk} = K_b \cdot SS_{act} \cdot (f_d + f_s \cdot a_{sorbed}) \quad [8.7]$$

Biofilm

The biofilm biodegradation model was taken from Melcer *et al.* (1995):

$$k_{biodeg}^{biofilm} = a_{b/w} \cdot K_L \cdot \frac{D_e \cdot r_1 \cdot \tanh(r_1 \cdot L_f)}{D_e \cdot r_1 \cdot \tanh(r_1 \cdot L_f) + K_L} \quad [8.8]$$

$$\text{with } r_1 = \sqrt{\frac{X_f \cdot K_b}{D_e}} \quad D_e = D_l * 0.8 \quad K_L = \frac{D_l}{L}$$

The biofilm / water interfacial area $a_{b/w}$ can be (roughly) estimated from river geometry as follows in equation [8.9] (assuming a rectangular cross-section). Note that a correction factor ($Z_{biofilm}$) is used to convert substratum surface to actual biomass surface.

$$d_{bed} > 0 \quad \Rightarrow \quad a_{b/w} = Z_{biofilm} \cdot \frac{2 \cdot d + w \cdot d_{bed} \cdot a_{bed}}{d \cdot w} \quad [8.9]$$

$$d_{bed} = 0 \quad \Rightarrow \quad a_{b/w} = Z_{biofilm} \cdot \frac{2 \cdot d + w}{d \cdot w}$$

2.3. Sensitivity Analysis

2.3.1. Sensitivity to Model Parameters

A hypothetical chemical was used to perform a sensitivity analysis of the model. Its double-first-order biodegradation rate coefficient K_b was set to $2.78 \cdot 10^{-7} \text{ (g/m}^3\text{)}^{-1} \cdot \text{s}^{-1}$ ($=0.001 \text{ (g/m}^3\text{)}^{-1} \cdot \text{h}^{-1}$). The diffusion coefficient D_l was fixed at $5.5 \cdot 10^{-5} \text{ m}^2/\text{s}$ (an average value from Melcer *et al.*, 1995). The applied biofilm parameter values are given in Table 8.2. Three hypothetical river types were defined. A is a small river with a pebbles bed; B is a medium-size river with similar bed; C is a large river with a muddy sediment (Table 8.2).

A sensitivity analysis was performed for all parameters, for the three test rivers. Relative sensitivities S_R were calculated numerically, based on the change in predicted removal rate coefficient k upon a 1% increase of each parameter P :

$$S_R = \frac{\Delta k_{biodeg} / k_{biodeg}}{\Delta P / P} = \frac{\Delta k_{biodeg} / k_{biodeg}}{0.01 \cdot P / P} = 100 \cdot \frac{\Delta k_{biodeg}}{k_{biodeg}} \quad [8.10]$$

Table 8.2. Sensitivity analysis of in-stream biodegradation model: biofilm and river parameters

L	0.0001			m
L_f	0.0001			m
X_f	40000			$\text{g}_{\text{dwt}}/\text{m}^3$
Z_{biofilm}	2			m^2/m^2
	River A	River B	River C	
d	0.1	1	5	m
w	1	10	100	m
SS_{act}	20	20	20	$\text{g}_{\text{dwt}}/\text{m}^3$
d_{bed}	0.05	0.1	0	m
a_{bed}	100	100	-	m^2/m^3
$A/V \text{ ratio}$	62	11.2	0.22	m^2/m^3

The calculated relative sensitivities are given below in Table 8.3.

Table 8.3. Sensitivity analysis of in-stream biodegradation model: results (relative sensitivities)

Parameter	S_R			
	River A	River B	River C	Average
Chemical properties				
K_b	<u>99.77%</u>	<u>99.81%</u>	<u>99.98%</u>	<u>99.85%</u>
D_l	0.23%	0.18%	0.02%	0.14%
River parameters				
d	<u>-89.79%</u>	<u>-74.26%</u>	-5.91%	<u>-56.65%</u>
w	-3.59%	-1.49%	-0.59%	-1.89%
SS_{act}	5.68%	<u>23.50%</u>	<u>93.44%</u>	<u>40.87%</u>
d_{bed}	<u>90.69%</u>	<u>75.00%</u>	0.00%	<u>55.23%</u>
a_{bed}	<u>90.69%</u>	<u>75.00%</u>	0.00%	<u>55.23%</u>
Biofilm properties				
L	0.00%	0.00%	0.00%	0.00%
L_f	<u>93.86%</u>	<u>76.13%</u>	6.53%	<u>58.84%</u>
X_f	<u>94.09%</u>	<u>76.32%</u>	6.55%	<u>58.99%</u>
$Z_{biofilm}$	<u>94.32%</u>	<u>76.50%</u>	6.56%	<u>59.13%</u>

Notation: $S_R > 10\%$, $1\% < S_R < 10\%$, $S_R < 1\%$

In all cases, a very high sensitivity was found for the biodegradation rate coefficient K_b . As expected, biofilm- and geometry-related parameters had a high sensitivity in smaller rivers (with a high A/V ratio), while the model was most sensitive to suspended biomass in the large river (with a low A/V ratio). A high sensitivity to width was never detected, and the sensitivities to the diffusion constant D_l and the stagnant water layer thickness L were negligible.

2.3.2. Effect of River Size on Predicted Biodegradation

By means of the Regime Theory (Simons & Albertson, 1960), river geometry (width, depth) can be estimated when flow is given (equation [8.11]). Using this theory, a set of river geometries were generated as a function of flow. For these geometries, the in-stream biodegradation half-life was predicted for the hypothetical chemical defined above. For these predictions, a zero bed depth was assumed. Hence only the true geometry effect was considered. The results are shown in Figure 8.3. Note that to illustrate the point, an unrealistically large range of flows was used.

$$\begin{aligned}
 p &= 6.312 \cdot \sqrt{Q} \\
 w &= \frac{0.9 \cdot p + 0.610}{0.92} \Rightarrow w = 6.175 \cdot \sqrt{Q} + 0.305 \\
 r &= 0.57 \cdot Q^{0.36} \\
 d &= \begin{cases} r > 2.13 & \Rightarrow d = 0.610 + 0.93 \cdot r \\ r \leq 2.13 & \Rightarrow d = 1.21 \cdot r \end{cases}
 \end{aligned}
 \tag{8.11}$$

With increasing flow, the fraction of biodegradation occurring in the biofilm decreased from almost 90 % (very small rivers, very low flow) to less than 10 % (very large rivers, very high flow). Together with this, the in-stream removal half-life increased from a very fast rate coefficient (½ hour half-life) in very small rivers to a much slower rate coefficient (>30 hours half-life) in very large rivers.

The direct relation between the predicted in-stream biodegradation half-life and the A/V ratio (which increases with decreasing river size) is shown in Figure 8.4.

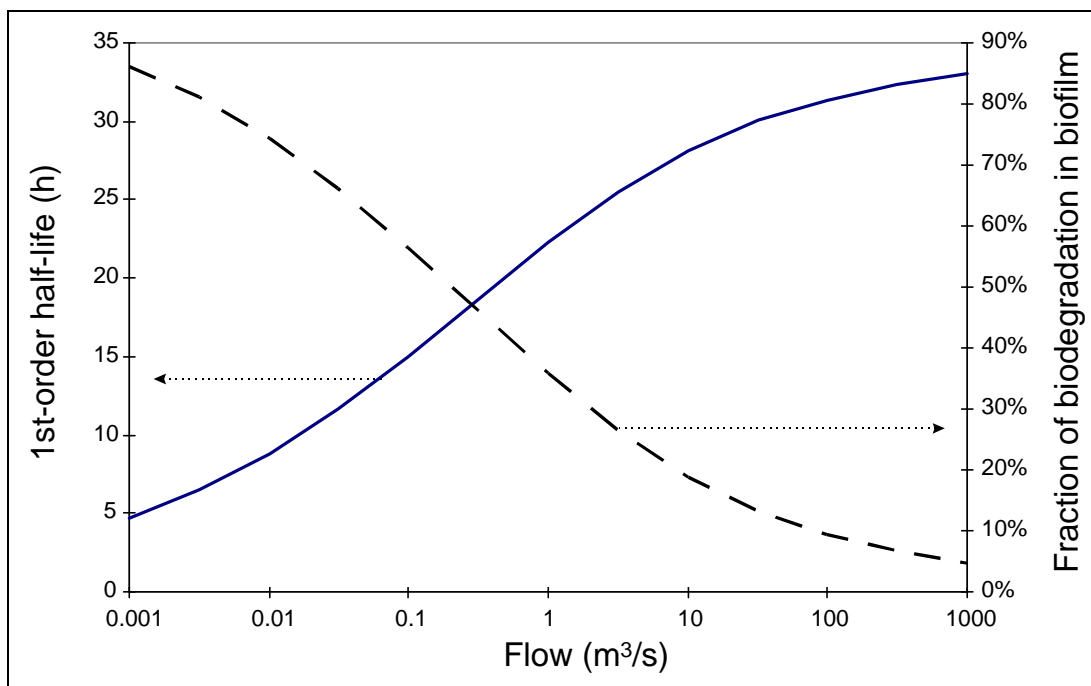


Figure 8.3. Predicted chemical in-stream biodegradation half-life as a function of river flow

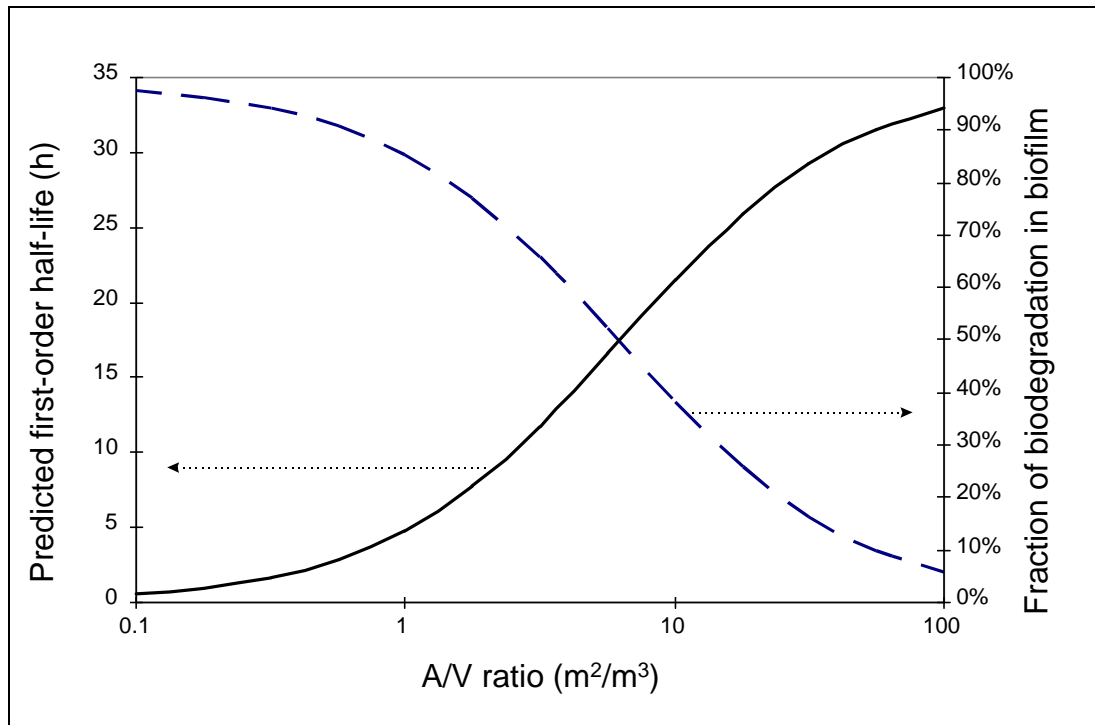


Figure 8.4. Predicted chemical in-stream biodegradation half-life as a function of river A/V ratio

2.4. Model Calibration: Artificial River Experiments

To calibrate the river biodegradation submodel, primary (parent) removal of LAS was measured in an artificial river setup, under complete steady-state conditions. As the artificial river setup allowed to quantify all relevant river and biofilm parameters, adequate information for a full calibration of the model could be sourced.

2.4.1. Experimental Methods

River system selection and design

Several river and biofilm characteristics are required for model calibration. Many of these cannot be (accurately) measured or are not homogeneous in the field. Experimentation with an artificial river was preferred, because [1] measurement of volumes, flows, velocities and residence times is straightforward; [2] a more homogeneous situation can be created; [3] the surface area for biofilm growth can be measured and manipulated; [4] chemical dosing is easy and harmless to the environment. Biodegradation experiments in artificial rivers have been conducted successfully in the past (e.g. Schröder, 1995; Steber, 1996; Guckert *et al.*, 1996; Koziollek *et al.*, 1996). As the research presented here was focused on microbial aspects, the limited macroscopic realism was not considered a disadvantage, especially because the model was subsequently corroborated using field measurements.

The artificial river was constructed as a cascade of 5 U-shaped gutters, each of 2 m length (Figure 8.5). The total river volume was 36 L. The design hydraulic residence time (HRT) was chosen to correspond with the half-life of LAS in small natural rivers. To achieve an HRT of approximately 3 h, the flow was set to 0.2 L/min. With this flow regime, a daily influent volume of ca. 300 L per day was needed. Two air diffusers were placed in each gutter, to provide oxygen and to counteract sedimentation (aeration intensity tuned manually, to allow maximal aeration without the spilling of water). The experiments were conducted at room temperature (20 °C).

To ensure a relatively constant and known composition, synthetic river water was used, rather than natural river water. This was prepared as a 50/50 mixture of a lab trickling filter's effluent with softened tap water. The trickling filter's influent was a synthetic sewage based on Boeije *et al.* (1998), containing LAS. A description of the trickling filter setup is given in chapter 6 of this thesis.

In the artificial river, biofilm could develop on the edges of the gutters, and on carrier material which was entered into the system to mimic the bed material or vegetation present in natural rivers. The total edges surface area was ca. 1.5 m² (area to volume ratio $A/V = 42 \text{ m}^2/\text{m}^3$). The total surface of the polypropylene biofilter carrier material (Filtermat, Temse, Belgium) (30 pieces per gutter) was ca. 3.4 m² ($A/V = 94 \text{ m}^2/\text{m}^3$) (specific surface area 220 m²/m³; density 61 kg/m³; 96% voids; surface area per piece 0.0225 m²; plastic volume per piece 5 mL). A schematic representation of this material is given in chapter 6 of this thesis.

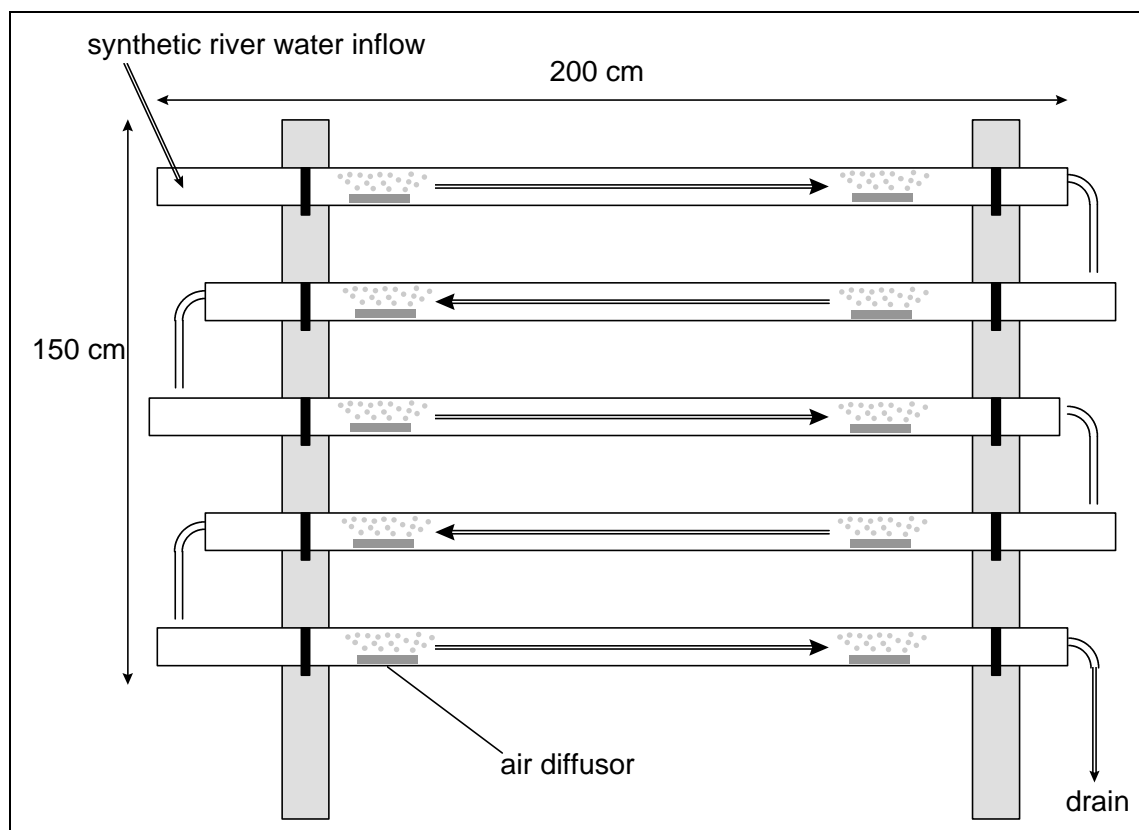


Figure 8.5. Artificial river construction (schematic drawing)

Hydraulic Characterization

Before the biological experiments, a hydraulic characterization was performed. Two fill-up tests were conducted, next to a tracer test.

Fill-up tests

By filling the different gutters until their overflow became operational, the volumes of the 5 stretches were determined: 8.50, 6.45, 7.00, 5.30 and 8.35 L. Hence, the total volume of the river was 35.6 L. The variation in volume between the stretches was due to imperfections of the construction (e.g. different height of the overflow). The mean hydraulic residence time after each stretch was estimated by recording the needed filling time (with a flow of 0.2 L/min). The results are given in Table 8.5.

Tracer test

A tracer test was performed by means of a pulse NaCl injection into the river's influent (river flow of 0.2 L/min). Conductivity was measured at approximately 20 cm before the end of each stretch. The tracer test's E-curve (with the surface areas below the curves normalized to 1) are shown in Figure 8.6. The open vessel dispersion model (Levenspiel, 1972) was used to describe the hydraulic response of the system. This model is described by:

$$E = \frac{v}{\sqrt{4p \cdot D \cdot t}} \cdot \exp\left(-\frac{(l - v \cdot t)^2}{4 \cdot D \cdot t}\right) \quad [8.12]$$

A 'Tanks-in-Series' model can also be used to describe the hydraulic behavior of the artificial river. The theoretical number of tanks can be derived from the dispersion model's parameters as follows:

$$N = \frac{v \cdot l}{2 \cdot D} \quad [8.13]$$

The length l was considered to be known, D and v were estimated by fitting the open vessel dispersion model to the tracer test data. An SSE minimization (using the Microsoft Excel solver tool) was used to fit the model. An excellent fit was found (Figure 8.6), with a coefficient of determination $R^2 = 99.5\%$. In Table 8.4, the parameters obtained by fitting the tracer test results to the open vessel dispersion model are given, as well as the corresponding theoretical number of tanks in series.

