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Department of Environmental Engineering

PhD Thesis
March 2009

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The thesis will be available as a pdf-file for downloading from the homepage of the department: www.env.dtu.dk

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Preface

This thesis contains my work on *Dynamic Modelling of Micropollutants in the Integrated Urban Wastewater System.* It was conducted at the Department of Environmental Engineering at the Technical University of Denmark (DTU Environment) during 2004-2008. Part of the material also developed during visits at the Department of Industrial Electrical Engineering and Automation (Lund University, Sweden) and at model*EAU* (Université Laval, Québec, Canada). The main supervisor was Associate Professor Peter Steen Mikkelsen while Professor Mogens Henze co-supervised.

The thesis consists of a summary and 7 papers, among which 5 have been published and 2 are submitted to international peer reviewed journals with ISI ranking.

Paper 1: **Lindblom**, **E**., Gernaey, K.V., Henze, M. and Mikkelsen, P.S. (2006). Integrated modelling of two xenobiotic organic compounds. *Water Sci. Technol*., **54**(6-7), 213-221.

Paper 2: **Lindblom**, **E**., Ahlman, S. and Mikkelsen P.S. (2007). How uncertain is model-based prediction of copper loads in stormwater runoff? *Water Sci. Technol.,* **56**(11), 65-72.

Paper 3: **Lindblom**, **E**., Madsen, H. and Mikkelsen, P.S. (2007). Comparative uncertainty analysis of copper loads in stormwater systems using GLUE and grey-box modeling. *Water Sci. Technol*., **56**(6), 11–18.

Paper 4: **Lindblom**, **E**., Ahlman, S. and Mikkelsen P.S. (2008). Uncertainty-based calibration of a stormwater surface accumulation-washout model using sampled Zn, Cu, Pb and Cd field data. *Submitted.*

Paper 5: Press-Kristensen, K., **Lindblom**, **E**., Schmidt, J.E. and Henze, M. (2008). Examining the biodegradation of endocrine disrupting bisphenol A and nonylphenol in WWTPs. *Water Sci. Technol*., **57**(8), 1253-1256.

Paper 6: Press-Kristensen, K. **Lindblom**, **E**. and Henze, M. (2007). Modelling as a tool when interpreting biodegradation of micro pollutants in activated sludge systems. *Water Sci. Technol*., **56**(11), 11-16.

Paper 7: **Lindblom**, **E**., Press-Kristensen, K., Vanrolleghem, P.A., Mikkelsen, P.S. and Henze, M. (2008). Dynamic experiments with high bisphenol-A concentrations modelled with an ASM model extended to include a separate XOC degrading microorganism. *Submitted.*

The papers above are included in the printed version of the thesis but not in the www-version. Copies of the papers may be obtained from the Library at the Department of Environmental Engineering, Technical University of Denmark (library@env.dtu.dk).

The following other publications were prepared during the PhD project but are not included as an integral part of the thesis:

Cloutier, F., **Lindblom**, **E**., Press-Kristensen K., Henze M., Mikkelsen P.S. and Vanrolleghem P.A. (2007). Modélisation dynamique du compartement de composés organiques xénobiotiques dans des stations d'épuration. In: *Proceedings 30e Symposium sur les Eaux Usées*. Saint-Hyacinthe, Canada, 16-17 October, 2007.

Ráduly, B., **Lindblom**, **E**. and Gernaey, K.V. (2007). A hybrid modelling approach in the simulation of integrated urban wastewater systems. Presented at: *European Congress of Chemical engineering – 6* (ECCE-6). Copenhagen, Denmark, 16-20 September, 2007.

Ráduly, B., Capodaglio, A. G., **Lindblom**, **E**. and Gernaey K.V. (2006). Model reduction using neural networks applied to the modelling of integrated urban wastewater systems. In: *Proceedings of the 20th European Conference on Modelling and Simulation ECMS 2006*. *Modelling Methodologies and Simulation Key Technologies in Academia and Industry*. Bonn, Germany, 28-31 May, 2006.

Benazzi, F., **Lindblom**, **E**. and Katebi, R. (2005). Software sensor application to WWT processes and future perspectives when applied to integrated urban wastewater systems. Presented at: *The 4th World Wide Workshop for Young Environmental Scientists*. Domaine de Chérioux, Vitry sur Seine, France, 10 – 13 May, 2005.

Lindblom, **E**., Raduly, B. and Mikkelsen, P.S. (Eds.). (2005). *System process modelling report*. Environment & Resources DTU, Technical University of Denmark, 116 pp. Incl. Annexes. EU research training network (contract HPRN-CT-2001-00200), http://www.env.dtu.dk/publications/fulltext/2005/MR2005-018.pdf.

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Dr Stefan Ahlman is acknowledged for sharing his results from the stormwater sampling campaign and for a nice long collaboration first at the Division of Water Environment Technology, Chalmers University of Technology in Sweden, and more recently at DHI Sweden.

Dr Kåre Press-Kristensen at DTU Environment is acknowledged for sharing experimental results from the Lynetten case study and for collaboration related to analysis of these. Lynettefællesskabet I/S kindly allowed us to dose bisphenol-A to their nice pilot plant at Lynetten.

Professor Peter Vanrolleghem hosted me at model*Eau* (Université Laval, Canada) and provided substantial input to the WWTP modelling part of the thesis.

Associate Professor Ulf Jeppsson and Dr Christian Rosén at IEA (Lund University, Sweden) always had time to listen and came up with good ideas and solutions for most things. It has been a pleasure to frequently visit you in Lund!

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Abstract

The focus of this thesis is dynamic modelling of micropollutants in the integrated urban wastewater system consisting of sewer catchments, wastewater treatment plants and receiving waters. Micropollutants are present in urban water due to manufacturing, disposal and use of man-made chemicals in all parts of the society as well as formation in e.g. combustion processes in connection with heating and traffic. From here, micropollutants leach into the natural environment to a large extent via pipe systems collecting both wastewater from household and industry and stormwater runoff from paved surfaces. The general hypothesis of the thesis is that models that realistically describe the fate of micropollutants in the system can be developed based on their inherent properties (e.g. biodegradability, liquid-solid partition coefficient) together with well-established mathematical descriptions of the physical, chemical and biological processes that occur in integrated urban wastewater systems. The hypothesis is examined by means of modelling three defined focus areas following the sequence of a generic model development procedure.

In *focus area 1, Integrated modelling*, a conceptual model for the fate of micropollutants in a simplified representation of the integrated urban wastewater system is developed. The presented model is capable of elucidating several frequently discussed integrated scale problems influencing the fate of micropollutants, e.g. induced re-suspension of particulates and overflow of detention basin structures during wet weather, and effects of external disturbances and operational conditions on the wastewater treatment performance. Thereby it is shown for the stormwater pollutants pyrene and the wastewater pollutant bisphenol-A that the developed model-based tool can enhance process-understanding, and the possibilities for using models for optimal design of monitoring programmes and emission control strategies on an integrated scale are outlined.