Table 8.4. Artificial river tracer test: fitted dispersion model parameters

Stretch	D (m ² /s)	u (m/s)	L (m)	N (-)
1	0.0007608	0.0011712	1.8	1.4
2	0.0003855	0.000986	3.8	4.9
3	0.0004147	0.0009746	5.8	6.8
4	0.000304	0.0009451	7.8	12.1
5	0.0003291	0.0009252	9.8	13.8

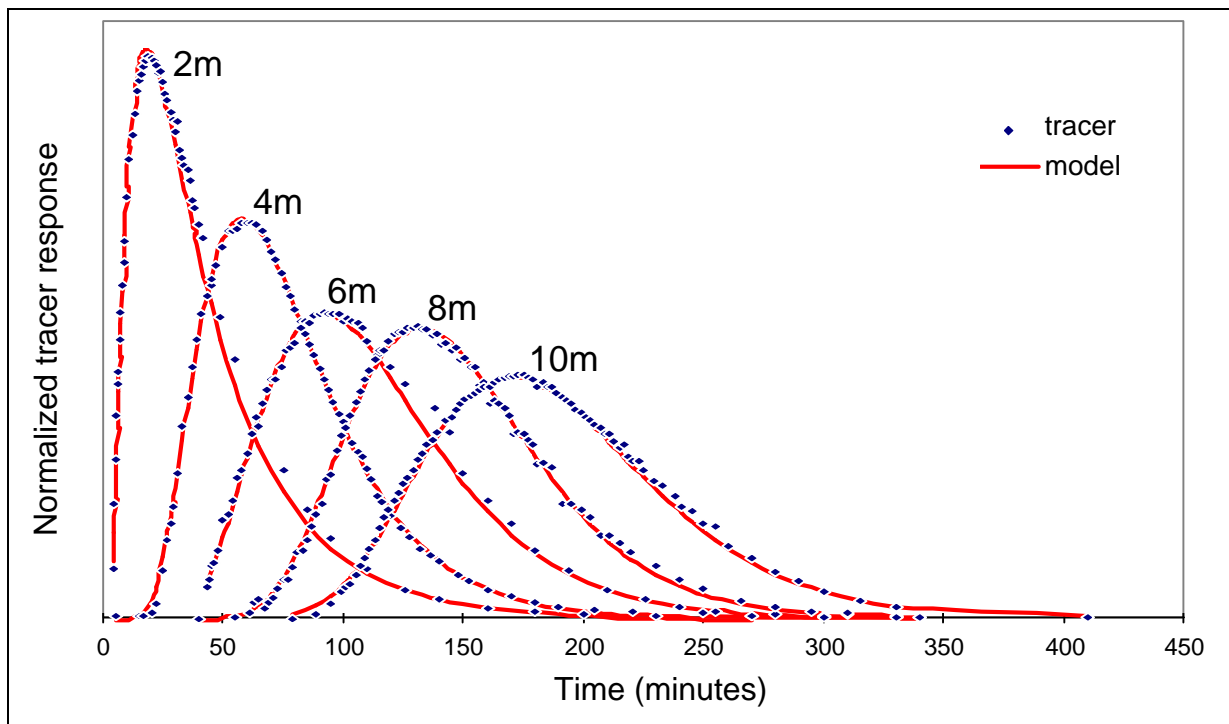


Figure 8.6. Artificial river NaCl tracer test: E-curves

The average hydraulic residence time (\bar{t}) at each point in the river can be obtained by solution of:

$$\bar{t} = \frac{\int_0^{\infty} \frac{v}{\sqrt{4p \cdot D \cdot t}} \cdot \exp\left(-\frac{(l - v \cdot t)^2}{4 \cdot D \cdot t}\right) \cdot t \cdot dt}{\int_0^{\infty} \frac{v}{\sqrt{4p \cdot D \cdot t}} \cdot \exp\left(-\frac{(l - v \cdot t)^2}{4 \cdot D \cdot t}\right) \cdot dt} = \int_0^{\infty} \frac{v}{\sqrt{4p \cdot D \cdot t}} \cdot \exp\left(-\frac{(l - v \cdot t)^2}{4 \cdot D \cdot t}\right) \cdot t \cdot dt \quad [8.14]$$

This integral was solved numerically, using Maple V software (Waterloo Maple Inc., Ontario, Canada). The obtained average residence times are given in Table 8.5, as well as the times of the tracer peak. The average HRT obtained by the dispersion model is very comparable to the experimentally determined HRT in the fill-up test.

Table 8.5. Artificial river: hydraulic residence times

Stretch	t_{peak} (min)	\bar{t} (tracer test) (min)	\bar{t} (fill-up test) (min)
1	24.00	44.12	42.50
2	60.00	77.47	74.75
3	90.00	113.70	109.75
4	131.00	148.91	136.25
5	173.00	189.39	178.00

HRT in the presence of biofilm

It was preferred not to repeat the tracer test during the biological experiments. The actual HRTs during each individual measurement were calculated as a correction of the tracer test HRTs. These corrections were based on the actual (measured) flow, and on the presence of biofilm and carrier material (volume reduction). Note that it was assumed that the river's mixing characteristics remained the same under the different experimental conditions and flows. The flow variation was limited: between 170 and 230 mL/min.

Measurements during biological experiments

LAS (total) was measured at 4 distances (0, 2, 5 and 10 m). No anionic surfactants other than LAS were present, hence the aspecific Azure-A analytical method (Den Tonkelaar & Bergshoeff, 1969) could be used reliably. COD samples (filtered) were taken at the same locations.

Three experimental series were conducted:

- [1] no biofilm present (i.e., only suspended biomass, originating from the trickling filter's effluent),
- [2] suspended biomass and biofilm on the gutters' edges, and
- [3] suspended biomass and biofilm on the edges and on carrier material.

The biofilm thickness on the carrier material was estimated from its wet (leaked out) mass. To estimate biofilm thickness on the gutter's edges, the mass of small plastic trays (4x4 cm), which were placed in the gutters, was measured. Biofilm growth on these trays was assumed to be similar to growth on the gutter walls.

Relative LAS and COD in-stream removal profiles were obtained by expressing the concentrations as % LAS and COD remaining. ANOVA (analysis of variance) was used to check whether any significant in-stream removal had taken place, by comparison of relative LAS and COD levels at the 4 different measurement locations. First-order in-stream removal rate coefficients were obtained by linear regression between the natural logarithms of the relative LAS and COD levels, and the HRTs for each experiment (imposing a zero-intercept). From all rate coefficients within one experimental series the mean and 95% confidence interval were determined.

2.4.2. In-stream Removal Results

The in-stream removal of LAS and of COD was determined in the artificial river system. LAS in-stream removal was assumed to be completely due to biodegradation. LAS is non-volatile; sorption to solids and subsequent sedimentation were assumed to be negligible because of the low suspended solids levels and the intensive aeration.

The mean initial LAS level for each experimental series varied between 1.2 and 2.5 mg/L. For COD, this variation was between 30 and 45 mg/L. The artificial river SS were on average 20 mg/L (with large variations: 5-35 mg/L).

No biofilm

The in-stream removal profile with only suspended biomass in the river (originating from the trickling filter's effluent) is shown in Figure 8.7 (top). No significant in-stream-removal was detected over the 3 hour period, neither for LAS nor for COD.

Biofilm on edges

The in-stream removal profile after one month of biofilm development on the gutters' edges is shown in Figure 8.7 (center). The measured biofilm thickness was ca. 400 μm . However, this may have been an overestimation because the plastic trays may have acted as sediment traps. Significant in-stream removal was observed for LAS and COD. The calculated decay rate coefficient of LAS was $0.38 (\pm 0.12) \text{ h}^{-1}$ (mean $r^2 = 0.855$); for COD, it was $0.19 (\pm 0.11) \text{ h}^{-1}$ (mean $r^2 = 0.755$). Hence, for COD the relative variability was higher, and the rate coefficient was only half that of LAS.

Biofilm on carriers and edges

Next, plastic carrier material was entered into the river. The in-stream removal profile after one month of further biofilm growth is shown in Figure 8.7 (bottom). The biofilm thickness on the carriers was measured to be ca. 50 μm . In-stream-removal was significant for LAS and COD. The LAS decay rate coefficient was $0.71 (\pm 0.17) \text{ h}^{-1}$ (mean $r^2 = 0.857$); for COD the rate coefficient was $0.18 (\pm 0.08) \text{ h}^{-1}$ (mean $r^2 = 0.62$). Again, the COD data had a higher relative variability than LAS and the rate coefficient was lower.

Comparison of experimental series

The in-stream removal rate coefficients recorded in the three experimental series were compared by means of a Tukey test (significance threshold $\alpha=0.05$) (using SPSS software, version 7.5, SPSS Inc.). This test showed that LAS in-stream removal was significantly different in all three experimental series, while for COD no significant difference between the three cases could be shown.

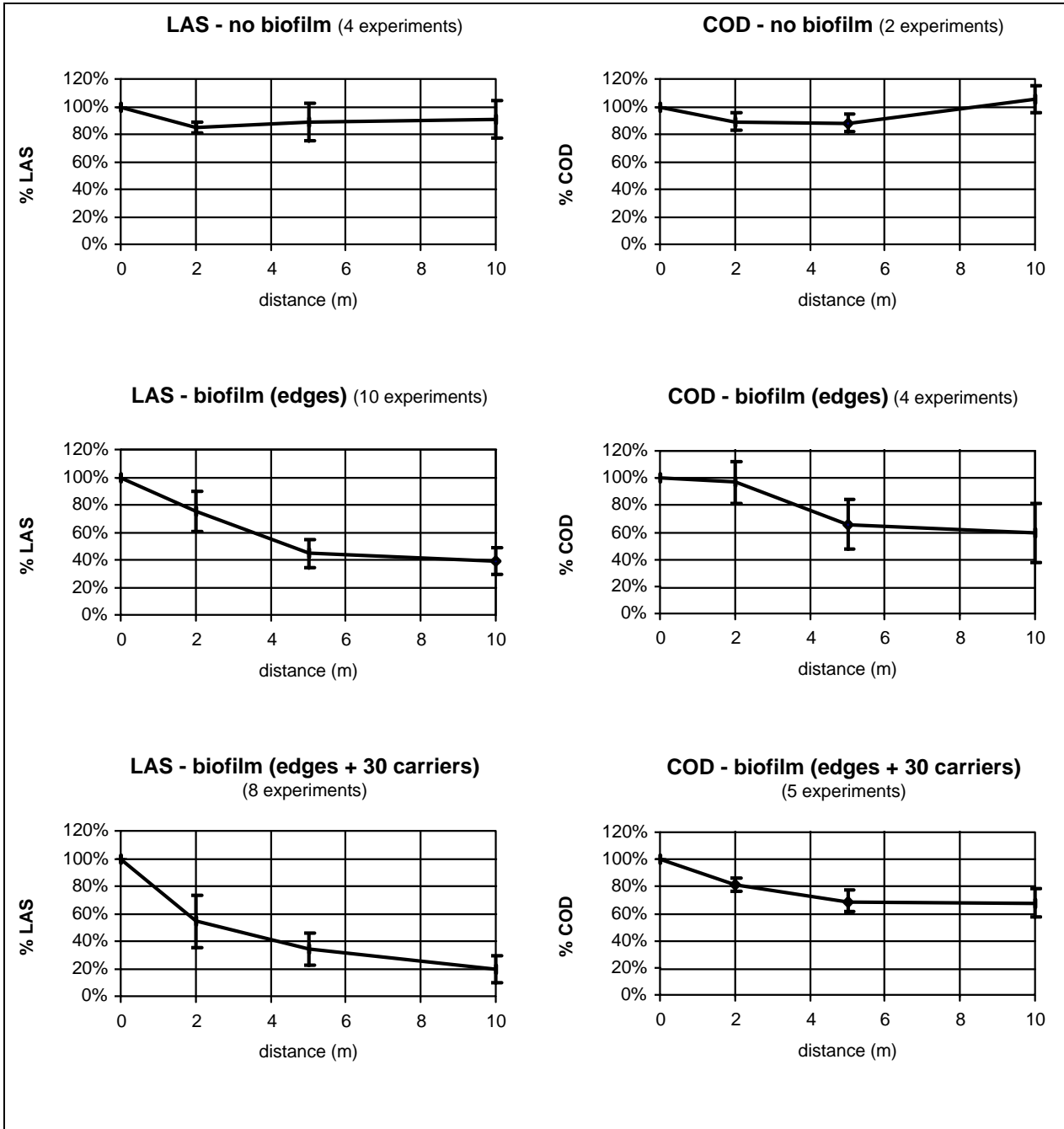


Figure 8.7. Artificial river in-stream removal measurements for LAS and COD

Discussion

No significant in-stream removal took place in the absence of biofilm. Hence, suspended biodegradation half-lives were much higher than the HRT (3 h). In the presence of biofilm, significant in-stream removal was shown. This indicates that in small rivers with a high surface area to volume ratio, biodegradation by biofilms can be much more important than by suspended biomass. The observed absence of in-stream removal in the ‘no biofilm’ case for LAS also indicates that biodegradation must have been the only significant in-stream removal process in the ‘with biofilm’ cases. LAS biodegradation was proportional to the amount of biofilm in the system. This trend was also observed for COD, but data variability prevented to support this statistically. In-stream degradation of LAS was always faster than COD decay. This can be explained by the good biodegradability of LAS, and also by the fact that the river water originated from a trickling filter’s effluent. In the filter, a nearly complete removal of the readily biodegradable COD (which is degraded faster than LAS) had been achieved. The COD remaining in the effluent consisted of less biodegradable fractions, which are degraded slower than LAS.

2.4.3. Model Calibration for LAS

For the purpose of calibration based on the experimental artificial river setup, the biodegradation model was slightly modified. Within the biofilm biodegradation, a further distinction was made between edge biofilm and biofilm on carriers. This distinction was necessary because the biofilm thickness was different. The calculation of the biofilm surface area was based on the actual geometry of the artificial river and on the actual surface area of the carrier material.

A temperature correction was not used, as the artificial river experiments were conducted at room temperature (ca. 20 °C).

The modified biodegradation model is formulated as:

$$k_{biodeg} = k_{biodeg}^{bulk} + k_{biodeg}^{edge\ biofilm} + k_{biodeg}^{carrier\ biofilm}$$

with $k_{biodeg}^{x\ biofilm} = a_{b/w}^x \cdot K_L \cdot \frac{D_e \cdot r_1 \cdot \tanh(r_1 \cdot L_f^x)}{D_e \cdot r_1 \cdot \tanh(r_1 \cdot L_f^x) + K_L}$ [8.15]

and

$$a_{b/w}^{edge\ biofilm} = Z_{biofilm} \cdot \frac{A_{edge}}{V_{river}}$$

$$a_{b/w}^{carrier\ biofilm} = Z_{biofilm} \cdot \frac{n_{carriers} \cdot A_{carrier}}{V_{river}}$$

The entire artificial river was modeled as one river stretch, hence homogeneous conditions (a.o. biofilm thickness) were assumed all over the river.

Model calibration for LAS

A number of parameters were taken from Melcer *et al.* (1995), because their actual value could not be determined within the scope of the described work (left part of Table 8.6): D_l , L , X_f . The correction factor $Z_{biofilm}$ was set to 2; this value represents the fact that a biofilm is not a flat surface but contains ‘peaks’ and ‘valleys’, and hence its total surface area is much higher than the surface area of the carrier onto which it grows (e.g. Lazarova & Manem, 1995).

(e.g. Struijs *et al.*, 1991). The model was calibrated only by tuning the (active) thickness of the edge and the carrier biofilm.

The parameters mentioned in the right part of Table 8.6 were known or could be measured. The K_b of LAS, $0.001 \text{ (g}_{dwt}/\text{m}^3)^{-1} \cdot \text{h}^{-1}$, was calculated from the first-order rate coefficient typically used for biodegradation by suspended biomass in activated sludge waste water treatment plants (3 h^{-1} , with mixed liquor SS = $3000 \text{ g}_{dwt}/\text{m}^3$) (e.g. Struijs *et al.*, 1991b).

The model was calibrated only by tuning the (active) thickness of the edge and the carrier biofilm, $L_f^{edge \text{ biofilm}}$ and $L_f^{carriers \text{ biofilm}}$. Although biofilm thickness was measured, the edges biofilm measurements showed a high variability, and hence only indicated an order of magnitude rather than absolute values. Moreover, a measured biofilm thickness includes both active and inactive layers (dead, or - in the case of LAS biodegradation - anoxic or anaerobic biofilm).

Table 8.6. In-stream biodegradation model calibration for LAS: fixed parameters

Default parameters			Measured or estimated parameters		
D_l	$5.5 \cdot 10^{-5}$	m^2/s	A_{edge}	0.308	m^2
L	0.0001	m	$A_{carrier}$	0.022492	m^2
X_f	40000	$\text{g}_{dwt}/\text{m}^3$	K_b	0.001	$(\text{g}_{dwt}/\text{m}^3)^{-1} \text{h}^{-1}$
$Z_{biofilm}$	2	m^2/m^2	$n_{carriers}$	0, 15 or 30	-
			SS	20	$\text{g}_{dwt}/\text{m}^3$
			V_{river}	0.00712	m^3

For the ‘no biofilm’ case no calibration was needed as all parameters were given. Next, the edge biofilm thickness was calibrated. The resulting value was fixed and used for the third case (edges + carriers), for which the carrier biofilm thickness was estimated. Calibration parameters, model predictions and corresponding measurements are given in Table 8.7.

Table 8.7. In-stream biodegradation model calibration for LAS: tuned parameters + results

		Edges	Edges + 30 carriers / stretch
Calibration			
$L_f^{edge\ biofilm}$	mm	106 [83, 129] *	106 **
$L_f^{carriers\ biofilm}$	mm	-	44 [28, 59] *
Model calculations			
$k_{biodeg}^{edge\ biofilm}$	h^{-1}	0.363	0.363
$k_{biodeg}^{carriers\ biofilm}$	h^{-1}	-	0.332
k_{biodeg}^{bulk}	h^{-1}	0.020	0.020
k_{biodeg}	h^{-1}	0.383	0.715
Measured			
k_{biodeg} (mean)	h^{-1}	0.382	0.711
k_{biodeg} (95% confidence)	h^{-1}	[0.305, 0.459]	[0.592, 0.830]

* calibrated L_f corresponding to 95 % interval of k_{biodeg} measurements

** from 'Edges' calibration

Discussion

It was possible to fit the biodegradation model to LAS in-stream removal measurements in the artificial river, using measured system information or realistic defaults as model parameters, and using an LAS biodegradation rate coefficient which was derived from activated sludge data. The calibrated edge biofilm thickness was 4 times lower than measured, which can on the one hand be explained by the low accuracy of the measurement. On the other hand, typically only the upper layer of a biofilm is aerobic (e.g. Horn & Hempel, 1997). Hence, since LAS biodegradation requires oxygen (e.g. Jimenez *et al.*, 1991), a calibrated active edge biofilm thickness of 100 μm is quite plausible. Finally, the calibrated carrier biofilm thickness was very close to the (accurately) measured value of 50 μm (which can be assumed completely active). Note that the carriers were only introduced at a later stage of the experiments, hence less time was available for biofilm growth compared to the edges.

2.5. Model Corroboration - Red Beck Field Study

The model was applied to the Red Beck, a small river in the Calder catchment (Yorkshire, UK). Within the GREAT-ER project, a detailed LAS in-stream removal monitoring campaign has been conducted (Fox *et al.*, submitted).

2.5.1. Model Parameters and River System

The same parameter values as in the artificial river calibration were used. However, the biodegradation rate coefficient was corrected for the low temperature (9 °C) by setting K_b to $0.0005 \text{ m}^3/\text{g}_{\text{dwt}}\cdot\text{h}$, which corresponds to a $Q10$ factor of 2. The biofilm thickness was set to 100 μm (cf. the calibrated edges biofilm thickness above).

The river was split into 2 stretches (average parameter values are given for each stretch):

- [1] Shibden Head (treatment plant) to Dam Head: 1.3 *km*, HRT 1.45 *h*, width 1.5 *m*, depth 15 *cm*, SS 16.5 *mg/L*.
- [2] Dam Head to Sunny Bank: 3.5 *km*, HRT 3.6 *h*, width 3.05 *m*, depth 22.5 *cm*, SS 11.2 *mg/L*.

For both sections, the bed material consisted of pebbles, with an average bed depth of 15 *cm*. Its specific surface area was estimated to be $100 \text{ m}^2/\text{m}^3$ (by assuming spherical pebbles with 2 *cm* radius and 33% voids).

From the river geometry and bed properties, it was possible to roughly estimate the surface available for biofilm growth, both on the river's 'edges' (area per length = width + 2 * depth) and on the pebbles (area per length = width * bed depth * specific surface area). For section [1] this was respectively 0.3 m^2 and 22.5 m^2 per *m* of river, for section [2] it was 0.45 m^2 and 45.75 m^2 per *m*. The estimated total surface area per unit of volume (A/V) was $100 \text{ m}^2/\text{m}^3$ in section [1] and $70 \text{ m}^2/\text{m}^3$ in section [2].

The LAS concentration in the Red Beck were a factor 2 to 3 lower than in the artificial river study, which was used for model calibration. The flow in the Red Beck was 0.1 m^3/s .

2.5.2. Model Predictions versus Measurements

The biodegradation model calculations were performed for both stretches, resulting in a 1st-order LAS half-life of 2.09 *h* in stretch [1] and 3.14 *h* in stretch [2]. In both cases, 97.5% of the biodegradation was predicted to take place in biofilms. By relating the initial level in [1] with the most downstream level in [2] (not considering the differences of the 2 sections), an 'overall' half-life value of 2.74 *h* was calculated.

In the Red Beck field study, an overall LAS half-life of 2.23h was found. For section [2] only, this was 2.67h. This corresponds well with the predictions: the model overestimated the overall half-life by merely 23% and the half-life in section [2] was overestimated by 18%. An overview of these measurements and predictions is given below in Table 8.8.

Table 8.8. Red Beck field study: predicted vs. measured LAS in-stream removal

	[1] Shibden Head to Dam Head	[2] Dam Head to Sunny bank	Overall
Predicted LAS half-life	2.09 h	3.14 h	2.74 h
Measured LAS half-life	-	2.67 h	2.23 h

Discussion

The predicted in-stream biodegradation of LAS in the Red Beck corresponds well with measured in-stream removal, even with many model parameters being rough estimates or default values. However, to allow a more general applicability, further validation for other situations and testing of the applied assumptions and defaults are required. As many parameters used in the model prediction were rough estimations, it would be speculative to draw any conclusions from the model's underestimation of the in-stream removal rate coefficient. A tentative explanation may be given by the fact that, next to biodegradation, also sorption / sedimentation took place in the Red Beck. This hypothesis is supported by the SS levels which decreased downstream, and by the fact that 10-25% of the measured LAS was associated with solids (Fox *et al.*, submitted).

The presented biodegradation modeling concept was also compared with measurements in the Emscher River (Germany) by Løkkegaard Bjerre *et al.* (1998). Based on the A/V ratio reported for this river ($1 \text{ m}^2/\text{m}^3$), the model presented in this paper predicts that the biofilm would account for 14 % of the total biodegradation activity (Figure 8.4). This prediction corresponds well with the measurements of relative oxygen transformation activity in the biofilm reported by Løkkegaard Bjerre *et al.* (1998).

3. Conclusions

Based on a review of the literature, a conceptual steady-state river fate model was selected for use within the GREAT-ER project. This model considers the processes degradation (hydrolysis, photolysis, biodegradation), sorption / sedimentation, and volatilization.

The existing models have a number of shortcomings. The photolysis models are relatively crude steady-state simplifications of a dynamic reality. The sorption / sedimentation model can only be as accurate as the applied suspended solids sedimentation rate coefficient. Finally, biodegradation is typically considered in a non-physically-based way.

In the artificial river experiments presented in this chapter, biodegradation was found to be the only significant in-stream removal process of LAS. In this specific case, measurable biodegradation only occurred when biofilm was present. The biodegradation rate was proportional to the amount of biofilm in the system.

A new biodegradation modeling concept, considering microbial activity both in biofilm and in bulk water, was presented. This model could be calibrated using the experimental data obtained in the artificial river experiments. Using this calibration, the model was able to predict the in-stream removal of LAS which was measured in the Red Beck field study (Fox *et al.*, submitted). The accuracy was more than satisfactory within the GREAT-ER approach, where a final accuracy of a factor < 5 is aimed for (Feijtel *et al.*, 1997). Hence, it can be concluded that the model was successfully corroborated for the fate prediction of LAS in the specific case of the Red Beck.

It is recommended that a further corroboration of the presented modeling approach be conducted, especially based on other detailed field study data. The range of validity of the model and its assumptions needs to be extended to other chemical substances and to other types of rivers.

Chapter 9

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***Fate of Biodegradable Chemicals in the Sewer:
Case Study for LAS***

Chapter 9

Fate of Biodegradable Chemicals in the Sewer: Case Study for LAS

1. Introduction

The degradability of LAS in sewers has been demonstrated in the past. Moreno *et al.* (1990) found 50% LAS removal in a southern Spanish sewer (during winter, under dry weather conditions). LAS was measured at the beginning and end of a long sewer line (travel time of approximately 9 hours, distance of 12 km), using 2-hourly composite samples over 24 hours. The in-sewer removal of LAS found by Matthijs *et al.* (1995, 1997) in The Netherlands ranged between 10% and 68%, with an average of 50% elimination. In this study, an indirect method was used: predicted raw sewage concentrations (based on consumption data) were compared to field measurements. Using the same approach, Holt *et al.* (1998) detected over 60% of LAS in-sewer removal in Yorkshire (UK).

To confirm and to further quantify the elimination of LAS (Linear Alkylbenzene Sulphonate) in sewer systems, an in-sewer removal experiment was conducted, by measuring the concentration of LAS at different points in a well-characterized sewer branch, following the plug of sewage using a dye tracer. To explain the results of this field study, a laboratory degradation experiment was also performed.

These experimental studies were in close co-operation with Aquafin (the company which is responsible for planning, design and operation of sewers and treatment infrastructure in Flanders) and Procter & Gamble Eurocor.

2. Field Study

2.1. Selection of Study Area

It was expected that relatively long hydraulic residence times in the sewer were required for the in-sewer removal experiments (order of magnitude: hours). Hence, a lowland area was preferred, with low slopes. Based on advice by Aquafin, the sewer system of Tielt (West Flanders) was selected for the study, because of past experiences with this well-characterized sewer.

The selected study area is a sewer branch in Aarsele (east of Tielt), which only receives one (minor) tributary input, approximately halfway its length. A calibrated hydraulic model was available (Heip *et al.*, 1997). The hydraulic residence time at dry weather was expected to be approximately 3 hours, based on hydraulic model results.

Three sampling locations were chosen, all of which are easily accessible by road: SP1 = Aarsele center (start of the sewer branch, next to CSO structure); SP2 = N35 road (confluence of main sewer line with Baudeloostraat sewer line); SP3 = Aarsele Railway Station (end of the sewer branch, next to CSO structure). At the SP2 location, 2 samples could be taken: SP2A = the main sewer line, upstream of the confluence with the Baudeloostraat sewer, and SP2B = the Baudeloostraat ‘tributary’ sewer outflow. The location of the sewer branch and of the sampling points is illustrated schematically in Figure 9.1.

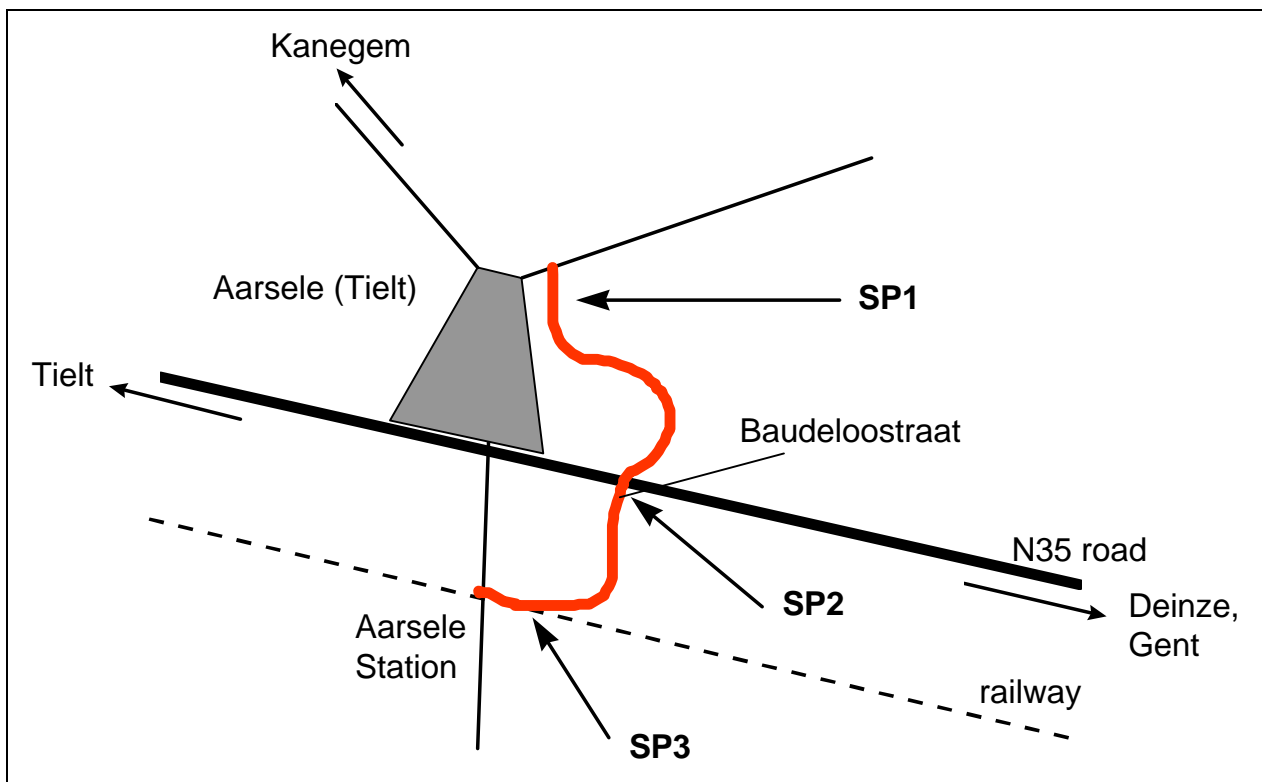


Figure 9.1. Sewer field study: schematic of sewer branch and sampling locations

Upstream of the selected sewer branch, is the sewer line between the villages of Kanegem and Aarsele. Waste water is intermittently pumped into this sewer, by means of a pump which is switched on for ca. 15 minutes every 2 hours.

2.2. Methods

Dry weather conditions were required both on the day of the study itself and at least 2 days before. Samples were taken 'following a plug of sewage'. To accomplish this, a dye tracer (Rhodamine B) was used. Next to LAS, Boron and BOD were also measured. Boron could be used as an inert tracer to check dilution effects, and BOD measurements allowed to compare LAS degradation with the degradation of 'typical' organic material.

2.2.1. Tracer

The bacterial acute EC-50 of Rhodamine B is ca. 750 mg/L (Verschueren, 1996). Hence a concentration of 10 mg/L could be assumed non-toxic, and it was aimed not to exceed this level in the sewer. Based on the hydraulic model, the sewer flow was expected to be ca. 5 L/s. To obtain maximally 10 mg/L of rhodamine in the sewer (without considering dispersion), 50 mg/s were to be spiked. Rhodamine was detected visually, by examining the color of sewage samples in glass vials. For the detection of the rhodamine peak, the color intensity in each vial was compared to the previous sample. It was possible to detect the peak within an accuracy of ca. 5 minutes, which was sufficiently accurate for the purposes of this work.

2.2.2. Sampling

A rhodamine pulse was spiked during 30 seconds. The rhodamine detection was used to determine the actual sampling time. LAS, Boron and BOD samples were taken 5 minutes after the rhodamine peak (to reduce rhodamine levels in the samples). Three bottles were filled for each sample (all in duplicate). For LAS, 1000 mL glass bottles were used. LAS samples were preserved using 3% of formaline solution. BOD samples were also put in 1000 mL glass bottles, which were stored in a cooling box. Boron samples were stored in plastic bottles of 100 mL. At the time of sampling, *t* (temperature), DO (dissolved oxygen) and pH were measured.

2.2.3. Laboratory Die-Away Test

Using sewage from SP3, which was sampled during the field study experiments, a lab die-away study was performed on a shaking device which provided aeration. An abiotic control (inactivated using 3% formaline solution) was run in parallel. This test was performed during 24 hours, which is approximately 8 times longer than the residence time in the sewer itself.

2.2.4. Analytical

Specific LAS analyses (after Holt *et al.*, 1995) and Boron analyses (after Environment Agency, 1996) were performed at the UK Environment Agency, Leeds Laboratories (UK). BOD was analyzed at the Laboratory of Microbial Ecology of the University of Gent (Belgium), using the Sapromat apparatus (e.g. Verstraete *et al.*, 1974).

2.3. Results

Field study results for LAS and BOD are shown below in Table 9.1. Boron levels did not decrease from upstream to downstream, and the tributary's LAS level was similar to that in the main sewer branch. Hence, corrections for dilution did not have to be taken into account. The sewage temperature was between 12 and 15 °C, DO varied between 3 and 6 mg/L, and pH was ca. 8.3.

Table 9.1. In-sewer removal study - LAS and BOD results

	Time	LAS (mg/L)	BOD (mg/L)
SP1	0h00m	11.7	465
SP2A	1h45m	14.5	467
SP3	2h55m	13.1	261
tributary (SP2B)	-	14.5	253

No primary elimination of LAS from the sewer was found. Toxicity of the tracer chemical could be eliminated as a possible reason. Sewage quality (DO, temperature, pH) was also not expected to have impaired biodegradation. BOD was not eliminated in the first stretch of sewer but was removed for ca. 45% in the second.

In the laboratory die-away test, it was found that primary LAS biodegradation during the 24 hour period was very limited. Less than 10% was removed. Note that the slight increase in measured LAS concentration during the first hour may have been due to desorption from suspended solids in the sewage.

2.4. Discussion

A toxic substance may have been present in this particular sewer, which inhibited biological degradation of LAS, and of BOD in the first stretch of the study area. This hypothesis is contradicted by the fact that a significant BOD elimination was found in the second part of the sewer, and by the fact that BOD could be measured at all, using a biological respirometry test. In toxic sewage, the BOD measurement is expected to be zero, as biological activity is inhibited.

Non-biodegradability of LAS under the specific conditions of the considered sewer system is unlikely, especially since temperature and the dissolved oxygen level were favorable.

The most plausible explanation is that the studied sewer branch did not contain sufficient amounts of (suitable) biomass to provide fast LAS degradation. This hypothesis is not contradicted by the fact that BOD could be measured, as for the BOD measurements an inoculum (activated sludge) was added. This hypothesis is also not contradicted by the laboratory die-away test, in which biodegradation was slow and hence very limited within a 24 hour time frame.

3. Laboratory Experiments

As the results of the field study did not meet the expectations based on literature, a further laboratory experiment was conducted to measure the biological degradation kinetics of LAS in Tielt sewage under different biomass conditions. To examine the effect of the specific sewage origin, a die-away experiment was also conducted with Gent sewage (WWTP influent).

3.1. Methods

3.1.1. Sampling

Tielt sewage: a composite sewage sample was taken at Tielt SP2A. In total, 10 L of sewage was collected and transported to the lab, stored in a cooling box. Next to the sewage sample, a sewer sediment sample (200 mL) was taken. Gent sewage: influent of the Gent WWTP (Ossemeersen) was sampled. 2 L of sewage was taken and transported to the lab, stored in a cooling box. Activated sludge, required for a die-away study with inoculum, was also taken from this WWTP in Gent (100 mL of recycle sludge).

3.1.2. Experiments

The die-away study was performed during 5 days. Different types and levels of bacterial inoculum were used for the different experiments (Table 9.2).

Table 9.2. Description of sewage die-away experiments

Name	Sewage	Description	
A, B	Tielt SP2A	sewage, as such	2x
C, D	Tielt SP2A	+ Tielt sewer sediment (5% v/v)	2x
E, F	Tielt SP2A	+ Ossemeersen activated sludge (5% v/v)	2x
G	Tielt SP2A	abiotic control (3% v/v formaline solution)	1x
H	Gent	influent, as such	1x

The sewage samples were put in open glass bottles, at room temperature, and were mixed (and aerated) on a shaking platform during 5 days. The sampling intensity was decreased towards the end of the experiments, as an exponential decay profile was expected. Samples for surfactant analysis (50 mL) were preserved with 3% formaline solution. pH, DO and temperature were regularly monitored and adjusted if needed. A DO level between 3 and 4 mg/L was aimed for, as this is representative of the situation in the considered sewer system.

At the start of the experiment, the water temperature was less than 20 °C, as the samples were previously stored in a refrigerator. During the first day temperature increased to > 27 °C, due to very high ambient temperatures. The next days temperature stabilized between 23 and 25 °C.

3.1.3. Analytical

To reduce the costs of the experiment, an aspecific analytical method for anionic surfactants was used: the Azure-A method (Den Tonkelaar & Bergshoeff, 1969). The measurements were performed at Procter & Gamble Euro-Analytical (Strombeek-Bever, Belgium). The BOD of Tielt SP2A was measured, using the Sapromat apparatus, without the addition of an inoculum (but with the normal addition of a nitrification inhibitor) (Laboratory of Microbial Ecology of the University of Gent, Belgium).

3.2. Results

The Tielt SP2A raw sewage, as such, was used for a non-inoculated BOD measurement. The 10 day BOD value (at 20 °C) was 565 mgO₂/L (average of duplicate analyses). From the BOD curves, it could be derived that sufficient numbers of competent micro-organisms were present in the raw sewage for the fast degradation of organics, without the need for an adaptation phase.

The results (expressed as % remaining Azure-A active substances) are plotted in Figure 9.2 (the mean value is given for duplicate experiments).

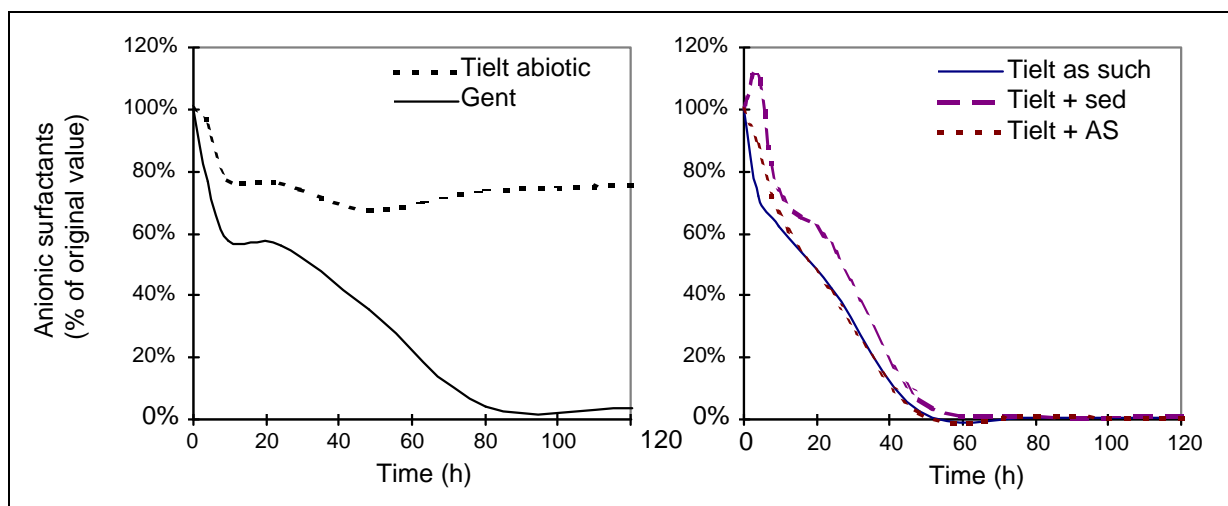


Figure 9.2. Sewage die-away experiments: % remaining anionic surfactants

Approximately 30% of the anionic surfactants was removed in the abiotic control. Anionic surfactants degradation in Tielt sewage was faster than in Gent sewage. The fitted first-order decay rate in Tielt (average for all 3 experiments) was 0.021 h⁻¹, while the fitted rate for the Gent experiment was only 0.013 h⁻¹. There was no influence of adding extra biomass (from sewer sediment or from activated sludge) on the rate of anionic surfactants degradation in Tielt sewage.

3.3. Discussion

It was found that Tielt sewage contained sufficient competent biomass for the degradation of BOD, as shown by the Sapromat experiment without inoculum. Tielt sewage showed no toxicity towards BOD degrading micro-organisms.

Elimination of anionic surfactants was faster in Tielt sewage than in Gent sewage. The primary surfactant removal was complete in both cases, but it required 50 hours for Tielt and 80 hours for Gent. From these kinetics, the field study results can be explained. The half-life time for the decay of anionic surfactants in Tielt sewage was 34.5 h. This is a factor 10 higher than the actual residence time in the studied sewer line, which explains the absence of any measurable LAS elimination.

There was no difference in anionic surfactants elimination between the sewage ‘as such’ experiments and the experiments with additional biomass. Apparently, the addition of only 5% (v/v) of an extra biomass source (sewer sediment or activated sludge) was not sufficient to speed up biodegradation.