In *focus area 2, Stormwater quality modelling*, an uncertainty-based model calibration methodology is developed and discussed in relation to model predictions of stormwater pollution loads. Rather than one optimally calibrated solution, the result of the method is a distribution of model parameters, which if propagated through the model generates model output predictions that are consistent with (bracket) the experimental observations. The method is discussed and applied in combination with data from a separate system in Gothenburg including one month's monitoring data of rainfall, stormwater runoff and zinc, copper, lead and cadmium concentrations. It is shown that the relatively few and uncertain experimental observations, together with the uncertainties of input data and model structures, involves that a wide range of parameters are able to yield similar and equally valid model outputs. The total observed loads of the case study elements could be predicted with an uncertainty of ±20-80%, conditional on the used model and monitoring data.

In *focus area 3, Wastewater treatment plant modelling*, process formulation extensions to state-of-the-art activated sludge models are shown and discussed. Compared to wastewater treatment plant models describing removal of traditional pollutants like organic matter and nutrients, at least sorption/desorption, volatilisation/stripping and biological degradation by specialised microorganisms must be considered if the fate of micropollutants are to be realistically simulated. A single-substrate growth and decay model is developed and recommended for describing biodegradation of the endocrine disrupting micropollutant bisphenol-A in a pilot scale wastewater treatment plant. A calibration methodology that combines steady-state data with dynamic step-response data is developed as well. The presence of a specific bisphenol-A degrading organism in the activated sludge is established.

In the thesis it is shown that not too complex lumped, conceptual and deterministic models can be used to elucidate several complex phenomena of importance to the fate of micropollutants in the integrated urban wastewater system. To be practical also for predictive purposes several sources of uncertainty should be considered, which can however be modelled as model parameter uncertainty using the developed uncertainty-based calibration method.

Dansk sammendrag

Hovedemnet for denne afhandling er dynamisk modellering af miljøfremmede stoffer ved lave koncentrationer i det integrerede urbane spildevandssystem bestående af kloakoplande, spildevandsrensningsanlæg og vandløb. Tilstedeværelse af miljøfremmede stoffer i urbant vand skyldes produktion, brug og bortskaffelse af menneskeskabte kemikalier i alle dele af samfundet samt f.eks. forbrændingsprocesser i forbindelse med opvarmning og trafik. Miljøfremmede stoffer opsamles i både spildevand fra husholdninger og industri og regnvand afstrømmet fra befæstede overflader og udledes i stort omfang til miljøet gennem byernes afløbs- og spildevandssystemer. Den grundlæggende hypotese er, at modeller som realistisk beskriver miljøfremmede stoffers skæbne i systemet kan udvikles med udgangspunkt i stoffernes iboende egenskaber (f.eks. bionedbrydelighed, væske-faststof fordelingskoefficient) samt veletablerede matematiske beskrivelser af de fysiske, kemiske og biologiske processer, som optræder i det integrerede spildevandssystem. Denne hypotese undersøges ved at gennemføre udvalgte trin fra en generisk modeludviklings procedure for tre definerede fokusområder indenfor afhandlingens hovedemne.

En konceptuel model for en forenklet repræsentation af det integrerede urbane spildevandssystem er udviklet og udbygget med processer, der beskriver miljøfremmede stoffers skæbne, specielt tilbageholdelse og transport samt sorption og bionedbrydning. Det er derved påvist for stofferne pyren, der forekommer hyppigt i afstrømmet regnvand, og bisphenol-A, der findes i spildevand, at denne form for simuleringsværktøj kan øge procesforståelsen og dermed mulighederne for at designe moniteringsprogrammer og emissions kontrol strategier på oplandsskala. Modellen er i stand til at belyse betydningen af adskillige integreret skala fænomener på skæbnen af miljøfremmede stoffer, f.eks. forøget resuspension af partikulært bundne stoffer under regn, overløb fra forsinkelsesbassiner og effekterne af varierende tilløb og driftforhold på funktionen af renseanlæg.

En usikkerheds-baseret kalibreringsmetode er udviklet og diskuteret i forbindelse med modelprædiktioner af forureningsmængder i regnvand afstrømmet fra urbane overflader. Frem for et optimalt parametersæt er resultatet en fordeling af modelparametre, som forplantes gennem modellen og giver resultater, der er i overensstemmelse med (dækker) de eksperimentelle observationer. Metoden anvendes og diskuteres i sammenhæng med data fra et separat kloakopland i Göteborg med en måneds moniteringsdata for nedbør og afstrømning samt zink, kobber, bly og cadmium koncentrationer. Det påvises, at de relativt få og usikre eksperimentelle observationer samt usikkerhed på input og modelstruktur resulterer i at et bredt område af modelparametre er i stand til at give tilsvarende og lige valide model output. Totalafstrømningen af disse tungmetaller kan prædikteres med en usikkerhed på ±20-

80% af middelværdien, betinget af den anvendte dynamiske model og moniteringskampagne.

Tilføjelser af specifikke processer til eksisterende aktiv slam modeller er diskuteret. Sammenlignet med traditionelle rensningsanlægs modeller, der beskriver fjernelse af organisk materiale og næringsstoffer, må sorption/desorption, fordampning/stripning og bionedbrydning ved hjælp af specifikke mikroorganismer som minimum tages i betragning for at simulere fjernelse af miljøfremmede stoffer realistisk. En Monod vækst- og nedbrydningsmodel baseret på et enkelt substrat er udviklet og anvendt til at beskrive nedbrydning af det østrogene stof bisphenol-A i et pilotskala renseanlæg. En kalibreringsmetode, som udnytter en kombination af steady-state og dynamiske step-respons data, er desuden udviklet og anvendt til at påvise tilstedeværelsen af specifikke bisphenol-A nedbrydende mikroorganismer.

Afhandlingen viser, at ikke-distribuerede, konceptuelle deterministiske modeller kan benyttes til at belyse adskillige komplekse fænomener af betydning for miljøfremmede stoffers skæbne i det integrerede spildevandssystem. I forbindelse med anvendelse af modellerne ved praktisk prædiktion er det vigtigt at tage højde for adskillige kilder til usikkerhed, som imidlertid kan modelleres som modelparameter usikkerhed ved at bruge den udviklede metode til usikkerheds-baseret kalibrering.

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1 Introduction

The conventional notation for low concentration substances that are not naturally present in the environment is micropollutants. Around 100 000 chemicals are registered in the European Union and are, as a result of manufacturing, disposal and use, emitted to the environment. A substantial proportion of the total load of micropollutants enters the receiving waters by discharge from urban areas (e.g. Eriksson *et al.*, 2002, 2003). The major discharge points are direct industrial discharges (with or without treatment), wastewater treatment plants (WWTPs), separate storm sewers, combined sewer overflows (CSOs), building drains and smaller discharge pipes and surface runoff. The primary sources of micropollutants are the products which contain them, such as household chemicals, personal care products, pesticides, vehicles, construction materials and road surfaces etc, as well as the chemicals used in manufacturing.

The discharge concentrations of most micropollutants are usually far below acute human toxic levels, and it is mainly adverse long-term effects and the ecological impact that is of concern. It has been established that some micropollutants have hormonal or endocrine disrupting potential and current studies report that specific xenobiotic organic compounds (XOCs) in the effluents of wastewater treatment plants (and consequently also in stormwater discharges, via CSOs) are responsible for effects such as sterile fish in certain recipients (Press-Kristensen *et al*., 2007).