4. Modeling Exercise

The method used by Matthijs *et al.* (1995, 1997) and Holt *et al.* (1998), based on market data and measured WWTP influent concentrations, was applied to the Tielt study area. Market data for anionic surfactants in the region of Tielt were provided by Procter & Gamble, Eurocor. Inhabitant numbers and water consumption were obtained from Aquafin. These data, together with the predicted concentration of anionic surfactants in the 2 sewer branches at the location SP2A, is given in Table 9.3.

Table 9.3. Prediction of anionic surfactants concentration in Tielt SP2A sewage

Sewer branch	Inhabitants (cap)	Water use (L.cap ⁻¹ .day ⁻¹)	Anionics use (g. cap ⁻¹ .day ⁻¹)	Anionics conc. (predicted - mg/L)
Aarsele center	1097	87	5.1	59
Baudeloostraat	269	136		38

The weighted average (by flow) of the anionics concentration in the 2 considered branches is 53 mg/L. The measured concentration was 17.5 mg/L. Based on this, a removal efficiency of 67% can be derived. This compares well with the removals mentioned in the literature.

It should be noted that the measured concentration only represents one point of the diurnal concentration curve. As the sample was taken around 11h00 AM, it is expected to represent a high but not the maximal value.

5. Discussion

The results of the field study presented in this chapter appear to be in contradiction with the in-sewer removal measurements described in the literature. On the other hand, based on a comparison of the predicted raw sewage concentration and the measured concentration, the anionic surfactants appeared to have been removed to a large extent upstream in the sewer system.

The field study described in this chapter indicated that in the main sewer line of Aarsele (Tielt), no LAS removal occurred. The laboratory sewage die-away studies showed a complete elimination of anionic surfactants, but at a relatively slow rate. This confirmed that, based on the activity of suspended biomass in the considered sewage, biodegradation was too slow to achieve any significant removal in the 3 hours residence time. On the other hand, the absence of in-sewer removal is contradicted by the modeling exercise.

None of the studies mentioned in the literature were conducted by means of a dye-tracer experiment. None of them gives a full confirmation about the processes which occurred in a specific 'packet' of sewage. The field study presented here showed no LAS removal following such a packet of sewage in a single stretch of the main sewer. However, the high LAS removal degrees found in the studies given in the literature were related to the entire sewer system, instead of one stretch. Considering the entire sewer system in Aarsele (using the market data modeling approach), a high degree of removal was also found.

A possible explanation is that no surfactant in-sewer removal took place in the main sewer line because no biofilm could be established there due to intermittent flushing by the upstream pump. On the other hand, biofilms are expected to be present and active in the slower flowing side branches of the system. Assuming the results of the market data approach are correct, a high degree of surfactant elimination must have taken place in these smaller side branches.

To gain a better understanding of the fate of chemicals in the sewer system, it is recommended that a detailed monitoring campaign be conducted. The chemical fate pathway should be followed from the households to the treatment plant or to the main sewer line. An entire sewer (sub)catchment should be evaluated, preferably under completely controlled conditions, and using tracer chemicals. Therefore, co-operation of the area's inhabitants is most probably required (cf. the experiments by Schowanek *et al.*, 1996).

Chapter 10

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New PEC Definitions for River Basins Applicable to GIS-based Environmental Exposure Assessment

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Chapter 10

New PEC Definitions for River Basins Applicable to GIS-based Environmental Exposure Assessment

1. Introduction

The initial output of a GREAT-ER simulation (Feijtel *et al.*, 1997; Boeijs *et al.*, 1997) for a specific catchment and chemical is a set of geo-referenced local predicted concentrations, linked to a digital river network. This can e.g. be presented as a color-coded map or as a concentration profile. Such output is directly applicable for local (or regional) water quality management purposes, and it allows model verification by means of site-specific monitoring programs. Moreover, it allows the identification of local high risk areas. However, for application in a regional environmental risk assessment context, there is a need to aggregate the geo-referenced output to a single value (or frequency distribution) which is representative of chemical exposure within the catchment.

In this chapter, two aggregation methods were studied: aggregation of all concentrations in the catchment, and aggregation of all ‘highest’ predicted concentrations (occurring immediately below waste water emission points).

2. Definitions

2.1. Nomenclature

Local (frequency distributions of) concentrations are linked to individual river stretches or waste water emission points. As the acronym ‘PEC’ is a regulatory term (e.g. EEC, 1994b), which is used in risk assessment for comparison with PNECs or NOECs, this is not to be used for predicted local geo-referenced concentrations. Instead, the term ‘ C_{SIM} ’ (simulated concentration) was applied.

For each stretch, GREAT-ER simulations produce the values $C_{SIM,start}$ (at the beginning of the stretch), $C_{SIM,end}$ (at the end of the stretch) and $C_{SIM,internal}$ (predicted average concentration in the stretch) (chapters 2 and 3 of this thesis).

In this chapter, aggregated concentration values - which can be used in a risk assessment context - are called PECs (Predicted Environmental Concentrations). Two aggregated PEC types were defined and tested: $PEC_{initial}$ and $PEC_{catchment}$.

2.2. $PEC_{initial}$

$PEC_{initial}$ is the spatial aggregation of concentrations in the river immediately after emissions. This is comparable to PEC_{local} as defined in the EU Technical Guidance Documents (EEC, 1994b), although its calculation method is different.

2.2.1. Local Basis for Spatial Aggregation

$C_{SIM,start}$ was selected as the starting point from which $PEC_{initial}$ can be calculated. This value can be monitored (albeit indirectly), by calculating the mass balance of upstream and waste water effluent measurements (both flow rate and concentrations), assuming complete instantaneous mixing. As no in-stream removal below the emission point is considered, $C_{SIM,start}$ is independent of the river segmentation (length of the stretches) and hence of the river network's scale. $C_{SIM,start}$ is totally scale independent if emissions are not aggregated into larger hypothetical emission points. However, if aggregated emissions are used (i.e., if several small emission points are aggregated into one hypothetical emission point), the $C_{SIM,start}$ value may increase.

The impact of the uncertainty around in-stream removal and flow velocity is limited to its impact on the upstream concentration - it has no effect on the concentration which is due to the considered waste water emissions. It can be concluded that $C_{SIM,start}$ offers the most stable and unambiguous starting point for a $PEC_{initial}$ aggregation.

The fact that in-stream removal is not taken into account for the considered emission points results in the use of the highest C_{SIM} values produced by GREAT-ER simulations. This is complementary to the $PEC_{catchment}$ approach (see below), where average values are used. It is stressed that $C_{SIM,start}$ of an emission-receiving river only represents the 'worst-case' predicted in the one-dimensional GREAT-ER river modeling approach. In reality, much higher concentrations can be found close to the emission point, due to incomplete mixing. The true worst-case situation in the river occurs at the exact location where the effluent is discharged into the river. At this point, no mixing or dilution have yet occurred, and hence the local concentration in the river is equal to the effluent concentration.

2.2.2. Spatial Aggregation

$PEC_{initial}$ is described by the spatial mean and spatial standard deviation of the local $C_{SIM,start}$ values. The aggregation can be based on local means, or on local high percentiles (e.g. 90th) if a variability analysis was included in the simulation. Weighting is not required in the spatial aggregation process, as the unweighted approach is already scale-independent ($C_{SIM,start}$ is scale-independent in itself). The unweighted approach warrants that all emission points are given equal importance.

2.3. $PEC_{\text{catchment}}$

$PEC_{\text{catchment}}$ is the spatial aggregation of concentrations representative of the entire catchment. Although this is a new concept typical for geo-referenced exposure assessment, but it could be compared to PEC_{regional} in the EU Technical Guidance Documents (EEC, 1994b).

2.3.1. Local Basis for Spatial Aggregation

$C_{SIM, \text{internal}}$ is the most representative value for the concentration in a stretch. As $PEC_{\text{catchment}}$ aims to provide a measure for the 'representative' concentration all over a catchment, it was based on this most representative value for individual stretches. The $C_{SIM, \text{internal}}$ value of individual stretches is scale dependent, as its calculation depends on the stretch length. The longer a stretch is, the more residence time is available for in-stream removal, hence the average concentration $C_{SIM, \text{internal}}$ will be lower in long stretches compared to short stretches (when all other conditions are equal). This scale-dependency needs to be compensated for in the aggregation process.

2.3.2. Spatial Aggregation

$PEC_{\text{catchment}}$ can be described by the spatial mean and spatial standard deviation of the local $C_{SIM, \text{internal}}$ (mean or high percentile) values.

Stretch selection

There are 2 plausible options for the selection of stretches which are to be included in the spatial aggregation: (1) selection of all stretches in the digital river network (entire digitized catchment), or (2) selection of only those stretches which are downstream of pollution sources.

Option (1) is the most comparable with the current regional exposure assessment approach ('unit world' models, e.g. Mackay *et al.*, 1992), in which all surface waters in a region are considered for the dilution of the chemical mass loading. It allows to compare the degree of chemical-specific pollution between catchments, and it also allows a quantitative evaluation of chemical-related water quality in a catchment, which is especially useful from a water quality management point of view.

Option (2) focuses on polluted surface waters only. This is significantly different from the currently used methods. However, this concept may also be appropriate for risk assessment: risk assessment of the aquatic environment should mainly focus on rivers that are actually at risk (because they are downstream of pollution points) and need not necessarily deal with pristine environments. A practical reason in favor of this option is the fact that data on upstream unpolluted rivers (headwaters) are generally scarce and/or of low quality, especially when large-scale databases and maps are used.

Scale-dependency

An unweighted spatial aggregation of predicted river concentrations can be identified as scale-dependent in two ways: (A) related to the level of geographical detail of the river network, and (B) related to the applied river stretch length:

(A) River network geographical detail

The unweighted aggregated $PEC_{catchment}$ is influenced by the number of upstream unpolluted rivers which are included in the digital river network. The more unpolluted headwaters are present, the lower the aggregated $PEC_{catchment}$ will be. The number of headwaters in the river network depends not only on the digitization but also on the type of catchment: mountainous catchments will typically have more (but smaller) sources than lowland catchments. This scale-dependency is illustrated by means of the example river network in Figure 10.1. If all headwater stretches are included (situation I), the unweighted average $PEC_{catchment}$ is 0.15. If on the other hand only the three most downstream stretches are considered in the network (situation II), the unweighted average $PEC_{catchment}$ is 0.50. This scale-dependency is resolved when headwater stretches are not considered (situation III): in this case the unweighted average $PEC_{catchment}$ is 0.75, independent of the upstream river network's level of detail.

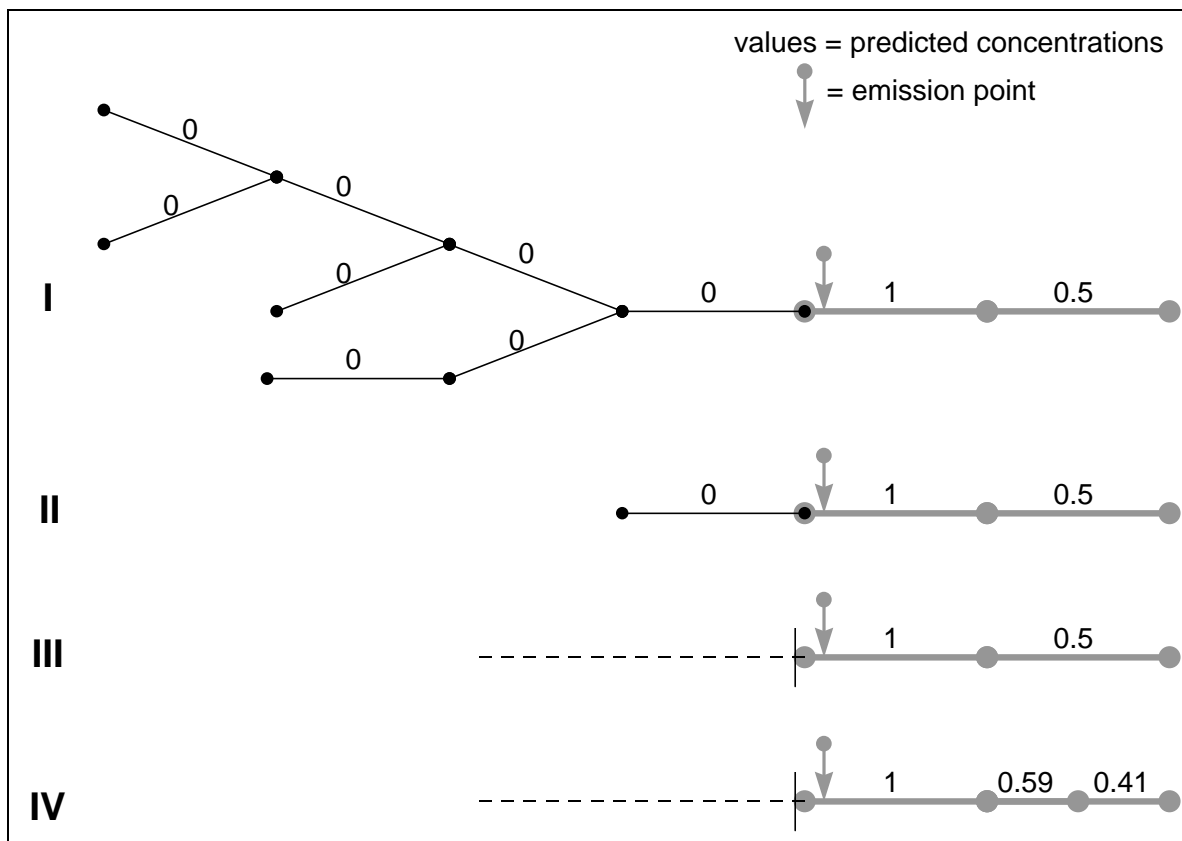


Figure 10.1. Scale-dependency of $PEC_{catchment}$ calculations: example river network

(B) Stretch length

In practice, river stretch length can not be fixed, e.g. due to the presence of confluences. Because of this, the unweighted aggregated $PEC_{catchment}$ is influenced by the river segmentation. If in the example river network of Figure 10.1 the most downstream stretch (with concentration 0.5) would be split up into 2 stretches (situation IV), the unweighted average $PEC_{catchment}$ (based on the selection of only those stretches downstream of pollution sources) would be 0.67 instead of 0.75.

Weighting

Because of both scale-dependencies, an unweighted spatial aggregation of $C_{SIM,internal}$ values can not be used for $PEC_{catchment}$ calculations. $PEC_{catchment}$ would not be comparable between catchments that were digitized at a different scale or using different stretch lengths, and would not be a constant within a single catchment if it would be modeled using different scales or river segmentations. Moreover, it would be possible to steer the value of $PEC_{catchment}$ by modifying the number of considered headwaters, or by modifying the river segmentation.

Weighted by stretch length

Weighting by stretch length obviously solves scale-dependency (B) mentioned above. However, it does not solve scale-dependency (A), related to the number of unpolluted headwaters that are considered in the aggregation. Hence, this approach can only be applied in combination with option (2) for stretch selection: only the stretches downstream of pollution sources.

The ecological interpretation is that equal importance is attached to rivers with equal length. Hence, small rivers are considered equally valuable as large rivers. This attaches importance to the entire aquatic ecosystem (the bulk water as well as the river’s edges), and also the terrestrial environment near the river which is influenced by it.

The weights w_i for each stretch i can be calculated as:

$$w_i = \frac{l_i}{\sum_{j=1}^{n_{stretches}} l_j} \quad [10.1]$$

Weighted by flow increment

Weighting by flow increment in a stretch solves both scale dependencies (A) and (B). For the PEC analysis, the flow increment in a stretch (i.e., the increase of flow in a stretch) is defined as the difference in mean flow between the considered stretch and the upstream stretch. After a confluence, the sum of both upstream flows is used. For the most upstream stretches in the digital river network (i.e., which are not connected to any further upstream stretches), the flow increment is equal to the flow itself. Hence, the flow increment in these most upstream stretches is equal to the flow increment in the entire headwaters subcatchment which - in reality - feeds into them.

This concept is illustrated in Figure 10.2 below. The flow increment ΔQ_3 in stretch 3 is calculated as the difference of the flow in stretch 3 with the upstream flow (i.e. the sum of flows in stretches 1 and 2). For stretches 1 and 2, there are no upstream stretches: the ‘upstream’ flows are zero, and consequently the flow increment values ΔQ_1 and ΔQ_2 are equal to the flows in stretches 1 and 2. For stretch 1, which in reality does receive the outflow of an upstream headwaters subcatchment, it is shown in Figure 10.2 that the flow increment ΔQ_1 corresponds with the entire headwaters catchment, rather than with the drainage area of only stretch 1 itself.

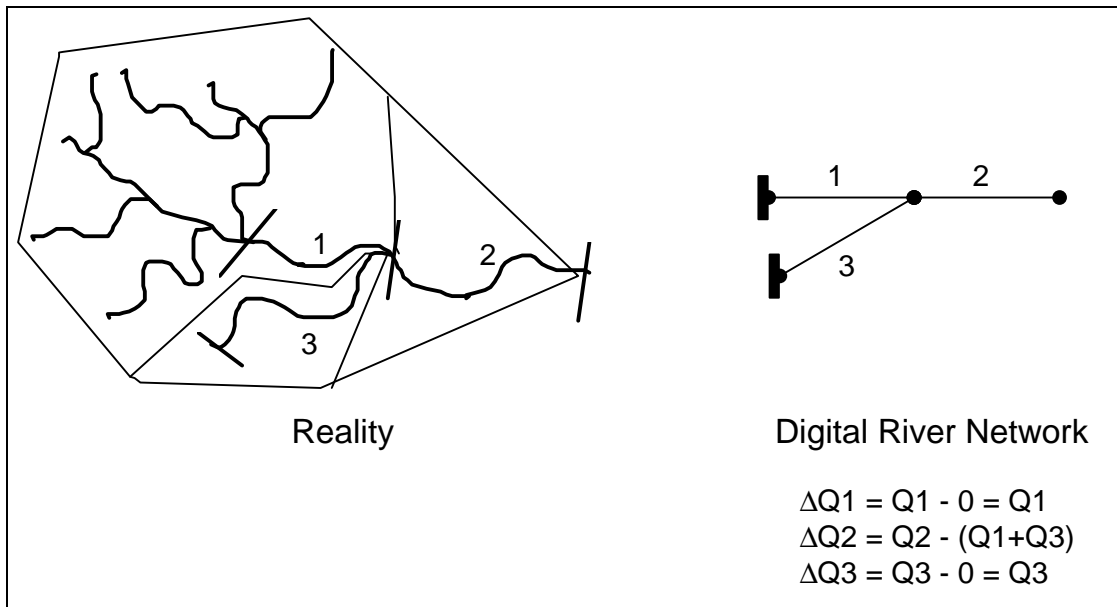


Figure 10.2. Flow increment: schematic illustration of the concept

Weighting by flow increment assigns the weight of all headwaters which are in reality at more upstream locations to the ‘most upstream’ stretches in the digital river network. This way, scale-dependency (A) is resolved: digitizing more or less unpolluted headwaters has no influence on the flow (= flow increment) in the most upstream stretch that is considered. However, it is crucial that these most upstream stretches be free of pollution. If not, the concentration of a single polluted stretch is given the weight of the entire (unpolluted) headwaters subcatchment feeding into this stretch, and hence the $PEC_{catchment}$ is a gross overestimation of the true situation.

As flow increment is correlated with the drainage area of a stretch and hence also with stretch length, scale-dependency (B) is also resolved. If a stretch is split into 2 sub-stretches, the sum of the flow increment in both stretches is equal to the flow increment in the original stretch.

The ecological interpretation of this weighting approach is similar to the ‘weighted by stretch length’ approach. However, stretches receiving emissions may have a higher weight, because the waste water emission adds to the flow increment in a stretch.