Nonylphenol (from e.g. car wash detergents) is an example of an endocrine disrupting chemical that has been found in stormwater (Björklund *et al*., 2007). Else, traditional stormwater micropollutants are often divided into (Ahlman, 2006) heavy metals (toxic to plants and animals), polycyclic aromatic hydrocarbons (PAHs) (carcinogenic) and herbicides/pesticides. In Eriksson *et al.* (2007), it is noticed that the list of interesting stormwater pollutants will need to be expanded in the future with the implementation of the EU Water Framework Directive (WFD) (European Commission, 2000). They therefore developed a methodology where “other miscellaneous organic compounds” (i.e. XOCs) were identified as well. Out of 233 investigated stormwater micropollutants their method judged 151 to be potentially hazardous considering either humans, animals or plants.

Water supply, urban drainage and wastewater treatment systems were originally designed to solve conventional problems (supply of potable water, flood protection and sanitation) and water quality research has mainly focused on organic matter and nutrients. The legislative requirement to achieve a reduction and/or elimination in the discharge of also some micropollutants within the extremely short time frame of 20 years, as set out in the WFD has therefore placed the water authorities and utilities responsible for the treatment and disposal of wastewater and stormwater, as well as industries which use and emit micropollutants across Europe, under enormous pressure.

1.1 Motivation

If the substances are not withdrawn from the market by legislation (which is an actively debated option, but a difficult one in the case of some compounds e.g. medicaments, that are needed for human welfare or PAHs, that are produced to a large extent in traffic), it is the layout and operation of the urban wastewater system that will be responsible for reaching the higher standards imposed by the new requirements, by being more efficient in reducing micropollutant discharges. Increased global urbanisation and the threats of possible climate effects of course don't simplify the problem. Complicating things even further, experimental procedures to investigate the fate of micropollutants in the urban wastewater system are difficult and expensive: the compounds are present at low concentrations, several processes occurring concurrently often contribute to one specific outcome (they are interrelated i.e. it might be difficult to see cause-relationships), the analytical methods are uncertain and expensive and numerous practical problems are related with the variability of the rainfall–runoff process and the aggressive wastewater environment.

A mathematical model is a practical way of summarizing the best available knowledge about how a certain substance behaves, and how it is affected by various processes in particular systems. This type of knowledge enhances the possibilities for optimising wastewater and stormwater operation and treatment processes, as well as monitoring programmes at an integrated urban catchment scale. Models are therefore important tools for gaining the understanding, which is necessary for reaching new discharge standards decided by society.

As pointed out in Rauch *et al.* (2002), the advance of models as tools for design and operation of the integrated urban wastewater system has followed the above-mentioned historical concerns (water supply, flood protection, sanitation). Thus, there are several hydraulic models which focus on flooding prevention as well as water quality models developed to describe removal of traditional pollutants, mainly organic matter, nitrogen and phosphorus. Some of these models are implemented in commercial simulation platforms (e.g. SWMM, MOUSE, WEST), but they are usually not concerned with specific chemical compounds and thus they cannot be applied directly to describe the fate and transport of micropollutants. For this purpose, the models must be extended.

1.2 Objectives and hypothesis

The overall aim of the thesis is to develop dynamic mathematical models that realistically describe the fate and transport of micropollutants in the integrated urban wastewater system. By the definition of three focus areas (FAs) a number of more specific objectives are stated.

FA1. In focus area 1, the objective is to develop a conceptual model structure that can help to further understand the fate of both wastewater and stormwater micropollutants from source (households, industry, urban surfaces) to destination

(CSOs, primary and secondary sludge and the effluent of the WWTP) in a simple representation of the integrated urban wastewater system.

FA2. In focus area 2, the objective is to discuss, develop and show suitable methods to analyse the uncertainty of a stormwater accumulation-washout model, especially considering that available dynamic micropollutant data for calibration are sparse.

FA3. In focus area 3, the objective is to develop and calibrate a model, which can be used to better understand and optimize WWTPs that are able to remove micropollutants in combination with removal of traditional pollutants.

The general hypothesis is that models to fulfil the objectives can be developed based on inherent properties of micropollutants (e.g. biodegradability, liquid-solid partition coefficient) together with well-established mathematical descriptions of the physical, chemical and biological processes that occur in integrated urban wastewater systems. The hypothesis is checked by means of modelling the defined focus areas following the sequence of a generic model development procedure. In this way each focus area sheds light on important aspects of importance also to the overall aim of the thesis.

1.3 Outline of the thesis

The thesis consists of a summary (Chapters 1-9) accompanied by 7 papers in the Appendices, among which 5 have been published and 2 are submitted to international peer reviewed journals with ISI ranking. In Chapter 1 the motivation and objectives are stated, and the author's publications are listed. In Chapter 2, the general methodology of the thesis is presented. Chapter 3 includes background information regarding the three focus areas of the thesis as well as more detailed problem specifications. The remainder of the summary presents and discusses the actual results of the research. Chapter 4 is concerned with the issues of model formulation and model performance analysis. Then in Chapters 5 and 6 the formulated models are evaluated against experimental data, and methods for model calibration and uncertainty analysis are developed and applied. Chapter 7 lists the conclusions of the thesis and in Chapter 8 suggestions for future work are discussed. Finally, Chapter 9 includes the bibliography.

2 Methodology

The methodology of the thesis, shown schematically in Figure 2.1, was developed at an early stage of the project and is described step-by-step in general terms in this chapter. The figure illustrates an "ideal" way of advancing while approaching problems with the help of a model. Since it has not been practically possible within the scope of the thesis to follow all steps in detail for each included topic, the figure also indicates where the focus of each focus area and included paper lies.

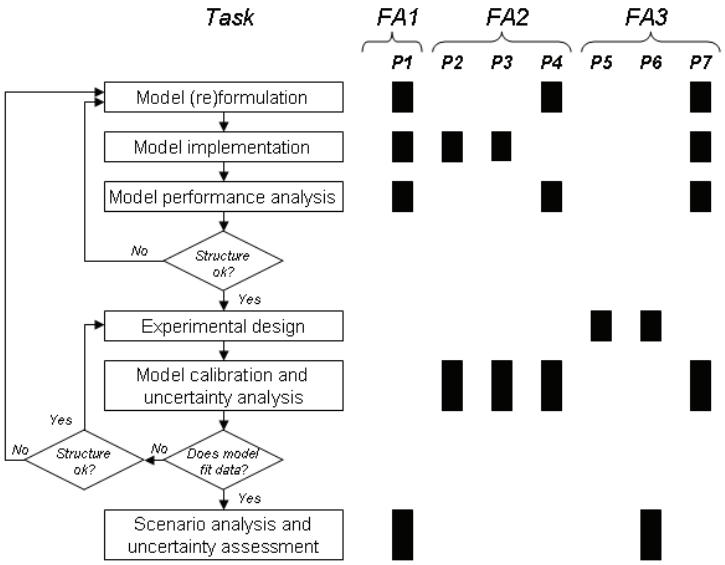

Figure 2.1. Schematic representation of the generic modelling methodology and the main focus of the 3 focus areas and 7 attached papers.

2.1 Model formulation

In the model formulation phase, problem specifications are used together with available material and a priori knowledge (from experience, literature) to define system boundaries, to characterise the incorporated processes which are of interest to consider and to chose a way of modelling these. The "appropriate" way will always depend on the stated model objectives, which are intimately related to the problem specifications shown in the following chapter. To facilitate the further discussion of the thesis the notation, which is used to classify mathematical models, are given below.

2.1.1 Dynamic versus static models

The following general notation for a continuous dynamic model is used:

$$\frac{dx}{dt} = f(t, x, u, \theta) \tag{2.1}$$

$$m = h(t, x, u, \theta) \tag{2.2}$$

Here t is time, x is a vector including the state variables, u is a vector including the model input variables and θ is the model parameter vector. The functions in f include the mathematical "rules" that describe how the model states are related with the inputs and the parameters. Most often not all state variables are observable and therefore a vector with observable model output variables m, which are related to the state variables through the functions in h, is introduced. The dynamic model can be converted to a static model by letting the derivatives in Equation 2.1 equal zero.

2.1.2 Distributed versus lumped models

Distributed dynamic models take into account both the time and spatial dimensions and need to be described with partial differential equations. In a lumped dynamic model the state variable x is distributed in time but not in space, which results in ordinary differential equations. The necessary simplification is the definition of regions where the processes are assumed to not vary in space.

2.1.3 Deterministic versus stochastic models

In a deterministic model the future outputs are uniquely determined by (1) the current states in x and (2) the future inputs u. A stochastic model contains random variables and the outputs are therefore not known with certainty, thus they are expressed as probability distributions.

2.1.4 Conceptual versus mechanistic models

If the functions in f are based on the laws of physics and include many details the model is referred to as a mechanistic (or reductionist) model. In contrast, conceptual models simplify the details of purely mechanistic models by using parameters for empirical relationships rather than for physical laws. The parameters of conceptual models can often not be measured directly and, to have predictive power, they therefore need to be calibrated with data until measurements and model output coincide.

2.1.5 Chosen model types of the thesis

Following the notation in the text above, most models that are hypothesised to be practical in this thesis are dynamic, lumped, deterministic and conceptual.

The general choice of using dynamic models is due to the involved phenomena, which all are dynamic, together with one of the major aims of the project, to provide improved understanding. The models are furthermore lumped, which is required for keeping the complexity at an acceptable level.

In environmental modelling in general, as well as here, the application of deterministic models dominates over stochastic modelling. In much, this depends on the scarce availability of data, which requires that some relationships are (at least assumed to be) deterministically known. An exception to the use of deterministic models is grey-box

modelling (Section 2.3.3)**,** which is an example of a stochastic model application of the thesis.

The chosen models are more or less conceptual models; “more or less” because it is often not possible to categorise a model as solely conceptual or mechanistic. To mention two examples:

- Parameters in mechanistic models are physically interpretable and thereby in theory possible to measure. However, it is often necessary to conduct such experiments in a laboratory scale and the results must then be extrapolated to other environmental conditions, which in itself can be seen as a conceptualisation.

- Due to the relatively high level of complexity of the activated sludge models (ASMs) of Henze *et al.*, 2000, these are often considered to be quite mechanistic. On the other hand, they describe thousands of different biomass families with two (ASM1, ASM3) or three (ASM2, ASM2d) state variables and are in this sense thus conceptual.

One reason for applying conceptual instead of mechanistic models is lack of knowledge, the details of the incorporated processes are simply not known. A second reason is that the mechanistic model would be very complex and not possible to validate because of lack of data.

2.1.6 Level of accuracy

It is important to decide upon the required level of accuracy. This level will depend upon the purpose of the modelling study and on project budget (money and time). Again, here are two examples:

- A WWTP model aimed at supporting model based control requires that only a limited part of the plant is modelled whereas a model of the same plant aimed at operator training would better be plant-wide (including all compartments e.g. screens). In the first case the model accuracy is important whereas for the second model calibration might not be required as long as the general behaviour of the plant is captured.

- A model for a sewer system aimed at improving detailed understanding needs to be mechanistic and distributed to study hydraulics and water quality processes in individual sewer stretches but does not necessarily require high accuracy. A model for the same system aimed at pollutant load or flow predictions based on rain data can very well be lumped, conceptual and completely stochastic, if it outputs sufficiently good predictions.

It is appropriate to question whether the formulation and implementation of a mathematical model to define and solve some of the problems in this thesis is overly complicated, and thereby a waste of time. Here, the obvious answer is no. A specific micropollutant is affected by not one but several inputs and processes at various locations within the system. Moreover, the number of micropollutants of interest is continuously growing. As the system size and number of studied compounds increases the involved problems will soon be un-manageable by solely traditional "paper and pen" methods.

2.2 Model implementation and performance analysis

Once formulated, the models have been implemented (coded) as C-file S-functions in MATLAB™ /Simulink™. The most often non-linear ordinary differential equations are solved with built in numerical solver methods (ode45 or ode15s). MATLAB™ was chosen as the simulation platform since it is considered to be one of the most fundamental software tools at research institutes all over the world. Simulink™ is an add-in to MATLAB™ that provides a graphical user interface for building dynamic models as block diagrams. Later in Chapter 4 (Figure 4.10) a Simulink flow-scheme is shown. The only exception to the use of MATLAB™ is found in the implementation of the grey-box model, which was done in the software CTSM (Kristensen and Madsen, 2003).

After implementation, the model performance is analysed, i.e. it is checked that the simulated outcomes are consistent with the presumed formulation. If not, the model formulation and implementation phases must be reconsidered. Several examples of model performance analyses (simulations) will be shown throughout Chapter 4.

2.3 Experimental design, model calibration and uncertainty analysis

This phase deals with the issue of analysing/evaluating the developed model structures by comparing them with experimental data. In Equations 2.1 and 2.2 the general dynamic model was formulated as a continuous model with regard to the time variable t. In practise, experimental data are only partially available, at instances k=1,2,…,N-1, N. A discrete experimental observation y_k will never exactly equal the associated model output m_k and therefore, to compare the model with the N real data, the following observation equation is introduced:

$$y_k = m_k(t, x, u, \theta) + e_k \tag{2.3}$$

The deviation between the experimental observation and the associated model output is given by the error, or residual, e_k, which is a result of a number of uncertainties:

- Uncertainty in the relationships f and h between model variables.

- Uncertainty in the model parameters θ.
- Uncertainty in the input data u.
- Uncertainty in the observations y_k, including uncertainty in the registered sampled time instances t_k.

2.3.1 Model calibration

The process of searching for a parameter set that minimises or optimises some objective function, which is often chosen to depend on the errors, is referred to as parameter estimation or model calibration. Throughout the thesis, the "goodness-of-fit" of a certain parameter set $\theta^{(i)}$ has been evaluated based on the following objective function:

$$SSE\left(\theta^{(i)}, y\right) = \sum_{k=1}^{N} \left(y_k - m_k\left(\theta^{(i)}\right)\right)^2 \tag{2.4}$$

i.e. based on the sum of squared errors (*SSE*).

2.3.2 Uncertainty analysis

With model uncertainty analysis, we mean an analysis aimed at providing information about the error e_k (e.g. influence on model predictive uncertainty, origin, structure, magnitude etc). Two approaches to model uncertainty analysis have been applied and are discussed below.

2.3.3 Grey-box modelling

A grey-box model takes into account the various uncertainties listed above by adding a stochastic noise term ($\sigma(\theta)\mathrm{d}\omega$) to the differential equations of the deterministic differential equation (Equation 2.1) and by modelling the error term in the observation equation (Equation 2.3) as a white noise process:

$$dx = f\left(t,x,u,\theta\right) dt + \sigma\left(\theta\right) d\omega \tag{2.5}$$

$$y_k = m_k\left(t,x,u,\theta\right) + e_k\left(\theta\right) \tag{2.6}$$

where ω is a standard Wiener process and $\sigma(\theta)$ a function as described in Kristensen *et al.*, (2004) and Madsen (2007).