The weights w_i for each stretch i can be calculated as follows in equation [10.2]. Note that the total flow increment in a catchment (i.e. the sum of the flow increments in all stretches) must necessarily be equal to the flow at the end of the catchment.

$$w_i = \frac{\Delta Q_i}{\sum_{j=1}^{n_{stretches}} \Delta Q_j} \equiv \frac{\Delta Q_i}{Q_{end}} \quad [10.2]$$

Weighted by stretch volume

The volume of a river stretch can be calculated from its flow, flow velocity and length. Hence, this approach implicitly contains a weighting by length, and hence it solves scale-dependency (B). Although this weighting approach decreases the importance of individual headwater stretches (due to the implicit weighting by flow) it does not solve scale-dependency (A): a large number of headwater stretches will - together - still contribute significantly to the weighted average. Hence, this approach can only be applied in combination with the selection of only the stretches downstream of pollution sources.

Weighting by stretch volume focuses on large rivers (because these have the largest volume). This may be of less ecological relevance, as smaller rivers are often more valuable or vulnerable than large ones. Also, weighting by volume stresses the importance of ‘bulk water’ organisms rather than the benthic or river edge ecosystem. From an exposure assessment point of view, weighting by volume focuses on high dilution situations, where risk and exposure levels may be lower than what is representative for the entire catchment.

The weights w_i for each stretch i can be calculated as:

$$w_i = \frac{V_{stretch\ i}}{\sum_{j=1}^{n_{stretches}} V_{stretch\ j}} = \frac{\frac{Q_i \cdot l_i}{v_i}}{\sum_{j=1}^{n_{stretches}} \left(\frac{Q_j \cdot l_j}{v_j} \right)} \quad [10.3]$$

Additional weighting factors

Additional weighting factors can be considered (to be used in combination with one of the already mentioned approaches). Additional weighting by flow directs the focus towards the main waterbodies of the catchment. As with the volume-weighting, this focuses on large rivers, on high dilution and on ‘bulk water’ organisms. Additional weighting by a water quality index will stress the importance of high-quality ecosystems in the catchment. This will typically increase the weight of stretches with a low degree of pollution and will hence decrease the aggregated $PEC_{catchment}$, possibly resulting in a too optimistic exposure assessment. Another problem with water quality weighting is that the required data may not be generally or readily available, or not related to the correct river network structure. Moreover, for different catchments the water quality indices may not be comparable.

In this chapter, additional weighting factors will not be further considered.

Calculation of weighted average and standard deviation

A weighted average is calculated as follows (\bar{x}_w = weighted average, x_i = individual values, n = number of values):

$$\bar{x}_w = \sum_{i=1}^n x_i \cdot w_i \quad \text{with} \quad \sum_{i=1}^n w_i = 1 \quad [10.4]$$

The weighted variance σ_w^2 is an estimator of the population's true variance, just like the 'normally calculated' variance σ^2 is one. However, a different probability function $f(x)$ is used, reflecting a non-aselective sampling approach of the population. For the 'traditional' calculation of variances, an aselective sampling is represented by assigning equal probability to each x_i : $f(x_i)=1/n$. For the weighted calculation, the probability for each x_i is equal to its weight: $f_w(x_i)=w_i$.

$$S^2(x) = \int_{-\infty}^{+\infty} (x - E(x))^2 \cdot f(x) \cdot dx = \int_{-\infty}^{+\infty} (x - E(x))^2 \cdot \frac{1}{n} \cdot dx \quad [10.5]$$

$$S_w^2(x) = \int_{-\infty}^{+\infty} (x - E(x))^2 \cdot f_w(x) \cdot dx = \int_{-\infty}^{+\infty} (x - E(x))^2 \cdot w_i \cdot dx$$

In the above integrals, the factors $1/n$ and w_i are not relevant as they approach zero. However, when the number of sampled values is finite, these integrals can be calculated as the corresponding sums. Because these estimators for the variance are only unbiased asymptotically with n going to infinity, a correction is required: the terms of the sums are to be multiplied by $n/(n-1)$:

$$S^2(x) = \sum_{i=1}^n \left((x - \bar{x})^2 \cdot \frac{1}{n} \cdot \frac{n}{n-1} \right) = \frac{\sum_{i=1}^n ((x - \bar{x})^2)}{n-1} \quad [10.6]$$

For the weighted calculation of the variance, the same correction was applied. Hence, when all weights are equal to $1/n$ (i.e., the unweighted case), the weighted variance is equal to the variance obtained in the 'traditional' calculation:

$$S_w^2(x) = \sum_{i=1}^n \left((x - \bar{x}_w)^2 \cdot w_i \cdot \frac{n}{n-1} \right) = \sum_{i=1}^n \left((x - \bar{x}_w)^2 \cdot w_i \right) \cdot \frac{n}{n-1} \quad [10.7]$$

3. Case Studies

3.1. Methods

The applied fate model used a chemical specific percentage elimination to describe removal in the sewer system and in waste water treatment (trickling filter or activated sludge). To calculate fate in rivers, a fixed first-order in-stream removal rate coefficient was used. A Monte Carlo simulation (1000 shots) was applied for simultaneous uncertainty and variability analysis. When uncertainty and variability are combined, this method only offers reliable calculations of the local C_{SIM} distribution means, because the uncertainty increases the spread of the distributions (see chapter 2 of this thesis). Consequently, only the mean C_{SIM} values could be used for spatial aggregation in these case studies.

A non-calibrated fate simulation was conducted for the surfactant LAS (Linear Alkylbenzene Sulphonate). Next to this, a simulation was also conducted for the hypothetical substance CONS: a completely conservative chemical with the same emission profile as LAS. The chemical properties and market data used for LAS were based on chemical industry data (ECETOC, personal communication). Together with the parameters for CONS, the LAS parameters are given in Table 10.1.

Table 10.1. Chemical parameters used in the case study simulations

	LAS	CONS
Product consumption	1 kg/(cap.year)	1 kg/(cap.year)
In-stream removal rate	0.006 - 1.71 h ⁻¹ *	0 h ⁻¹
Removal in primary treatment	45 %	0 %
Removal in activated sludge treatment	98 %	0 %
Removal in trickling filter treatment	85 %	0 %
Removal in the sewer	25 %	0 %

* uniform distribution

The PEC calculations were applied to two Yorkshire catchments, the Went and the Calder. The datasets were not yet completely quality-controlled, and may hence have contained errors. Therefore, the analysis presented here should not be interpreted as a reliable exposure assessment, but merely as a test of the proposed PEC definitions and calculation methodologies.

For the $PEC_{catchment}$ calculations, three different stretch selection options were used: 1A all stretches; 1B a reduced catchment containing all polluted stretches plus one stretch for each unpolluted subcatchment; and (2) a reduced catchment containing only polluted stretches (Figure 10.3). 1A and 1B are two cases representing the same concept ('all stretches'), but applied at a different level of geographical detail. A description of both catchments and the effect of the applied stretch selection is given in Table 10.2 below.

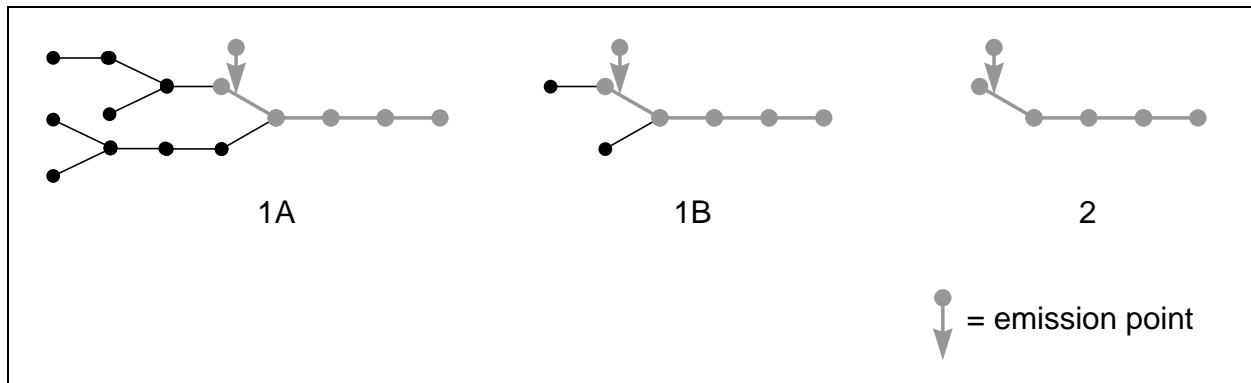


Figure 10.3. Stretch selection: 3 options applied for the case studies

Table 10.2. Case studies: test catchment description and stretch selection

	Went	Calder
River flow at the end of the catchment	$0.98 \text{ m}^3/\text{s}$	$19 \text{ m}^3/\text{s}$
Number of waste water emission points	7	21
Total population	28053	798458
Population per unit of flow at the end of the catchment ($\text{cap} / (\text{m}^3/\text{s})$)	28625	42024
Stretch selection 1A		
number of stretches	105	1562
cumulative stretch length	112 km	1103 km
cumulative river volume	$78.6 \cdot 10^3 \text{ m}^3$	$2400 \cdot 10^3 \text{ m}^3$
Stretch selection 1B		
number of stretches	46	164
cumulative stretch length	52 km	215 km
cumulative river volume	$64.4 \cdot 10^3 \text{ m}^3$	$1900 \cdot 10^3 \text{ m}^3$
Stretch selection 2		
number of stretches	28	93
cumulative stretch length	36 km	118 km
cumulative river volume (calculated)	$55.8 \cdot 10^3 \text{ m}^3$	$1800 \cdot 10^3 \text{ m}^3$

The Went catchment is much smaller than the Calder catchment. In the Calder, the flow at the end of the catchment is 20 times higher than in the Went, its total cumulative stretch length is a factor 10 higher, and its cumulative volume is 30 times higher. The total population of the Calder catchment is also 30 times higher than that of the Went catchment. Still, the Calder only has 3 times more waste water emission points, which can be explained by the (on average) smaller size of

the emissions into the Went. The total population divided by the river flow at the end of the catchment is 1.5 times higher in the Calder than in the Went. Hence, the total domestic pollution load in the Calder receives (in total) 1.5 times less dilution than that in the Went.

The number of stretches in selection 1A (all stretches of the 1:50,000 river network) was strongly reduced when instead only the polluted stretches plus one unpolluted stretch per headwater subcatchment, or strictly only the polluted stretches were used (stretch selection 1B;2). In the Went, 56;73 % of the stretches and cumulative stretch length disappeared. However, only 18;29 % of the cumulative volume was lost. In the Calder, 90;94 % of the stretches and 80;89 % of the cumulative length were removed, but again only 20;25 % of the cumulative volume. In the Calder catchment, pollution is concentrated in the most downstream 6 % of the stretches, while in the Went more than 25 % of the stretches is influenced by pollution. The unpolluted volume fraction is much smaller, which can be explained by the smaller volume of headwater stretches compared to the more downstream parts of the rivers.

3.2. Results

The geo-referenced simulation results are illustrated in Figure 10.4 (Went) and Figure 10.5 (Calder) (concentrations quartiles color-coded by means of gray-scale) (geographical projection).

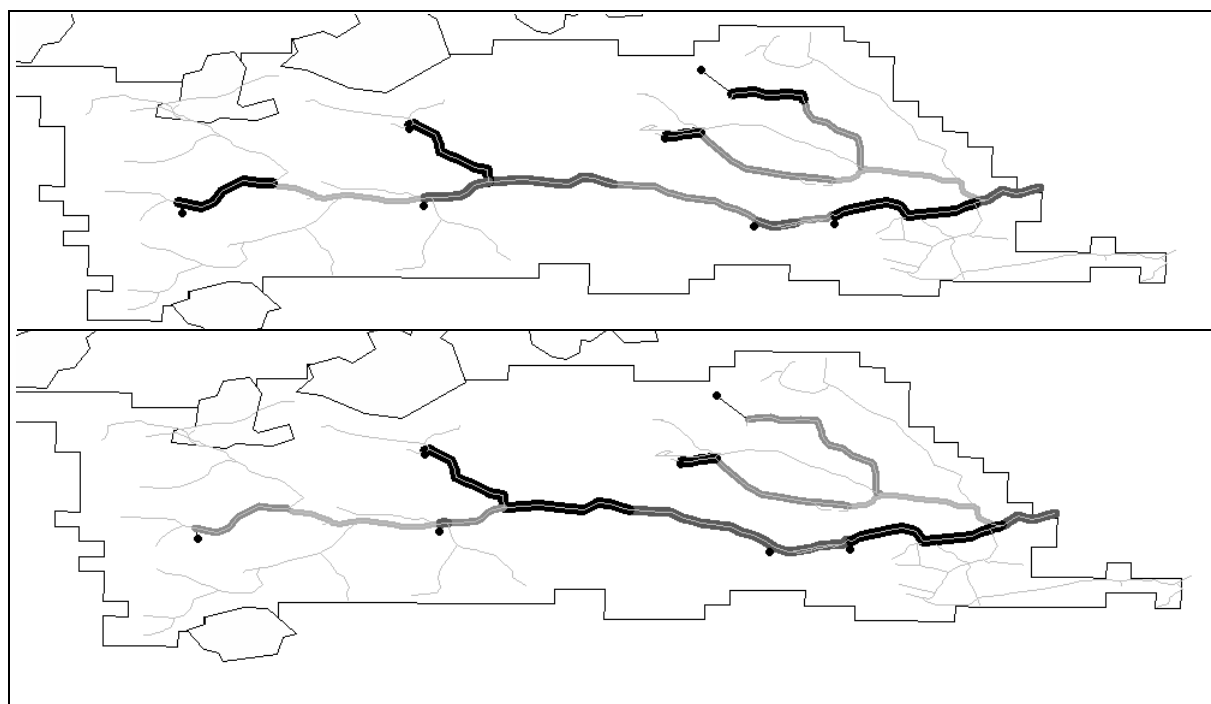


Figure 10.4. Went simulation: LAS (top) and CONS (bottom)

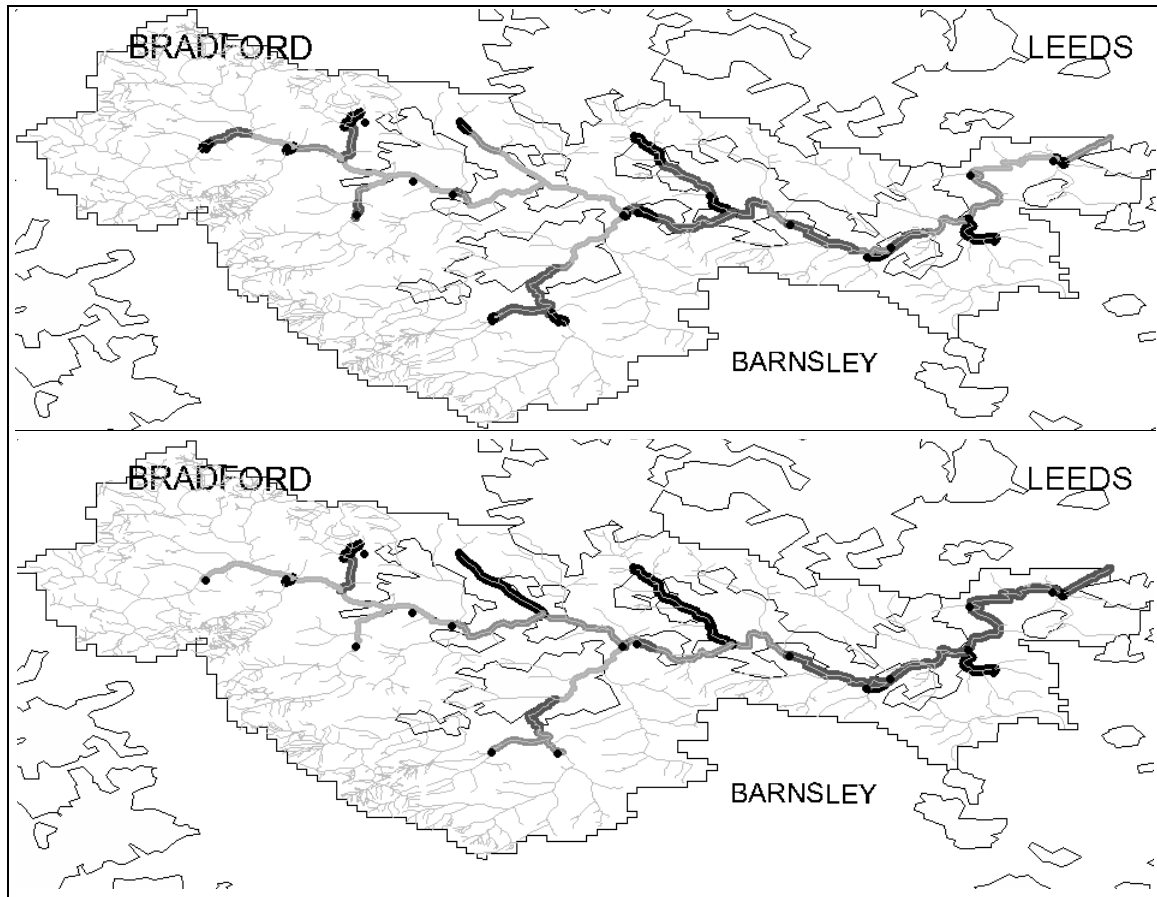


Figure 10.5. Calder simulation: LAS (top) and CONS (bottom)

3.2.1. $PEC_{initial}$

$PEC_{initial}$ was defined as the unweighted spatial aggregation of $C_{SIM,start}$ for all stretches in the catchment which directly receive an emission of waste water. The results of the $PEC_{initial}$ calculation are given below in Table 10.3.

Table 10.3. $PEC_{initial}$ calculations (in mg/L)

	Went		Calder	
	mean	st. dev.	mean	st. dev.
LAS	0.65	1.44	0.089	0.178
CONS	8.3	17.3	2.2	3.6

3.2.2. $PEC_{catchment}$

$PEC_{catchment}$ was defined as the spatial aggregation of $C_{SIM,internal}$ values over the entire catchment, or over the polluted section of the catchment. For the first option, weighting by flow increment is required, while for the second option weighting by length or by volume is needed.

For LAS, the spatial variability of $C_{SIM,internal}$ values is shown in Figure 10.6. These histograms were weighted by flow increment ('all stretches' case) or by stretch length ('only polluted stretches' case) - similar to the $PEC_{catchment}$ calculations (weighted histograms were obtained by counting the cumulative weight instead of the frequency in each class). The left part of Figure 10.6 shows the importance of unpolluted headwaters in the 'all stretches' case (peak at concentration zero); the spatial distribution does not have a specific "standard" shape. In the right half of Figure 10.6, a lognormal-like shape can be recognized for the Calder but not for the Went.

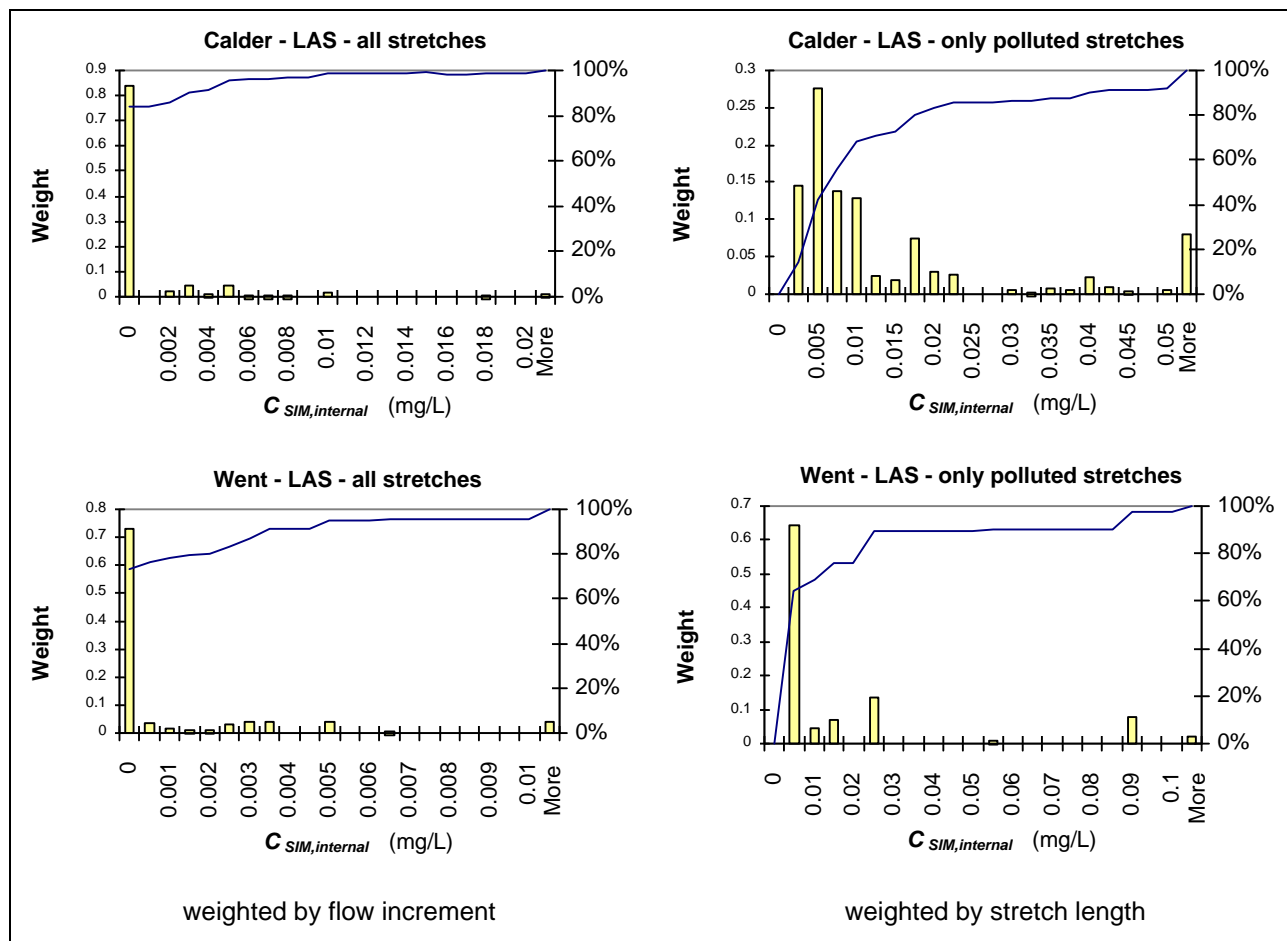


Figure 10.6. Spatial variability of $C_{SIM,internal}$ values (for LAS) (weighted histograms)

In the $PEC_{catchment}$ calculations presented here, four different weightings (unweighted, by length, by flow increment and by volume) were used in combination with the three different stretch selections (see higher, section 3.1). Only the weighting techniques described above in the $PEC_{catchment}$ definitions (section 2.3.2) are considered relevant; the results obtained with the other techniques are given to illustrate their scale-dependency and hence their irrelevance. $PEC_{catchment}$ values are listed in Table 10.4. Results obtained with scale-dependent calculations are printed in italics.

3.3. Discussion

3.3.1. Scale Dependencies in $PEC_{catchment}$ Calculations

Effect of reduction in catchment detail (1A versus 1B)

The type-A scale-dependency (linked to the number of unpolluted upstream stretches that are considered in the river network) of the unweighted, weighted-by-length and weighted-by-volume calculation approaches can be observed by comparing $PEC_{catchment}$ for stretch selection 1A and 1B. When the number of unpolluted headwater stretches in the digital river network was reduced (i.e., when the network's level of detail was decreased), $PEC_{catchment}$ increased in all cases. The volume-weighted $PEC_{catchment}$ was least affected because the total volume of the headwater stretches has a relatively low weight compared to the entire catchment's volume: the reduction of the headwater stretches only caused a 25-30 % decrease in total volume.

$PEC_{catchment}$ weighted by flow increment was independent of the number of considered unpolluted headwater stretches. The minor differences between stretch selection 1A and 1B for the Calder were due to inconsistencies in the flow data, which caused a negative flow increment for some stretches. This also led to the not strictly monotonous behavior of the weighted cumulative frequency distribution curves for the Calder in Figure 10.6.

The results confirm the theoretical considerations about scale dependency in section 2.3.2. It can be concluded that for a $PEC_{catchment}$ calculation which aims to consider the entire catchment (both the polluted and the unpolluted parts), weighting of $C_{SIM,internal}$ by flow increment is required.

Table 10.4. $PEC_{catchment}$ calculations (in mg/L)

	Went		Calder	
	mean	st. dev.	mean	st. dev.
LAS				
Stretch selection 1A				
<i>not weighted</i>	0.036	0.32	0.00130	0.0137
<i>weighted by length</i>	0.0088	0.103	0.0021	0.0159
weighted by flow increment	0.0030	0.0136	0.00147	0.0138
<i>weighted by volume</i>	0.0075	0.041	0.0023	0.0117
Stretch selection 1B				
<i>not weighted</i>	0.083	0.49	0.0124	0.041
<i>weighted by length</i>	0.0189	0.151	0.0105	0.035
weighted by flow increment	0.0030	0.0136	0.00151	0.0140
<i>weighted by volume</i>	0.0094	0.046	0.0073	0.0121
Stretch selection 2				
<i>not weighted</i>	0.136	0.62	0.022	0.052
weighted by length	0.027	0.182	0.0191	0.045
<i>weighted by flow increment</i>	0.032	0.26	0.0190	0.040
weighted by volume	0.0105	0.049	0.0075	0.0123
CONS				
Stretch selection 1A				
<i>not weighted</i>	0.72	4.6	0.081	0.60
<i>weighted by length</i>	0.40	1.67	0.162	0.91
weighted by flow increment	0.28	0.72	0.144	0.73
<i>weighted by volume</i>	0.74	0.94	0.184	0.81
Stretch selection 1B				
<i>not weighted</i>	1.64	7.0	0.77	1.72
<i>weighted by length</i>	0.86	2.4	0.82	1.93
weighted by flow increment	0.28	0.72	0.158	0.73
<i>weighted by volume</i>	0.93	0.97	0.89	0.55
Stretch selection 2				
<i>not weighted</i>	2.7	8.8	1.37	2.1
weighted by length	1.23	2.8	1.51	2.4
<i>weighted by flow increment</i>	1.09	3.85	0.73	1.00
weighted by volume	1.04	0.98	0.94	0.52

Effect of stretch selection: all stretches (1A) versus only polluted stretches (2)

$PEC_{catchment}$ increased when only polluted stretches were used instead of the entire catchment. This is straightforward, as average exposure levels are necessarily higher in the polluted sections of a catchment compared to the zero-exposure in the unpolluted sections. In all cases, the $PEC_{catchment}$ increase was higher in the Calder than in the Went. This can be explained by the catchments' structure: as there are more unpolluted headwater stretches in the Calder compared to the Went, dropping these headwaters from the calculations obviously has a stronger impact for a catchment with more headwaters.

For the flow-increment weighted case, this was by more than a factor 10 for LAS and by a factor 4-5 for CONS. However, this calculation method is irrelevant in combination with stretch selection 2. When only polluted stretches are considered, the weight of entire unpolluted headwater sub-catchments is assigned to the situation of the most upstream polluted stretches into which these headwaters feed (cf. Figure 10.2, assuming that stretch 1 would be polluted). Hence, such calculations result in a strong overestimation of true exposure levels.

The spread of the spatial distributions decreased (in the Calder by a factor 3-8; in the Went by a factor 1-2). This can be ascribed to the reduction in spatial variability when a large number of 'extreme' cases (zero concentration) are removed from the population. This can also be observed in Figure 10.6.

For both catchments, the LAS $PEC_{catchment}$ based on only polluted stretches and weighted by volume was a factor 2.5 lower than the corresponding $PEC_{catchment}$ weighted by length. This is in line with the expectation that weighting by volume focuses the attention to larger rivers with higher dilution and after more in-stream removal has taken place. For CONS a similar effect was seen (factor 1.6 for the Calder, factor 1.2 for the Went). The effect was less extensive because CONS is only affected by dilution, not by in-stream removal. The spread of the volume-weighted $PEC_{catchment}$ was also lower for both chemicals and catchments, which can be explained by the leveling out of very high or low concentrations in the more downstream rivers.

Effect of river segmentation

The type-B scale-dependency (linked to the variable stretch length) of the unweighted $PEC_{catchment}$ calculation (see section 2.3.2) could not be illustrated in this work, because the river network segmentation itself was not modified.

3.3.2. Comparison of PEC Calculations and Catchments

$PEC_{initial}$

For LAS, $PEC_{initial}$ was a factor 7 higher in the Went compared to the Calder. For CONS, the difference between $PEC_{initial}$ in both catchments was smaller than for LAS (a factor 4). The higher $PEC_{initial}$ of CONS in Went versus Calder can not be due to a different waste water treatment

infrastructure as the chemical is conservative. Also for LAS this is not probable, as in both catchments the sewage is mainly treated by trickling filter plants. A plausible explanation is the difference in catchment structure. On average, the emission points in the Went are at a more upstream location than those in the Calder, hence they generally receive a lower dilution.

For LAS, the spread of the spatial $PEC_{initial}$ distribution was similar in both catchments (standard deviation / mean $\cong 2$). For CONS, the spread of the distribution in the Went was similar to the LAS case, while for the Calder it was more narrow (st.dev. / mean $\cong 1.6$).

The $PEC_{initial}$ for CONS was much higher than for LAS, which is obvious as CONS is not eliminated in waste water treatment. Furthermore, as CONS undergoes no in-stream removal, $C_{SIM,start}$ values associated with more downstream emission points also contain a major component of upstream pollution, which further increases $PEC_{initial}$.

$PEC_{initial}$ versus $PEC_{catchment}$

As expected, $PEC_{initial}$ was always higher than $PEC_{catchment}$. Compared to the weighted-by-flow-increment $PEC_{catchment}$ considering all stretches, this difference was more than a factor 200;30 (LAS;CONS) for the Went and a factor 60;15 (LAS;CONS) for the Calder. The spread of $PEC_{initial}$ was a factor 2-5 lower for LAS and a factor 1-3 for CONS. The lower spread is caused by the relative similarity of concentrations immediately after emissions compared to the much larger variability of concentrations all over the catchment.

When only the polluted stretches are considered, the difference with $PEC_{initial}$ is less spectacular. For LAS;CONS in the Went, these $PEC_{catchment}$ values were lower by a factor 24;7 (weighted-by-length) and 60;8 (weighted-by-length). In the Calder, the difference was limited to a factor 5;1.4 and 12;2.3. The difference between Went and Calder indicates that the pollution in the Calder is more concentrated in the downstream sections of the catchment, resulting in a 'polluted-only' $PEC_{catchment}$ which is closer to $PEC_{initial}$. In the Went, pollution is more spread out, hence relatively more in-stream removal (for LAS) and extra dilution can take place, resulting in a 'polluted-only' $PEC_{catchment}$ which is farther away from $PEC_{initial}$. The difference between LAS and CONS is due to the absence of in-stream removal for the latter. For CONS, the difference between $PEC_{initial}$ and the 'polluted-only' $PEC_{catchment}$ is only due to additional dilution downstream of the emission points.

$PEC_{catchment}$ weighted by length, considering only polluted stretches

A neutral view on the situation in the polluted parts of a catchment (assuming equal importance for all locations in the river) is represented by $PEC_{catchment}$ weighted by length, considering only polluted stretches.

LAS exposure levels calculated for the polluted part of the Went are a factor 1.4 higher than those in the Calder. This can mainly be explained by the higher $PEC_{initial}$ in the Went. The fact that the ratio between $PEC_{catchment}$ values of the Went and the Calder is much lower than the ratio between their $PEC_{initial}$ values (factor 7), is mainly due to the different dilution properties in both catchments. Contrary to LAS, the exposure to CONS in the polluted parts of the Went was slightly lower than in the polluted parts of the Calder - even though $PEC_{initial}$ was higher in the Went by a factor 4. This can only be ascribed to the different dilution in both catchments.

$PEC_{catchment}$ weighted by volume, considering only polluted stretches

When stretch volume is used for weighting instead of stretch length, the aggregated exposure level dropped by a factor 2.5 for LAS and 1.2-1.6 for CONS. As mentioned higher, this is due to the fact that weighting by volume attaches most attention to downstream stretches with high dilution and after more in-stream removal. Note that in this weighting case, the exposure to CONS in the Calder was slightly lower than in the Went (contrary to the weighted-by-length case presented above).

$PEC_{catchment}$ weighted by flow increment, considering all stretches

The overall exposure situation in a catchment can be measured by means of $PEC_{catchment}$ weighted by flow increment, considering all stretches (polluted as well as unpolluted).

Both for LAS and CONS, $PEC_{catchment}$ weighted by flow increment in the Calder was a factor 2 lower than in the Went. This is due to two factors: it is directly determined by the lower $PEC_{initial}$ in the Calder, and it is also influenced by the location of the emission points. As most emissions are situated in the downstream regions, most of the Calder's upstream sections are unpolluted, which significantly reduces the average exposure over the entire catchment. This explains why the ratio between the 'all stretches' $PEC_{catchment}$ values in the Went and the Calder is higher than the ratio between the 'polluted-only' $PEC_{catchment}$ values. The difference in catchment structure also explains why $PEC_{catchment}$ for CONS based on all stretches is lower in the Calder than in the Went, while $PEC_{catchment}$ based on only the polluted stretches has a similar value in both catchments.

4. Conclusions

Two spatially aggregated PEC types were defined and tested: $PEC_{initial}$ and $PEC_{catchment}$.

$PEC_{initial}$ was defined as the spatial aggregation of initial river concentrations after each waste water emission in the catchment, by means of an unweighted average, based on mean or high percentile concentrations.

$PEC_{catchment}$ was defined as the spatial aggregation of all ‘internal’ river concentrations (i.e., the average value in a stretch), by means of a weighted average, based on mean or high percentile concentrations. To obtain an aggregated exposure value representative of the entire catchment, all stretches (polluted and unpolluted) have to be considered. In this case, weighting by flow increment is needed to resolve scale-dependency. To produce an aggregated exposure value representative of the polluted parts of the catchment, only the polluted stretches should be considered. In this case, weighting by stretch length or by stretch volume is required to resolve scale-dependency. Weighting by length results in a ‘neutral’ aggregation which attaches identical importance to all locations in the river network. Weighting by volume stresses the importance of downstream parts of the river with a higher dilution and after more in-stream removal, hence resulting in a lower exposure estimate.

A higher $PEC_{catchment}$ in the polluted part of the catchment compared to the entire catchment is obvious, and inherently part of the concept. It must be stressed that a $PEC_{catchment}$ based on only polluted stretches is not representative of the entire catchment, and this should be taken into account when such a PEC is applied in a risk assessment framework.

The irrelevance due to scale-dependency of an unweighted $PEC_{catchment}$ was illustrated. The need for an adequate stretch selection as a function of the selected weighting technique was also shown. It is stressed that the use of an inappropriate stretch selection / weighting combination results in an aggregation which depends on the level of detail of the digital river network or on the geographical scale. Such aggregations are irrelevant because they can not be compared between catchments or between different digital versions of a single catchment. Consequently, as such values are not unambiguously determined, they can not be compared with effects levels, and hence they can not be used in environmental risk assessment.

Both proposed $PEC_{catchment}$ calculation methodologies do not require data about the entire river network that is being studied. When only polluted stretches are considered, no data is needed about the unpolluted sections of the catchment. When the entire catchment is considered, only the most downstream unpolluted stretches are required to obtain a $PEC_{catchment}$ weighted by flow increment. Hence, for the proposed $PEC_{catchment}$ calculations, fate simulations, flow data collection and river network digitization are not required for the entire catchment, but only for a limited (downstream) part. This may reduce the effort needed to implement the GREAT-ER methodology for new regions, and it will strongly decrease the required simulation time.

Chapter 11

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Conclusions and Perspectives

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Conclusions and Perspectives

1. Introduction

The work described in this thesis was conducted in the framework of the GREAT-ER project (Geography-referenced Regional Exposure Assessment Tool for European Rivers). The objective of this international project was to develop, test and corroborate an accurate exposure prediction tool, to estimate chemical exposure concentrations in surface waters. Such tool could be used to enhance the realism and accuracy of environmental risk assessment schemes used in the European Union. Current techniques to calculate regional predicted environmental concentrations (PECs) use a generic multimedia ‘unit world’ approach and do not account for spatial and temporal variability in environmental characteristics and chemical emissions. Since these methods do not offer realistic predictions of actual concentrations, the results are merely applicable on a generic screening level.

In the GREAT-ER project, a software system was developed to calculate predicted concentrations of ‘down-the-drain’ chemicals (i.e., consumer chemicals which mainly enter the environment via the domestic waste water route, e.g. detergents) in surface waters, using a Geographic Information System (GIS) for data storage and visualization, combined with simple mathematical models for the prediction of chemical fate.

The work described in this thesis was focused on chemical fate modeling and simulation, and on interpretation of simulation results. First, the development and testing of the simulation methodology was described. Next the selection, adaptation and/or development of appropriate chemical fate prediction models, supported by new measurement methods, was discussed. Finally, a method to obtain spatially aggregated PECs for catchment simulations was worked out.

2. Methodology

A geo-referenced simulation methodology for the prediction of aquatic exposure to individual ‘down-the-drain’ chemicals was developed. This method uses real-world data, including their spatial and temporal variability. By means of a hybrid stochastic / deterministic simulation approach, statistical frequency distributions of predicted concentrations in the aquatic environment are obtained. Steady-state deterministic models, which describe chemical fate, form the system’s core. From chemical market data, combined with information on the location of consumers and their emission habits, geo-referenced domestic chemical emissions are predicted. These emissions

are further processed in sewer and treatment models, to obtain predicted chemical mass fluxes into rivers. These emission fluxes are entered into a river model, resulting in geo-referenced predictions of chemical concentrations in the considered river systems. A stochastic (Monte Carlo) simulation, which deals with the natural variability and/or the uncertainty in the required information, is applied on top of these deterministic models. This finally results in statistical distributions of predicted concentrations, which can be used for risk assessment.

A prototype of the presented simulation system was tested by means of a (hypothetical) large sample data set, containing 16,000 geographical segments. A 1,000 shot Monte Carlo simulation took less than 1.5 hours on a low-end Windows NT personal computer (Intel Pentium processor, 150 MHz). From a computing power point of view, this indicates the feasibility of the approach for detailed regional or large-scale pan-European simulations.

The currently implemented stochastic simulation approach does not allow to split variability and uncertainty analysis. To achieve this, a “two-dimensional” stochastic simulation will have to be built into the concept. As this will quadratically increase the total number of iterations and hence also the required computing time, such technique may necessitate to replace the Monte Carlo simulation by more efficient sampling techniques, e.g. stratified sampling (“Latin hypercube”).

The practical applicability of the GREAT-ER simulation methodology was illustrated by means of a hypothetical but realistic case study. The simulation approach allowed to analyze the impact of different discharges and tributaries on the temporal and spatial distributions of predicted concentrations in the hypothetical catchment. The resulting distributions were log-normal. For the prediction of seasonality (i.e. the variability of river flows through the year), Monte Carlo simulation was found to be superior to the alternative (discrete) ‘flow scenario’ approach. Also for a complete uncertainty or variability analysis, Monte Carlo simulation is needed. However, to quickly obtain initial results, the ‘flow scenario’ method may be useful. Finally, the scale-independent character of the approach was explored, by upscaling from a detailed to a larger geographical scale.

3. Measurement and Prediction of Chemical Fate

The three main steps in the fate pathway of ‘down-the-drain’ chemicals were dealt with: sewers, waste water treatment, and rivers. For activated sludge waste water treatment, the *SimpleTreat* model was adapted to biological nutrient removal (BNR) plants. This adaptation was supported by measurements in modified versions of the standard CAS test (Continuous Activated Sludge), also incorporating BNR. For trickling filters, a new model was developed. The model was tested using measurements obtained in a laboratory pilot-scale (200 L) trickling filter, and in full-scale plants. To predict chemical fate in rivers, a novel modeling approach was worked out, including biofilm activity. This development was supported by a lab-scale artificial river experiment and a field study. Finally, a preliminary field study was conducted to analyze chemical fate in the sewer.

3.1. Chemical Fate in Waste Water Treatment Plants

3.1.1. Biological Nutrient Removal Activated Sludge WWTPs

There is a global increase of biological nutrient removal (BNR) ability in waste water treatment practice. This caused the need to modify both the Continuous Activated Sludge (CAS) laboratory test system and the mathematical fate model *SimpleTreat*, which are used to routinely assess the elimination of substances in activated sludge waste water treatment plants.