The uncertainty of a model prediction is given by simulating the grey-box model (Equations 2.5-2.6) with the maximum-likelihood estimate $\hat{\theta}$, i.e. with the parameter set that is most likely to predict the data. The software CTSM (Kristensen and Madsen, 2003) was used to find this estimate. Note that compared to the deterministic model, the grey-box model contains additional model parameters in the two *stochastic* noise terms, which makes it possible to model the uncertainty.

2.3.4 Uncertainty-based model calibration

The second approach to model uncertainty analysis, here entitled "uncertainty-based model calibration", does not as above involve a model reformulation. The uncertainty is instead projected on the already existing deterministic model and its parameters θ, which are seen as random. Essentially this means that, conditional on the model structure, states, time and input data, the model output m (Equation 2.2) is modelled as depending only on the values of the *deterministic* model parameters. The concept that several combinations of parameters are able to yield similar and equally valid outputs is referred to as *equifinality* (Beven and Freer, 2001; Beven, 2006).

The model parameter vector is defined by the so called joint posterior parameter distribution $g(\theta|y)$, which is obtained by updating the prior parameter distribution $\pi(\theta)$ with a likelihood measure $L(y|\theta)$, indicating how well different parameter sets from the prior perform as compared to the experimental observations:

$$g(\theta \mid y) = \frac{1}{K} \cdot L(y \mid \theta) \cdot \pi(\theta) \tag{2.7}$$

Here K is a normalising constant ensuring that g is a true probability distribution (the integral of $g(\theta|y)$ over all θ should be unity). The posterior parameter distribution is assumed to include all knowledge about the statistical properties of a certain model output. The model prediction uncertainty is given by Monte Carlo propagation of the posterior through the model followed by analysis of the empirical prediction quantiles. For example, with N draws of θ from $g(\theta|y)$ the probability P of that a model output m_k lies in a certain region A_k is calculated by simply counting and averaging the times this happens:

$$P(m_k(\theta) \in A_k) = \frac{1}{N} \sum_{n=1}^{N} \mathbf{1}\left\{m_k\left(\theta^{(n)}\right) \in A_k\right\} \tag{2.8}$$

where the function $\mathbf{1}$ takes the value 0 or 1:

$$\mathbf{1}\left\{m_k(\theta) \in A_p\right\} = \begin{cases} 1 & \text{if} \quad m_k(\theta) \in A_k \\ 0 & \text{else} \end{cases} \tag{2.9}$$

The region A_k in which 95% of the model outputs fall yields P=0.95 and the empirical 95% model prediction quantile. Throughout the thesis it has been presumed that when these 95% quantiles bracket approximately 95% of the observations y_k the model output uncertainty is adequately described. Following the basic idea if the GLUE methodology (see below) the parameter sets that that in this manner yield outputs in the region A_k are hence denoted *behavioural*.

An obvious difficulty with Equation 2.8 is that it requires access to draws of θ from $g(\theta|y)$ to be solved. The Metropolis algorithm (Metropolis *et al*., 1953) is one way of directly generating such draws based on Markov Chain Monte Carlo (MCMC) sampling that has been applied. A second way is to reformulate the equation so that draws from a known distribution, e.g. $\pi(\theta)$, are sufficient. This trick is utilised by the importance sampling methodology (e.g. Robert and Casella, 2000). The Metropolis algorithm and importance sampling are further discussed in Section 6.5.

The way of expressing model uncertainty as parameter uncertainty is closely connected to the Bayesian statistical paradigm in general and to the generalized likelihood uncertainty analysis method (GLUE) of Beven and Binley (1992) in particular. According to Beven (2008), "GLUE is a form of Bayesian model conditioning methodology without the need for defining a formal structure for the errors". The same author moreover states that "Bayesian identification of models is a special case of GLUE…" (Beven *et al*. 2008). Mantovan and Todini (2006) on the other hand baptize GLUE as "pseudo-Bayesian" and criticize the method for being an inconsistent and incoherent statistical inference process. The main difference between GLUE and the Bayesian method is the interpretation of the likelihood function. In formal Bayesian statistics the likelihood function is defined as "… any function proportional to the density of the data, conditional on the parameters" (Tanner, 1996). It thus includes information about the probability of predicting the data with a certain parameters set. In GLUE as well as in the current approach the likelihood function is replaced with a less formal likelihood function, which is interpreted as a measure that reflects the degree of belief the modeller has in various parameter values (conditional on the model structure) as a simulator of the data.

In the following, the intention is to keep theoretical discussions like the ones above at a minimum. McIntyre *et al.* (2002) refers the conversion of the likelihood response surface into a "calibrated" parameter distribution like in Equation 2.7 as "uncertainty-based model calibration"; this notation is hereby used.

2.4 Model reformulation

During the model calibration and uncertainty analysis phase, the model structure is continuously checked. This activity is similar to the model performance analysis (Section 2.2), but considers exhaustively the obtained data: if the model/s cannot simulate the experimental observations, or if data and prior knowledge cannot motivate the model structure, this is reformulated. Else, the best model/s is/are evaluated in the scenario analysis phase.

2.5 Scenario analysis and uncertainty assessment

To assess the influence of the model structure and parameter uncertainty, the models can be exposed to scenarios. Scenarios are here defined as plausible descriptions of how

the system (including its inputs) might behave outside the environment of the experimental activity. Although the scenario analysis phase have not been completed yet for all three focus areas the methods for uncertainty analysis were selected bearing in mind that the results should be applicable in scenario analysis. An attractive feature of the uncertainty based calibration methodology is that the predictive distributions follow directly from propagating the posterior parameter distribution through the model. Thus, having derived the posterior and defined the scenario, much of the work is done!

3 Description of focus areas

As outlined in section 1.2 the research in this thesis is focused around three areas (Figure 3.1). It started out with focus area 1 (FA1), in which an integrated model for the fate of stormwater and wastewater micropollutants in a simple representation of the urban wastewater system was developed. From here it was decided to study stormwater quality modelling in focus area 2 (FA2) and wastewater treatment plant modelling in focus area 3 (FA3). The reason for these prioritisations was partly, as will be seen below, due to collaboration opportunities.

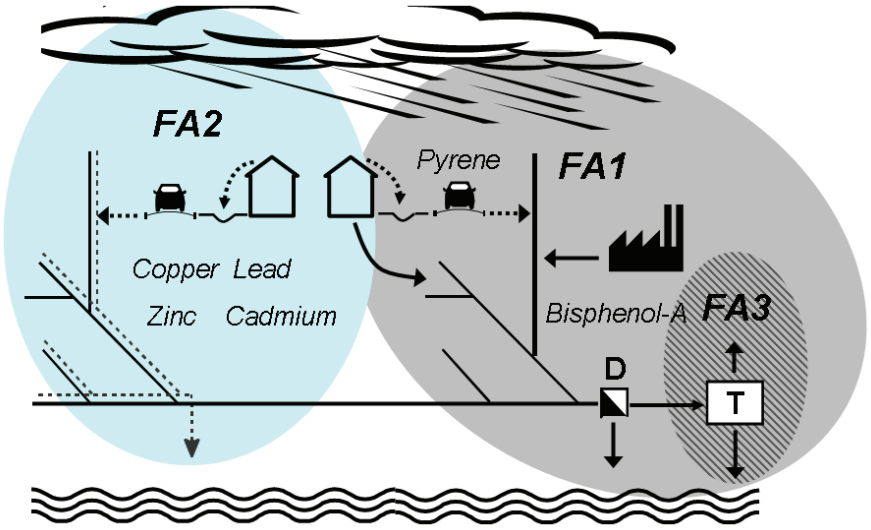

Figure 3.1. Locations of the three focus areas within the integrated urban wastewater system and the selected model compounds. FA2 concerns the stormwater of a separate sewer system whereas FA1 and FA3 concern combined sewer systems. D: Detention. T: Treatment.