Adaptation of the CAS Test

Two novel 'single-sludge' BNR bench-scale test systems were compared to the standard CAS unit: the Behr and the CAS-UCT unit, with respectively 2 (anoxic / aerobic) and 3 (anaerobic / anoxic / aerobic) biological reactors. Both units proved to be easy to handle and operate. A similar degree of COD, N and P removal was achieved with the Behr and the CAS-UCT. The experimental results compared well with IAWQ Activated Sludge Model No. 2 simulations and with similar full-scale plants. A new synthetic sewage was designed for the modified CAS units: to be more representative of real sewage than the standard OECD synthetic medium, to allow a good degree of BNR, and to support stable unit operation. A batch respiration test indicated that the new medium is a reasonable approximation of real domestic sewage. Although sludge settling was superior when real sewage was used, it remained sufficiently stable with the synthetic sewage to permit a 3 month test duration. The longer residence times applied in the BNR systems led to a reduction in effluent levels of biodegradable chemicals (like the surfactant LAS) compared to the CAS test. A parent LAS removal efficiency of 99.4% was found in both units, while the standard CAS was observed to have 98.6% removal. The role of the system's different redox zones in the overall removal requires further investigation for various types of chemicals.

The BNR units hold potential to be included in standard testing, complementary to the CAS system. As nutrient removal performance was similar in both units, the less complex Behr system may be preferable for standardization. As the CAS-UCT allows a higher flexibility, it has better perspectives for research applications.

Adaptation of the SimpleTreat Model

Most chemical fate models which are used to predict the elimination of individual chemicals in waste water treatment plants, have until now not incorporated biological nutrient removal aspects. Two modified versions of the standardized model *SimpleTreat* were developed, to increase its applicability to BNR plants. The modifications mainly focus on an improved description of sludge recycling, and on the presence of different redox zones in the biological reactor (aerobic, anoxic, anaerobic).

A more realistic description of sludge recycling, taking into account the water phase of these cycles and the actual recycling ratios, was proposed. It was shown that this may have an impact

on the fate prediction of highly volatile chemicals. To deal with BNR plant designs, two modeling approaches were presented, both based on the UCT process template: a 6-box model derived directly from *SimpleTreat*, and a more detailed 10-box model. Simulation results of both models were compared to measured LAS removals in the three bench-scale CAS test units. The LAS degradation rate coefficient was calibrated only using standard CAS test data, and was subsequently used to predict the fate of LAS in two BNR plants. Both modified models were more accurate than the standard *SimpleTreat*. The 10-box model was more accurate than the 6-box model, which (slightly) underestimated removal. In general, this illustrated the improved predictive power of the adapted models for the fate of readily biodegradable chemicals.

It is recommended to focus further research on the corroboration of these models for different chemical types. Especially simulation and laboratory measurements of volatile and / or less easily degradable substances would allow to further test the underlying assumptions. This should also give more conclusive evidence on the relative performance of the 6-box versus the 10-box model.

3.1.2. Trickling Filter WWTPs

The development of a chemical fate model for trickling filters was presented, based on the *SIMPLEBOX* / *SimpleTreat* approach combined with an existing biofilm diffusion / biodegradation model. By means of a sensitivity analysis, it was shown that the properties of the chemical under study determine which parameters are most important for the model. Flow, volume and suspended solids data are needed for the specific plant that is modeled. For biodegradable substances, biofilm thickness is a crucial parameter which is generally not measured - hence this value typically has to be estimated from defaults. For volatile chemicals it is required to estimate the air flow through the filter, which may also be difficult. Finally, the fraction of water in the filter's pores is an important parameter, which can be derived from hydraulic measurements.

To test the new model, LAS removal experiments were conducted in the laboratory using a 200 L pilot-scale high-rate trickling filter unit. The design of this unit allowed a characterization of all relevant model parameters (e.g. measurement of hydraulics and biofilm characteristics by continuously recording the filter unit's mass, biofilm analysis by examining carrier material taken from the filter). Moreover it allowed an easy monitoring of the system's performance. Using this setup, steady-state removal of LAS was measured under different well-characterized operating conditions, at high and normal LAS influent levels. The effect of the operating conditions (short versus long recycle, high versus low recycle ratio) was insignificant. At normal LAS influent levels (4 mg/L), LAS removal was in the order of 50 %, while a higher COD removal efficiency (70 - 90 %) was found. When a 3-4 times higher LAS level was present in the influent, the LAS elimination increased to 90 %. This may be ascribed to biological adaptation, but it may also indicate a different kinetic behavior at high concentrations. Further research (preferably using dynamic experiments) is required to study the effect of biological adaptation to different LAS influent concentrations on removal efficiency.

The new fate model was able to describe LAS removal in the pilot-scale filter using measured, estimated or default (literature) parameter values. The same biodegradation rate constant K_b (derived from activated sludge data) could be used in all experiments with a normal LAS influent concentration. However, for the experiments with 3-4 times more LAS in the influent, a 3.5 times higher K_b value was needed. This indicates a shortcoming of the fate model: it can only deal with this situation by recalibration of the biodegradation rate coefficient.

The model was also successfully applied to predict the fate of LAS in two full-scale low rate domestic trickling filter plants. A plant-specific calibration produced more accurate predictions than the extrapolation of another plant's calibration. However, if a relative deviation in the order of 10 % is deemed acceptable, such a plant-specific calibration appeared to be not strictly required.

In this work, only the biodegradation and sorption aspects of the model were confronted with measurements, since only LAS was used as test chemical. To test the relevance and validity of volatilization aspects, further research is needed. Furthermore, it is recommended to focus additional detailed research on the effect of influent concentrations on LAS biodegradation rates, and on the effect on these rates of adaptation to different concentrations.

After a further validation for different types of substances, the newly developed fate model may be used to complement the activated sludge model *SimpleTreat*. The bottleneck to apply the model is the characterization of hydraulic and biofilm related parameters: generally such information is not available or even measurable, hence realistic default values need to be applied. In the worst case, this may heavily increase the predictive uncertainty, and hence it may lead to questioning the usefulness of the model as such.

The main design criterion for the presented pilot-scale trickling filter unit was that it should allow a characterization of biofilm and hydraulic parameters. Because of its dimensions, high influent and effluent flows, and maintenance requirements, its operation is too laborious and complex to allow easy standardization. Moreover, it is not representative of low-rate domestic trickling filter plants. From this, it can be concluded that this system has no potential for use in standard chemical fate assessments.

3.2. Chemical Fate in Rivers

Based on a literature review, a conceptual steady-state river fate model was selected, considering the processes degradation (hydrolysis, photolysis, biodegradation), sorption / sedimentation, and volatilization. The existing river fate models have a number of shortcomings: photolysis is described as a crude simplification; sorption / sedimentation can only be modeled as accurate as the applied suspended solids sedimentation rate coefficient (which is often not known); and biodegradation is typically considered in a non-physically-based way, requiring site-specific calibration. In this thesis, a new in-stream biodegradation model, which considers both biofilm and suspended biomass activity, was developed.

To calibrate this model for the surfactant LAS, experimental data were obtained in a lab-scale artificial river system, which allowed to collect accurate and reproducible in-stream biodegradation data next to the required river characteristics. In these experiments, biodegradation was found to be the only significant in-stream removal process of LAS. In this specific case (with a high biofilm surface to water volume ratio) measurable biodegradation only occurred when biofilm was present. Moreover, the biodegradation rate was proportional to the amount of biofilm in the system.

The parameters of the new in-stream biodegradation model, calibrated on the series of experimental data obtained in the artificial river experiments, had realistic values. Using these calibrated parameters as such, the model was subsequently corroborated by comparing its predictions to an in-stream removal field study in the Red Beck, a small Yorkshire river. Only easy to collect or default data were used as site-specific model parameters. The predicted overall LAS half-life (without any calibration using the field data) was 2¾ h. This is less than 25 % slower than the in-stream removal half-life measured in the field. Hence, the model's accuracy was acceptable for use in the GREAT-ER concept.

It is recommended that a further corroboration of the presented modeling approach be conducted, especially based on other detailed field study data. The range of validity of the model and its assumptions needs to be extended to other chemical substances and to other types of rivers. If such further validation would be successful, the newly developed modeling concept may be an important step forward in predicting in-stream removal of biodegradable chemicals (or BOD in general) in rivers.

3.3. Chemical Fate in Sewers

To confirm and to further quantify the elimination of LAS in sewers, an in-sewer removal experiment was conducted. The concentration of LAS was measured at different points in a well-characterized sewer branch, following the plug of sewage using a dye tracer. Next to this, a laboratory sewage die-away experiment was performed. No in-sewer removal of LAS was found. The laboratory studies confirmed that, based on the activity of suspended biomass in the considered sewage, biodegradation was too slow to achieve any significant removal in the 3 hours residence time in this sewer. These findings appear to be in contradiction with literature data. They were also contradicted by a modeling exercise based on market data, which considered the entire sewer system rather than only the main branch. To gain a better understanding of the fate of chemicals in the sewer system, further detailed research is recommended.

4. Calculation of Predicted Environmental Concentrations

By means of GREAT-ER, accurate chemical fate simulations can be performed for the aquatic environment. However, the resulting digital maps with predicted concentrations for individual river stretches may contain too much local detail for practical risk assessment applications and decision making. To increase the applicability of GREAT-ER in a regional risk assessment context, it is

desirable that the geo-referenced output be aggregated to a single value (or at most a frequency distribution), which is representative of chemical exposure within a catchment.

Two spatially aggregated PEC types were developed. $PEC_{initial}$ is defined as the unweighted spatial aggregation of river concentrations just downstream of waste water emissions. $PEC_{catchment}$ is defined as the spatial aggregation of all average stretch concentrations. To be representative of the entire catchment, all stretches have to be considered. In this case, weighting by flow increment (i.e. the difference of outflow and inflow for each stretch) is needed to resolve scale-dependency. To produce a value representative of the polluted parts of the catchment, only the polluted stretches should be considered, and weighting by stretch length or volume is required. Weighting by length or by flow increment results in a 'neutral' aggregation, which attaches identical importance to all locations in the river network. Weighting by volume stresses the importance of downstream parts of the river with a higher dilution and after more in-stream removal, hence resulting in a lower exposure estimate. It is obvious that a higher $PEC_{catchment}$ will be obtained when considering only the polluted part of the catchment compared to the entire catchment. This should be taken into account when these PECs are applied in a risk assessment framework.

The new PEC definitions were tested using simulations for 2 case study catchments (Calder and Went, Yorkshire, UK). This confirmed the theoretical considerations which led to the different definitions, and illustrated the need for weighting to resolve scale-dependencies.

It was shown that both proposed $PEC_{catchment}$ calculation methodologies do not require data about the entire river network that is being studied. As no or very limited information is needed about unpolluted headwaters, relatively coarse digital river networks can be sufficient. This may reduce the cost and effort needed to implement the GREAT-ER methodology for new regions, and it will strongly decrease the required simulation time.

The new approaches to calculate PECs offer a scale-independent method to compare geo-referenced exposure predictions of a chemical between different catchments. Because of the scale-independence and the standardization of the calculations, they also allow the comparison of geo-referenced exposure predictions with standardized effects data. Hence, the new PECs can be applied in environmental risk assessments. However, additional research will be required to delineate which effects data are most relevant for specific views on exposure in a catchment. For example, organisms present in the sections of the catchment directly downstream of emissions (cf. $PEC_{initial}$) may be less sensitive or ecologically valuable than those in the unpolluted headwaters. This issue also holds true for comparison between catchments: some catchments may deserve a higher degree of protection than others.

5. General Conclusions and Perspectives

The simulation methodology and chemical fate models presented in this thesis were incorporated in the GREAT-ER system. They were linked with an ArcView based GIS / data base / user interface and a hydrological model, which were developed by other partners in this project.

Outside the scope of this thesis, the system was (or is being) applied to several pilot study catchments: e.g. in the UK (Yorkshire Ouse, 15,000 km²), in Italy (northern Lambro, 1,000 km²), in Germany (Itter, 100 km²) and in Belgium (Rupel, 7,500 km²). An initial model calibration and corroboration exercise for Boron and LAS indicated that GREAT-ER was able to predict environmental exposure to these chemicals with an accuracy well within the originally required factor 5. Generally, the predicted mean concentrations were within one standard deviation of the monitored means. It can be concluded that GREAT-ER has the potential to complement the current generic 'unit world' models (of which the realism and accuracy are much lower) in higher-tier exposure assessments. Note that the calibration exercise also indicated that GREAT-ER simulations can be used to track errors or inconsistencies in the geo-referenced environmental data sets.

The main bottleneck to apply GREAT-ER is the difficulty and cost of geographical data collection, due to the generally inhomogeneous formats in which environmental data are stored by different authorities and institutes in different regions and countries. Because of this, a standardized approach towards the implementation of new catchments in GREAT-ER can currently not be completely defined. For the application of fate models with a higher complexity, like those described in this thesis, a further bottleneck may be the absence of any centralized detailed information related to the treatment infrastructure, the emissions and the rivers.

This indicates that a complete pan-European application of GREAT-ER, as suggested for the second phase of the project, is only feasible when important resources are made available. In practice, it may be preferable to limit the application to different regions within Europe that are 'typical' for specific situations (e.g. from an environmental, treatment infrastructure, product marketing or political point of view). Alternatively, it may also be a reasonable option to apply GREAT-ER to a hypothetical but realistic geo-referenced evaluative environment, representative of the main exposure scenarios in the European Union. This approach could be positioned as a step between the 'unit world' techniques and geo-referenced exposure assessment.

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Notation

Notation

$a_{a/w}$	specific air / water interfacial area	m^2/m^3
$a_{b/w}$	specific biofilm / pore water interfacial area	m^2/m^3
a_{bed}	bed material specific surface area	m^2/m^3
A	biofilm / pore water interfacial area	m^2
$A_{act.sludge}$	surface area of the activated sludge tank	m^2
$A_{a/w}^{L_i}$	interfacial area between pore air water in 1 horizontal layer	m^2
$A_{carrier}$	surface area of a piece of carrier material	m^2
A_{edge}	surface area of edges (bed + sides) in one river stretch	m^2
A_{sec}	secondary settler surface area	m^2
A_{ff}	cross-sectional surface area of the filter unit	m^2
A_{total}	entire WWTP surface area (act. sludge + settler)	m^2
$ADV_{i,j}$	advective flow rate from compartment i to compartment j	m^3/s
b	competent biomass cell decay rate coefficient	d^{-1}
B_A	hydraulic surface loading rate	$(m^3/d)/m^2$
BNR	biological nutrient removal	-
BOD	Biochemical Oxygen Demand	mgO_2/L
B_V	volumetric loading rate	$kg_{BOD}.m^{-3}.d^{-1}$
B_X	biomass loading rate	$kg_{BOD}.kg_{dwt}^{-1}.d^{-1}$
$c_{i,j}$	advection / exchange / conversion coefficient	m^3/s
C	chemical concentration	g/m^3
C_0	chemical concentration at the start of a river stretch	g/m^3
C_d	chemical concentration (dissolved)	g/m^3
C_i	chemical concentration in compartment i	g/m^3
$C_{influent}$	chemical concentration (total, in influent)	g/m^3
C_s	chemical concentration (sorbed)	g/m^3
$C_{st.st.}$	chemical conc. (total, at steady-state in mixed liquor)	g/m^3
C_x	chemical concentration at distance x	g/m^3
\bar{C}	concentrations vector	-
COD	Chemical Oxygen Demand	mgO_2/L
\overline{COEF}	coefficients matrix	-
d	river depth	m
d_{bed}	river bed material depth	m
D	dispersion coefficient	m^2/s
D_e	chemical diffusion coefficient in biofilm	m^2/s
$D_{i,j}$	interphase transfer (diffusion) coeff. from box i to box j	$mol.s^{-1}.Pa^{-1}$

Notation

D_l	chemical diffusion coefficient in water	m^2/s
DO_{sat}	saturation dissolved oxygen concentration	gO_2/m^3
DO	dissolved oxygen concentration	gO_2/m^3
E	normalized tracer response	-
f	fugacity	Pa
f_{air}^e	fraction of filter unit pores filled with air	-
$f_{biofilm}^e$	fraction of filter unit pores filled with biofilm	-
$f_{anaerobic}$	anaerobic volume fraction	-
f_{anoxic}	anoxic volume fraction	-
$f_{aerobic}$	anaerobic volume fraction	-
f_d	dissolved chemical fraction	-
f_s	sorbed chemical fraction	-
$f_d^{primary}$	primary settler's effluent - dissolved fraction	-
$f_s^{primary}$	primary settler's effluent - sorbed fraction	-
f_{rec}^1	trickling filter short effluent recycle ratio - before settler	-
f_{rec}^2	trickling filter long effluent recycle ratio - after settler	-
$f_{treated}^{wwtp}$	WWTP influent fraction which is actually treated	-
$f_{untreat/wwtp}$	sewer flow fraction which (is / is not) sent to the WWTP	-
f_{water}^e	fraction of filter unit pores filled with water	-
GPC	surface aeration gas phase correction	-
$h_{act.sludge}$	activated sludge tank depth	m
h_{air}	air mixing height	m
h_{sec}	secondary settler depth	m
h_{tf}	filter unit depth	m
H	Henry's law coefficient	$Pa.m^3.mol^{-1}$
HRT	hydraulic residence time in river stretch	h
$HRT_{act.sludge}$	hydraulic residence time in the activated sludge tank	h
k	1 st -order chemical in-stream removal rate coefficient	s^{-1}
k_1^d	1 st -order decay rate coefficient (in dissolved phase)	s^{-1}
k_2^d	double 1 st -order decay rate coefficient (in dissolved phase)	$(g_{dwt}/m^3)^{-1}s^{-1}$
k_1^s	1 st -order decay rate coefficient (in sorbed phase)	s^{-1}
k_{biodeg}	1 st -order chemical biodegradation rate coefficient	s^{-1}
$k_{biodeg}^{biofilm}$	1 st -order chemical biodegradation rate coeff. in the biofilm	s^{-1}
k_{biodeg}^{bulk}	1 st -order chemical biodegr. rate coeff. in the 'bulk water phase'	s^{-1}
$k_{biofilm}$	1 st -order chemical elimination rate to the biofilm	s^{-1}

k_{bulk}	1 st -order chemical elimination rate by suspended biomass	s^{-1}
k_{deg}	1 st -order chemical degradation rate coefficient	s^{-1}
k_{diff}	1 st -order diffusive transfer kinetics rate	s^{-1}
k_{Ga}/k_{La}	ratio of chemical mass transfer rates in air and water (40)	-
$k_{hydrolysis}$	1 st -order chemical hydrolysis rate coefficient	s^{-1}
k_i	1 st -order chemical elimination rate coefficient in comp. i	s^{-1}
k_{max}	maximal biodegradation rate coefficient (Monod kinetics)	s^{-1}
k_{monod}	1 st -order biodegr. rate coefficient based on Monod kinetics	s^{-1}
$k_{photolysis}$	1 st -order chemical photolysis rate coefficient	s^{-1}
k_{sed}	1 st -order net suspended solids settling rate coefficient	s^{-1}
$k_{act.sludge}^{sorb}$	1 st -order (de)sorption rate coefficient in the act. sludge tank	s^{-1}
k_{sec}^{sorb}	1 st -order (de)sorption rate coefficient in the sec. settler	s^{-1}
k_{tf}^{sorb}	1 st -order (de)sorption rate in the trickling filter unit	s^{-1}
k_{str}	1 st -order rate coefficient for stripping in the aeration tank	s^{-1}
$k_{str}^{surface}$	1 st -order stripping rate coefficient - surface aeration	s^{-1}
k_{str}^{bubble}	1 st -order stripping rate coefficient - bubble aeration	s^{-1}
k_v, k_v^i	1 st -order rate coeff. for volatilization in act. sludge tank (i)	s^{-1}
k_{vol}	1 st -order chemical volatilization rate coefficient	s^{-1}
K_{air}	mass transfer coefficient in air ($2.78 \cdot 10^{-3}$)	m/s
K_b	double 1 st -order biodegradation rate coefficient	$(g_{dwt}/m^3)^{-1} s^{-1}$
K_d	dissolved / sorbed partitioning coefficient	L/kg
K_d^{ML}	solids / liquid partitioning coefficient for mixed liquor	L/kg_{dwt}
K_d^{sewage}	solids/liquid partitioning coefficient for sewage	L/kg_{dwt}
K_d^{tf}	solids / liquid partitioning coefficient for filter solids	L/kg_{dwt}
K_{DO}	oxygen saturation constant for aerobic biodegradation	g_{O_2}/m^3
K_H	air / water partitioning coeff. (dimensionless Henry coeff.)	-
K_L	external mass transfer coefficient	m/s
K_s	Monod kinetics half-saturation constant	g/m^3
K_{water}	mass transfer coefficient in water ($2.78 \cdot 10^{-5}$)	m/s
l	length	m
l_i	length of stretch i	m
L	stagnant water film thickness	m
LAS	Linear Alkylbenzene Sulphonate	-
L_f	biofilm thickness	m
L_i	box numbering index for filter unit layer i	-
M	chemical market (sales) data	$kg/(cap.year)$
n	number of horizontal layers	-