3.1 Selected model compounds

While studying micropollutants in urban storm- and wastewater a significant number of substances, each having specific inherent properties and thus behaving differently, need to be considered. This fact introduces an obvious difficulty as compared to traditional urban water quality research and motivates further the formulation of, like here, general models that simulate the fate of specific chemicals (which we know little about) by the adjustment of parameter values according to their inherent chemical properties (which we often know more about). Although generality is aimed for, both considering the developed models and methods, each focus area constitute a case study with specific micropollutants as shown below.

3.1.1 The PAH pyrene

Polycyclic aromatic hydrocarbons (PAHs), are compounds that carry carcinogenic and/or mutagenic activity. Main sources of PAHs are traffic activities (vehicular component wear, fluid leakage and pavement degradation) and PAHs such as pyrene are

consequently found in runoff water from urban areas (Shinya *et al.*, 2000). Pyrene is affected by sorption to suspended solids but is not easily degraded (Eriksson *et al.*, 2005) and was chosen as an example of an organic stormwater micropollutant in FA1.

3.1.2 Bisphenol A

Bisphenol A (BPA) from polycarbonate was selected as a wastewater micropollutant in FA1 and FA3 since BPA has been detected in treated wastewater on a global scale in potentially endocrine disrupting concentrations (Press-Kristensen *et al.*, 2007). BPA is an intermediate in the production of, and a residual in, polycarbonate, epoxy resins, flame retardants etc. BPA is manufactured in large quantities in the plastic industry, for the production of polycarbonates and epoxy resins. Studies have shown that BPA, when present in for example food packaging, can leach into the products and result in estrogenic activity (Birkett and Lester, 2003). BPA is reported to be easily degraded in WWTPs and is affected by sorption to particulate organic matter (Clara *et al*., 2005).

3.1.3 Heavy metals

Heavy metals are of particular interest in stormwater runoff and wastewater due to their toxicity, ubiquitous feature, and the fact that metals cannot be biologically transformed. The National Urban Runoff Program (NURP) conducted by the U.S. Environmental Protection Agency, concluded that heavy metals were the most common priority pollutants found in urban runoff (USEPA, 1983). The heavy metals copper (Cu), zinc (Zn), lead (Pb) and cadmium (Cd) are studied in FA2.

3.2 Focus area 1 – Integrated modelling

The long term goal of focus area 1 (**Paper 1**) is to deliver a model-based tool that can enhance process understanding and thereby the possibilities for optimising monitoring programmes and emission control strategies on an integrated scale. The objective comprises the description of fate and transport of micropollutants in the integrated urban wastewater system, from source to destination during both dry and wet weather conditions. An important sub-objective was also to establish an initial integrated modelling platform that can potentially be used as a basis for further research activities at DTU Environment.

FA1 provides an example where models are used to improve system understanding; a context in which it is relevant to formulate the model detailed enough to capture the system behaviour qualitatively, whereas the numerical accuracy of the model outputs is of less importance. The work in FA1 is conducted without access to case-specific experimental data, but with experience from other studies and literature.

Being an introductory study the following reasonably ambitious specifications were defined: To achieve a model capable of elucidating

(1) relevant phenomena influencing the fate of micropollutants in the integrated urban wastewater system environment and
(2) how these phenomena are related to the pollutant origin (stormwater or wastewater) and the inherent chemical properties of micropollutants.

3.3 Focus area 2 – Stormwater quality modelling

The objective of focus area 2 (**Papers 2, 3** and **4**) is to systematically analyse the uncertainty related with estimating the total load of pollution (heavy metals) from a separate stormwater drainage system without making strong prior assumptions. Several computer models have been developed for analysing stormwater quality problems and if applied in an appropriate way, these can be used to achieve further understanding for predicting flow and water quality in sewer systems and receiving waters and thereby for decision support. The true and correct meaning of 'appropriate' is likely to be discussed by model users always, because one certain model output will never equal a unique and perfect solution to a practical problem. To post a statement grounded on a model output you will be asked about the reliability and validity of this, e.g. we have to know how uncertain the model is. Therefore it is relevant to define a (practical) method that can give quantitative information about uncertainty conditional on the available information (models and data).

The results of this focus area are conditional on results of a parallel PhD study (Ahlman, 2006), which included a measurement campaign conducted in the densely populated 6 ha Vasastaden urban catchment in the city of Göteborg, Sweden. The generated data include measurements of rainfall intensity, runoff flow and flow-proportional concentration analyses of Cu, Zn, Pb and Cd in the stormwater. The referenced parallel PhD study also presents a dynamic conceptual stormwater model named SEWSYS, which to a large degree acts as a basis for the stormwater model that is developed and used in FA2.

3.4 Focus area 3 – WWTP modelling

Conventional WWTPs are not designed for removing micropollutants but are known to remove micropollutants and to reduce the estrogenic effect of wastewater (e.g. Poseidon, 2005). Consequently, if urban wastewater passes through a WWTP on its' way to the recipient, this compartment may constitute an important micropollutant barrier in the integrated system. The ability to optimize and control micropollutant removal in activated sludge systems depends on the understanding of the important processes and on how these interact with operational parameters (e.g. plant configuration, the hydraulic retention time (HRT), the sludge retention time (SRT)), as well as environmental (e.g. temperature) and compound-specific (e.g. sorption potential, degradability) parameters.

The specific objective of FA3 (**Papers 5**, **6** and **7**) is to formulate and validate a process model for the removal of BPA in activated sludge systems using data from experiments designed to, as a first step, investigate the possible presence of specific BPA-degrading biomass. The focus area benefits from a parallel PhD study (Press-Kristensen, 2007), in which the fate of BPA in WWTPs is studied following an experimental approach. The experiments are performed in a pilot plant placed next to the Lynetten WWTP receiving a mixture of urban and industrial wastewater from Copenhagen, Denmark. The pilot plant configuration mimics the activated sludge system of the full scale plant and includes an anaerobic reactor (1.65 m^3) and two aerobic/anoxic reactors (5 m^3 each) operated according to the BioDenitro principle (see Figures 1 and 2 in **Paper 6**), and one secondary clarifier.

The aim is to suggest a simple model that can easily be combined with the traditional growth-based activated sludge models (ASMs), which are defined in Henze *et al.*, (2000). The model must include traditional wastewater variables and the physical characteristics of the system (volumes, flows, the concentration of mixed liquor suspended solids (MLSS) etc.) to be capable of describing operational parameters (e.g. HRT, SRT). The behaviour of BPA, e.g. model variables and the additional biological and physico-chemical fate processes should be included as well.

4 Model formulation and performance analysis

In the urban wastewater system, micropollutants are affected by on the one hand physico-chemical processes such as sorption/desorption, volatilisation and stripping and on the other hand, by biological processes like biodegradation. Moreover, physical transport processes such as flow, sedimentation and re-suspension have a secondary impact on the fate of micropollutants via the physico-chemical processes. The degree of influence from the physico-chemical processes on the fate of a micropollutant depends on the inherent properties of the micropollutant in question as well as of the physical transport and storage processes in the particular system, which will in their turn depend on the configuration of the studied system, i.e. on the included compartments (type, dimension) and on the way they are linked.

This chapter starts with Section 4.1 where a literature review and discussion on how to model the important physico-chemical and biological processes are given. In Section 4.2. the equations for the various transport processes used throughout the thesis are then worked through. Finally in Section 4.3 the configuration of the models in the three focus areas are outlined. The selections of physico-chemical, biological and physical process models in each compartment are also discussed and motivated. In connection with the model formulations a number of simulations, which illustrate the proceeding of the model performance analysis phase are shown.

4.1 Physico-chemical and biological process modelling

For physico-chemical and biological processes in WWTPs, the ASM models prepared by the International Water Association (IWA) Task Group on Mathematical Modelling for Design and Operation of Biological Wastewater Treatment (see Henze *et al.,* 2000) are the most widespread. The popularity of these, especially the activated sludge model no. 1 (ASM1), have also inspired the development of river and sewer water quality models based on the same concepts (Reichert *et al.*, 2001; Vollertsen and Hvitved-Jacobsen, 2000).

The water quality process modelling described below follows the concept of the above-mentioned ASM-type models. Organic material is described in chemical oxygen demand (COD) units. One gram particulate COD is assumed to represent 0.75 g volatile suspended solids (VSS). Only physico-chemical and biological process modelling of organic micropollutants, or xenobiotic organic compounds (XOCs), are considered in the thesis and therefore XOC is used as a subscript referring to a generic XOC.

4.1.1 Sorption

Sorption of substances in the environment may be caused by adsorption of compounds on the surface of particulate material or by absorption of hydrophobic compounds in the lipophilic cell membrane of biomass and the fat fraction of sludge (Siegrist *et al*., 2003).

Adsorption to inorganic suspended solids has not been modelled in the thesis. Normally, only the non-dissociated fraction of hydrophobic compounds is assumed to be affected by sorption. Dependent upon the total concentration of the compound under study and the composition and concentration of the solid material, a certain equilibrium between the concentration of sorbed and dissolved micropollutant will be established.

A majority of previously published models for the environmental fate of micropollutants (and chemicals in general) assume that this equilibrium is reached instantaneously. The main reason for the assumption, in otherwise often dynamic models, is that the solid-liquid equilibrium is reached in a short time compared to the time scales of the competing processes. This is also the main reason for why in literature only solid-liquid partition coefficients (e.g. the K_d [$L^3 \cdot M\ VSS^{-1}$] value) are given; information about dynamics is not. Another reason is probably that an experiment where a dynamic process is sampled at N time-instances is approximately N times more expensive than a similar steady state experiment. In the literature, it has however been experimentally shown that the dynamics of the sorption process might influence e.g. the biodegradation potential of a treatment process (Wang and Grady, 1995).

In this thesis it is argued that, as well as assuming instantaneous (0 minutes) equilibrium, it is equally well-grounded to assume a time constant of say, 5, 10 or 15 minutes. To allow for possible slowly established equilibrium, the proposed general model for the solid-liquid distribution of a XOC is formulated with two reverse dynamic processes. Sorption is modelled as a mixed second order expression including a sorption rate k_{sor} [$L^3 \cdot M\ VSS^{-1} \cdot T^{-1}$], the concentration of soluble XOC S_{XOC} [$M\ COD \cdot L^{-3}$] and the concentration of volatile suspended solids X_{VSS} [$M\ VSS \cdot L^{-3}$]. Desorption is assumed to be proportional to the concentration of sorbed XOC, X_{XOC} [$M\ COD \cdot L^{-3}$] in a first order manner with a desorption rate k_{des} [T^{-1}]. As shown in the example below (Figure 4.1, Equations 4.1-5), following addition of a hypothetical non-volatile XOC to a vessel operating in batch mode with a constant concentration of VSS, k_{sor}/k_{des} will equal $X_{XOC} \cdot (S_{XOC} \cdot VSS)^{-1}$ at equilibrium, i.e. equal the K_d value, and this insight can be used for calibration.

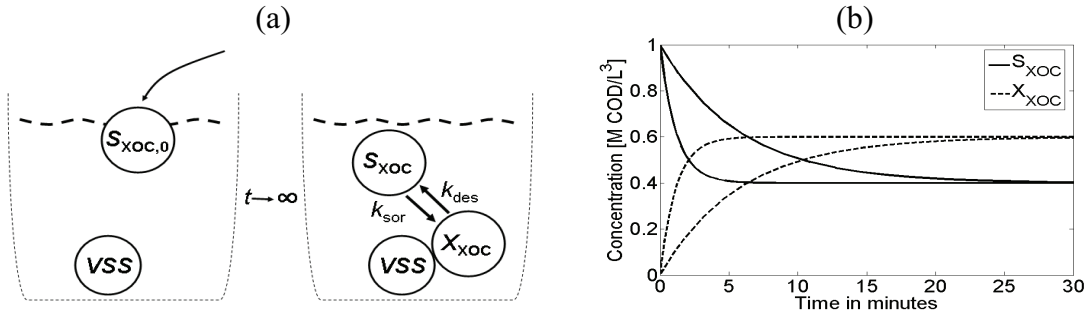

Figure 4.1: (a) A hypothetical experiment where a XOC, only affected by sorption is added to a vessel with constant concentration of *VSS*. (b) Simulation of the experiment with $S_{XOC,0}$=1 $M\ COD \cdot L^{-3}$and X_{VSS}=3000 mg/l. Fast dynamics (k_{sor}=0.25 $l \cdot mg\ VSS^{-1} \cdot d^{-1}$, k_{des} = 500 d^{-1}). Slow dynamics (k_{sor}=0.05 $l \cdot mg\ VSS^{-1} \cdot d^{-1}$, k_{des} = 100 d^{-1}). In both cases K_d=k_{sor}/k_{des}=0.5 $l \cdot g\ VSS^{-1}$.