Notation

$n_{carriers}$	number of carrier material units	-
$n_{stretches}$	number of stretches	-
N	number of tanks in series	-
N_b	mass flux into biofilm, per unit of interfacial area	$g.m^{-2}.s^{-1}$
$OxReq$	oxygen requirement in the activated sludge tank	g_{O_2}/m^3
P	parameter value	-
p	river's wetted perimeter	m
Pop	population	cap
\overline{PHI}	system in-/outflux vector	-
Q	flow	m^3/s
Q_{10}	biodegr. Q10 factor (rate coefficient change factor per 10°C)	-
$Q_{in}^{act.sludge}$	WWTP influent flow	m^3/s
Q^{air}	ventilation air flow due to chimney effect or forced aeration	m^3/s
Q_{out}^{dom}	water flow out of the domestic emission process	m^3/s
Q_{dwf}	dry weather waste water flow	m^3/s
Q_{end}	mean flow at the end of the catchment	m^3/s
Q_i	mean flow in stretch i	m^3/s
δQ_i	flow increment (based on mean flow) in stretch i	m^3/s
Q^{river}	river flow (from database)	m^3/s
Q_{actual}^{river}	actual (Monte Carlo realization) value of river flow	m^3/s
$Q_{in/out}^{river}$	water flow into/out of the river process	m^3/s
Q_{mean}^{river}	mean river flow	m^3/s
Q^{sec}	flow through secondary settler	m^3/s
$Q_{in/out}^{sewer}$	water flow into / out of the sewer process	m^3/s
$Q_{in/out}^{untreat/wwtp}$	water flow into/out of the untreated/treated WWTP process	m^3/s
Q_{waste}	waste sludge flow	m^3/s
r	river hydraulic radius	m
r_{end}	endogenous respiration rate	$g_{O_2} \cdot g_{dwt}^{-1} \cdot d^{-1}$
R	universal gas constant (= 8.314)	$J.mol^{-1}.K^{-1}$
$R(R_{i,j})$	sludge or effluent recycle ratio (from compartment i to j)	-
R^*	predicted chemical removal efficiency	-
R_{sec}^{SS}	secondary settler suspended solids removal efficiency	-
$R_{act.sludge}^{BOD}$	BOD removal efficiency in the activated sludge tank	-
R_{prim}^{BOD}	BOD removal efficiency in the primary settler	-
R_{prim}^N	N removal efficiency in the primary settler	-

R_{WWTP}	chemical elimination in waste water treatment plant	-
s	distance	m
S	box numbering index for settler	-
S_R	relative sensitivity	-
SRT	sludge residence time	d
SRT_{crit}	critical sludge residence time	d
SS_{act}	biologically active suspended solids concentration	g_{dwt}/m^3
SS_i	suspended solids level in compartment i	g_{dwt}/m^3
SS_{sewage}	influent suspended solids concentration	g_{dwt}/m^3
SS_{tf}	filter water suspended solids concentration	g_{dwt}/m^3
SSA	Specific Surface Area	m^3/m^2
SVI	Sludge Volume Index	L/g
t	time	s
t_{air}	air temperature	$^{\circ}C$
t_{ML}	mixed liquor temperature	$^{\circ}C$
t_{water}	water temperature	$^{\circ}C$
TRT	tracer residence time	min
v	flow velocity	m/s
v_i	flow velocity at mean flow in stretch i	m/s
$v_{sec}^{overflow}$	secondary settler overflow rate (at dry weather)	$m^3 \cdot m^{-2} \cdot s^{-1}$
v_{wind}	wind speed above the WWTP	m/s
V	volume of a trickling filter layer	m^3
V_i	volume of box i	m^3
V_{river}	volume of artificial river	m^3
V_{sec}	secondary settler volume	m^3
$V_{stretch\ i}$	mean volume in stretch i	m^3
V_{tf}	volume of the filter unit	m^3
w	river width	m
w_i	weight for stretch i	-
W	per capita water consumption	$L/(cap.d)$
$WWTP$	waste water treatment plant	-
x	river stretch length	m
X	competent biomass level	g_{dwt}/m^3
X_f	biofilm density	g/m^3
$XCH_{i,j}$	diffusive exchange flow rate from comp. i to comp. j	m^3/s
Y	competent biomass yield coefficient	-
$Z (Z_i)$	fugacity capacity (of box / medium i)	$mol \cdot m^{-3} \cdot Pa^{-1}$
a	ratio between actual and dry weather sewer flow	-
a_l	empirical parameter (minimal SS level in effluent)	g_{dwt}/m^3

Notation

a_2	empirical parameter (effect of flow on effluent solids level)	$g_{dwt}.m^{-3}.s.m^{-3}$
a_{anoxic}	degradation correction factor for anoxic conditions	-
$a_{anaerobic}$	degradation correction factor for anaerobic conditions	-
a_{redox}	degradation correction factor for different redox zones	-
a_{sorbed}	degradation correction factor for sorbed phase biodegradation	-
e_N, e_{DN}	efficiency of nitrification, denitrification	-
e_{tf}	filter unit porosity	-
$\Phi_{in/out}^{act.sludge}$	influent/effluent chemical mass flux	g/s
Φ_{BOD}	influent BOD flux	g_{BOD}/s
$\Phi_{degradation}$	chemical mass flux out of the box due to degradation	g/s
Φ_{in}^i	chemical mass flux into the system (into box i)	g/s
Φ_{out}^i	chemical mass flux from box i out of the system	g/s
Φ_{out}^{dom}	chemical flux out of the domestic emission process	g/s
Φ_N	influent N flux	g_N/s
$\Phi_{in/out}^{river}$	chemical flux into/out of the river process	g/s
$\Phi_{upstream}^{river}$	chemical flux from the upstream segment	g/s
$\Phi_{in/out}^{sewer}$	chemical flux into / out of the sewer process	g/s
$\Phi_{surplus}^{SS}$	surplus mixed liquor (waste sludge) suspended solids flux	g_{dwt}/s
Φ_{in}^{tf}	influent chemical mass flux	g/s
$\Phi_{in/out}^{untreat/wwtp}$	chemical flux into/out of the untreated/treated WWTP proc.	g/s
y	surface aeration empirical constant	-
r_{solids}^{ML}	density of mixed liquor (act. sludge) solids	kg_{dwt}/L
r_{solids}^{sewage}	density of sewage (influent) solids	kg_{dwt}/L
r_{solids}^{tf}	density of filter water suspended solids	kg_{dwt}/L
$Z_{biofilm}$	correction factor from specific surface area to biofilm area	-

Summary
Samenvatting

Summary

The work described in this thesis was conducted in the framework of the GREAT-ER project (Geography-referenced Regional Exposure Assessment Tool for European Rivers). The objective of this international project was to develop a tool to accurately predict chemical exposure in the aquatic environment, for use in environmental risk assessment. As the current generic ‘unit world’ techniques to assess regional exposure do not account for spatial and temporal variability and do not offer realistic predictions of actual concentrations, they are merely applicable on a screening level. In GREAT-ER, a software system was developed to calculate predicted concentrations of ‘down-the-drain’ chemicals (e.g. detergents) in surface waters, using a Geographic Information System (GIS) for data storage and visualization, combined with simple mathematical models for the prediction of chemical fate. In this thesis, the development of the simulation methodology used within GREAT-ER is described. Models to be used for the prediction of chemical fate are subsequently selected, adapted or newly developed. Also, new measurement methods are proposed and evaluated. Finally, a method to obtain spatially aggregated predicted environmental concentrations (PECs) for a catchment simulation was worked out.

Methodology

A geo-referenced simulation methodology for the prediction of aquatic exposure to individual ‘down-the-drain’ chemicals, which uses real-world data, was developed. By combining steady-state deterministic chemical fate models with a Monte Carlo simulation methodology, statistical frequency distributions of predicted concentrations in the aquatic environment are obtained. Emissions are predicted from chemical market data, and are further processed in sewer, treatment and river models. This results in geo-referenced predictions of chemical concentrations in the considered river systems. The practical applicability and the scale-independent character of this simulation methodology was illustrated by means of a hypothetical but realistic case study.

Measurement and Prediction of Chemical Fate

The standardized CAS (Continuous Activated Sludge) laboratory test system and the mathematical fate model *SimpleTreat* are used to routinely assess the elimination of substances in activated sludge waste water treatment plants. As these do not incorporate the effects of biological nutrient removal (BNR), which is rapidly gaining importance, a number of modifications were presented. The CAS test was adapted to include BNR processes. The performance of two modified CAS units, which were fed with an improved synthetic sewage, was monitored, and was also compared with model predictions. Next to this, primary removal of the surfactant LAS was also measured. It could be concluded that the proposed systems hold potential to complement the standard CAS. Similarly, the *SimpleTreat* model was modified to increase its applicability to BNR plants. The adaptations

Summary

focused on an improved description of sludge recycling and on the presence of different redox zones (anaerobic, anoxic, aerobic) in the biological reactor. Two updated models were applied to the modified CAS units, and tested using the LAS measurements. This illustrated the improved predictive power of the adapted models for the fate of readily biodegradable chemicals. However, further research is recommended for other substances.

For trickling filter waste water treatment plants, no standardized chemical fate model exists. A new fate model was developed, based on the approach used in *SimpleTreat* in combination with an existing biofilm model. To test the new model, a pilot-scale (200 L) trickling filter was built and operated. Using this setup, removal of LAS was measured under different well-characterized steady-state operating conditions. The new model could be fitted to LAS removal in the pilot-scale trickling filter as well as in two full-scale domestic filter plants. The same biodegradation rate coefficient (derived from activated sludge data) could be used in all cases, except for the laboratory experiments with higher LAS influent levels. As only the biodegradation and sorption aspects of the model could be confronted with measurements (because LAS was used as test substance), further research is needed to test the relevance of volatilization aspects. It is also recommended to focus additional research on the effect of the influent concentration on the biodegradation rate.

To predict the biodegradation of chemicals in rivers, a mathematical model was developed which considers both biofilm and suspended biomass activity. This model was calibrated for LAS using experimental data obtained in a small artificial river. Biofilm processes were shown to be by far the most significant removal mechanism in the considered system. The model was further tested by comparing its predictions to a field study in the Red Beck, a small Yorkshire river. The predicted overall LAS half-life (without any calibration using the field data) was within 25% of the in-stream removal measured in the field.

In a tentative in-sewer removal field experiment, no removal of LAS could be measured. This is in contradiction with literature information and with a modeling exercise based on consumption data. To gain a better understanding of chemical fate in the sewer system, further detailed research is recommended.

Calculation of Predicted Environmental Concentrations (PEC)

GREAT-ER simulations result in digital maps with predicted concentrations for individual river stretches. This output may contain too much local detail for practical risk assessment applications and decision making, for which a spatial aggregation of the results is desirable. Two spatially aggregated PEC types were developed: $PEC_{initial}$ (aggregation of river concentrations just downstream of waste water emissions) and $PEC_{catchment}$ (aggregation of all average stretch concentrations). Potential scale-dependencies and issues related to stretch selection were discussed and resolved. Testing for 2 case study catchments confirmed the theoretical considerations which led to the different definitions, and illustrated the need for appropriate weighting to resolve scale-dependencies.

Samenvatting

Dit proefschrift kaderde binnen het GREAT-ER project (*Geography-referenced Regional Exposure Assessment Tool for European Rivers*). Het doel van dit internationale project was de ontwikkeling van een voorspellingssysteem om nauwkeurig de blootstelling van het aquatische milieu aan chemicaliën te kunnen bepalen. Deze ontwikkeling moest bruikbaar zijn binnen het kader van milieurisicoanalyses. Aangezien de technieken die momenteel gebruikt worden om regionale blootstelling in te schatten ('eenheidswereld' modellen) geen rekening houden met variabiliteit in ruimte en tijd, en geen realistische voorspellingen van werkelijke concentraties kunnen leveren, zijn ze enkel geschikt voor *screening* doeleinden. In GREAT-ER werd een softwaresysteem ontwikkeld om concentraties van 'down-the-drain' chemicaliën (stoffen die vooral via huishoudelijk afvalwater in het milieu terecht komen, bv. detergents) in oppervlaktewater te voorspellen. Hiervoor werd een GIS (geografisch informatiesysteem) aangewend voor gegevensbeheer en -visualisatie, gecombineerd met eenvoudige wiskundige modellen voor de lotsvoorspelling van chemicaliën.

In deze thesis wordt de ontwikkeling beschreven van de simulatiemethodologie die gebruikt wordt in GREAT-ER. Vervolgens wordt de selectie, aanpassing of nieuwe ontwikkeling van geschikte lotsmodellen voor chemicaliën beschreven. Daarnaast worden ook nieuwe meetmethoden voorgesteld. Tot slot wordt een methode gepresenteerd om een ruimtelijke aggregatie van de gemaakte voorspellingen te verkrijgen.

Methodiek

Een geografisch gerefereerde simulatiemethode voor de voorspelling van milieublootstelling aan individuele 'down-the-drain' chemicaliën werd ontwikkeld. Deze techniek maakt gebruik van gegevens uit de realiteit. Door niet-dynamische deterministische lotsmodellen te combineren met een Monte Carlo simulatiemethode worden statistische frequentiedistributies van voorspelde concentraties in oppervlaktewater berekend. Emissies worden voorspeld op basis van marktgegevens, en worden verder verwerkt in riool-, waterzuiverings- en riviermodellen. Deze modelberekeningen resulteren in geografisch gerefereerde voorspellingen van chemische concentraties in de beschouwde riviersystemen. De praktische toepasbaarheid en het schaalonafhankelijke karakter van deze simulatiemethode werd geïllustreerd door middel van een hypothetische (maar realistische) gevalstudie.

Meting en voorspelling van het lot van chemicaliën

De gestandaardizeerde CAS (continu actiefslib) laboratoriumtest en het wiskundig lotsmodel *SimpleTreat* worden gebruikt om routinematig de verwijdering van chemische stoffen in actiefslibwaterzuiveringsinstallaties in te schatten. Deze nemen de effecten van biologische nutriëntverwijdering (BNV) niet in beschouwing. Aangezien BNV globaal sterk in belang toeneemt werden een aantal wijzigingen aan deze tests voorgesteld. BNV processen werden ingebouwd in de CAS test. De prestaties van twee omgebouwde CAS eenheden, die gevoed werden met een verbeterd synthetisch afvalwater, werden opgevolgd en vergeleken met modelvoorspellingen. Daarnaast werd ook de primaire verwijdering van de oppervlakte-actieve stof LAS in de omgebouwde testeenheden gemeten. Uit dit onderzoek kon besloten worden dat de voorgestelde systemen potentieel de CAS test kunnen aanvullen. Een vergelijkbare aanpassing werd uitgewerkt voor *SimpleTreat*, om de toepasbaarheid van dit wiskundig model voor BNV zuiveringsstations te verhogen. De aanpassingen waren gericht op een verbeterde beschrijving van de slibrecirculatie en op de aanwezigheid van verschillende redoxzones (anaeroob, anoxisch, aeroob) in de biologische reactor. Twee aangepaste modellen werden ontwikkeld. Deze modellen werden toegepast op de gewijzigde CAS eenheden, en konden getest worden door middel van de LAS metingen. Dit illustreerde de verbeterde voorspellingskracht van de aangepaste modellen voor het lot van vlug biodegradeerbare stoffen. Verder onderzoek is echter aangewezen voor chemicaliën met andere eigenschappen.

Voor oxydatiebedwaterzuiveringsinstallaties bestaat geen gestandaardiseerd lotsmodel. Op basis van de *SimpleTreat* benadering, in combinatie met een bestaand biofilmmodel, werd een nieuw model ontwikkeld. Om dit model te testen werd een pilotschaal (200 L) oxydatiebed gebouwd in het laboratorium. In deze opstelling werd de verwijdering van LAS gemeten onder verschillende goed gekarakteriseerde en stabiele omstandigheden. Het nieuwe model kon de LAS verwijdering in de pilootinstallatie goed beschrijven. Dit was ook mogelijk bij twee volleschaal oxydatiebedden voor huishoudelijk afvalwater. Eenzelfde biodegradatiesnelheidscoëfficiënt (afgeleid van actiefslibgegevens) kon gebruikt worden voor alle gevallen, behalve bij één labo-experiment waar verhoogde LAS niveaus in het influent voorkwamen. Enkel de biodegradatie- en sorptieaspecten van het model konden getoetst worden aan de werkelijkheid, aangezien LAS gebruikt werd als teststof. Daarom is het aangewezen verder onderzoek te verrichten om de relevantie van de vervluchtigingsaspecten na te gaan. Er wordt ook aangeraden om additioneel onderzoek uit te voeren naar het effect van de influentconcentratie op de biodegradatiesnelheid.

Om de biodegradatie van chemicaliën in rivieren te voorspellen werd een wiskundig model ontwikkeld dat de activiteit in rekening brengt van zowel biofilms als gesuspendeerde biomassa. Om dit model te calibreren voor LAS werd gebruik gemaakt van gegevens die verkregen waren in een kleinschalige kunstmatige rivier. Er werd aangetoond dat biofilmprocessen verreweg het belangrijkste verwijderingsmechanisme waren in het beschouwde systeem. Het model werd verder uitgetest door de voorspellingen te vergelijken met een veldstudie in de Red Beck (een kleine rivier in Yorkshire). De voorspelde halveringstijd voor LAS (zonder enige calibratie op basis van de veldgegevens) week minder dan 25 % af van de metingen in het veld.

In een beperkte veldstudie kon geen verwijdering van LAS in de riool worden vastgesteld. Dit is in tegenspraak met de literatuur en ook met een modelleeroefening gebaseerd op consumptiegegevens. Om het lot van chemicaliën in de riool beter te begrijpen is verder gedetailleerd onderzoek noodzakelijk.

Berekening van voorspelde milieuconcentraties (PECs)

Het resultaat van GREAT-ER simulaties bestaat uit digitale kaarten met voorspelde concentraties voor individuele riviersegmenten. Deze bevatten mogelijks te veel plaatselijke details voor praktische risicobeoordelingstoepassingen en beleidsondersteuning. Een ruimtelijke aggregatie van de resultaten is dus wenselijk. Twee geaggregeerde PECs (*predicted environmental concentrations*, voorspelde milieuconcentraties) werden ontwikkeld: $PEC_{initial}$ (aggregatie van rivierconcentraties onmiddellijk stroomafwaarts van afvalwaterlozingen), en $PEC_{catchment}$ (aggregatie van de gemiddelde concentraties in alle riviersegmenten). Potentiële schaalafhankelijkheden en problemen betreffende de selectie van segmenten werden besproken en opgelost. Een test voor twee gevalstroombeekbassins bevestigde de theoretische bedenkingen die leidden tot de verschillende definities. Ook werd de noodzaak van gewogen gemiddelden aangetoond, teneinde schaalafhankelijkheid van de berekeningen te vermijden.

Curriculum Vitae

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2. Education

- 1989 - 1994: Bio-engineer Environmental Technology (Universiteit Gent)
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- 1983 - 1989: ASO Wet. A (Mathematics) (Sint-Laurensinstituut, Zelzate)

3. Career

- from 2/1999: Procter & Gamble (Strombeek-Bever): ecotoxicologist
- 2/1996 - 2/1999: Universiteit Gent (BIOMATH Department, FLTBW): doctoral researcher
- 9/1995 - 2/1996: EPAS (Zwijnaarde): scientific researcher
- 8/1994 - 8/1995: Procter & Gamble (Strombeek-Bever): scientific research associate

4. Publications and Participation to Symposia

International Publications

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