The mass balance equation for the hypothetical experiment is

$$\frac{dS_{XOC}}{dt} = -k_{sor} \cdot X_{VSS} \cdot S_{XOC} + k_{des} \cdot \left(S_{XOC,0} - S_{XOC}\right) \quad , \quad S_{XOC}(0) = S_{XOC,0} \tag{4.1}$$

with the analytical solution:

$$S_{XOC}(t) = \left(\frac{k_{des}}{k_{sor} \cdot X_{VSS} + k_{des}} + \frac{k_{sor} \cdot X_{VSS}}{k_{sor} \cdot X_{VSS} + k_{des}} \cdot e^{-\left(k_{sor} \cdot X_{VSS} + k_{des}\right) \cdot t} \right) \cdot S_{XOC,0} \tag{4.2}$$

and

$$\frac{S_{XOC}}{S_{XOC,0}} \rightarrow \frac{k_{des}}{k_{sor} \cdot X_{VSS} + k_{des}} \quad , \quad t \rightarrow \infty \tag{4.3}$$

$$\frac{X_{XOC}}{S_{XOC,0}} = 1 - \frac{S_{XOC}}{S_{XOC,0}} \rightarrow \frac{k_{sor} \cdot X_{VSS}}{k_{sor} \cdot X_{VSS} + k_{des}} \quad , \quad t \rightarrow \infty \tag{4.4}$$

and

$$\frac{X_{XOC}}{S_{XOC} \cdot X_{VSS}} \rightarrow \frac{k_{sor}}{k_{des}} \quad , \quad t \rightarrow \infty \tag{4.5}$$

i.e. the equilibrium (the K_d-value) is given by the quota k_{sor}/k_{des}. The dynamics can be assumed to be fast if no other information is available. This structure mimics the one applied in Jacobsen and Arvin (1996), as well as the way chemical phosphorus precipitation is described in ASM2d (Henze *et al*., 2000).

4.1.2 Volatilisation and stripping

Transport across the free surface of flowing water is critical to the movement of numerous compounds in the environment. The most rigorously investigated compound in this context is the transfer of oxygen from air into water, in sewer and river models a process referred to as reaeration. None of the model compounds (Section 3.1) of this thesis are significantly affected by removal to air processes and consequently these have not received attention in the attached papers. However, for many other micropollutants transport from water to air is an important fate process and therefore a short discussion of how it can be modelled is given below.

Non-forced transport of a substance from the water phase to the gas phase is generally termed volatilisation. The transformation can be modelled as $K_L a_{XOC} \cdot (S_{XOC} - C_{G,XOC})$ where $K_L a_{XOC}$ [T^{-1}] is the overall mass transfer rate and $C_{G,XOC}$ the bulk gas concentration of the XOC. Most technical and environmental systems such as ponds, sewers and rivers are relatively well ventilated and therefore $C_{G,XOC}$ is often negligible

and assumed to be zero. A relatively good knowledge about oxygen transfer rates in the sewer, the river and the WWTP can be utilised to model volatile chemicals with a dimensionless Henry law constant $H>4\cdot10^{-2}$, through the two-film boundary-layer theory (the rate at which a chemical volatilises can be correlated to the oxygen reaeration rate based on its diffusivity). Diffusivities for various compounds in water can be approximated in several ways e.g. by the Wilke and Chang method (see Bird et al. (2002) for a description). For slowly volatilising compounds ($H<4\cdot10^{-6}$) volatilisation can be neglected. In the case of moderately volatile compounds ($4\cdot10^{-6}<H<4\cdot10^{-2}$) both the liquid film and gas film influences the mass transfer (Trapp and Harland, 1995). The mass transfer rate related to the gas phase must then be estimated.

In turbulent vessels, such as the aeration basin in activated sludge systems, the aeration process accounts for the majority of volatile micropollutant losses by mass transfer (Melcer *et al*., 1994). Such forced removal is usually termed stripping.

4.1.3 Biological degradation

Degradation converts the micropollutants into other chemical structures and can occur either biologically by the activity of viable biomass or by the surrounding chemical/physical environment, e.g. (natural) sunlight or (forced) advanced oxidation, abiotic degradation. For the modelled organic compounds (pyrene and bisphenol-A) and the considered systems possible abiotic degradation processes are assumed to not be relevant, and are dismissed in the thesis. Although biological degradation might occur everywhere in the integrated urban wastewater system (in Vollertsen and Hvitved-Jacobsen (2000) the sewer is compared to a chemical/biological reactor), the forthcoming analysis is limited to consider biological degradation in WWTPs, which are actually designed to enhance these processes. Hence, the upcoming discussion is focused on biological degradation of XOCs in WWTPs.

Biological degradation is a complex process, and several equations are used to describe it, e.g. by assuming zero order, first order, pseudo first order (also referred to as mixed second order) kinetics or by using various types of growth-based Monod model formulations. A number of different approaches for modelling biological XOC degradation in WWTPs found in the literature are shown in Table 4.1 and Table 4.2. The most simple zero- and first-order models (processes A and B) assume that, given a certain hydraulic retention time (reaction time), a fixed amount (in A) or a fixed fraction (in B) of the XOC in the influent is removed, independently of other water quality variables. In a zero-order reaction model, the removed amount is independent of the influent concentration while in the first-order case it is not. The *SimpleTreat* model of Struijs *et al.* (1991) assumes that XOCs are exclusively biologically degraded in the water phase of the aeration tank, a process that is modelled as a first order reaction with respect to S_{XOC}. In an attempt to provide a generalised fate model for the fate of XOCs in biological treatment plants, Byrns (2001) use this type of kinetics as well. Cowan *et al.* (1993) found that the specific degradation cannot be explained by the soluble chemical alone. In their model (*WW-TREAT*) the biodegradation was therefore

described (Process C) with two first order reactions: (1) biodegradation of S_{XOC} and (2) biodegradation of X_{XOC}. This is the only reference of the thesis where the particulate XOC fraction is affected by degradation.

A common feature of both the zero and first order formulations is that the organisms responsible for the degradation, are not explicitly modelled. The rate coefficients k_0 [M COD·L^{-3}·T^{-1}] and k_1 [T^{-1}] are instead lumped parameters, which in one way or another assumes a constant concentration of active XOC degrading biomass, $X_{B,XOC}$ [M COD·L^{-3}], in the activated sludge. If this assumption does not hold, or if the XOC degradation is affected by other environmental factors as well (e.g. redox conditions, the suspended solids concentration or DO-levels of the aeration tanks), the extrapolation of an estimate of k_0 or k_1 from one configuration to another looses sense. On the other hand, if the influence of the HRT is dominant and knowledge about other factors are scarce, the zero or first order formulation might be a good choice and they probably also constitute the most commonly applied equations for reactions in environmental systems.

Assuming that nutrients are present in sufficient concentrations, and that the metabolites from the degradation process do not inhibit the degradation, the *TOXCHEM* model (Melcer *et al.,* 1994) describes degradation as a pseudo first order reaction proportional to S_{XOC} and the concentration of volatile suspended solids (X_{VSS}), see process D1. In a recent EU project about removal of pharmaceuticals (Poseidon, 2005) process D2 was proposed, including the concentration of total suspended solids X_{TSS} [M·L^{-3}] instead of X_{VSS}. In Jacobsen *et al.* (1996) a similar reaction, but with suspended solids concentration replaced by the concentration of total active heterotrophic biomass, $X_{B,H}$ [M COD·L^{-3}], was used (Process D3). In the model proposed by Govind *et al.* (1991), only the part of $X_{B,H}$ actually capable of degrading the XOC, $X_{B,XOC}$ [M COD·L^{-3}], is included in the degradation equation (Process D4). They propose to estimate the active biomass concentration by the introduction of a yield parameter.

Table 4.1. Zero, first and pseudo first order models for biological degradation of XOCs found in the literature.

Process		Removal rate [M COD M^{-3} T^{-1}]	Reference
A	Zero order	$-k_0$	
B	First order	$-k_1 \cdot S_{XOC}$	Struijs *et al.* (1991), Byrns (2001)
C	Two first order	$-k_1 \cdot S_{XOC} - k_{1,X} \cdot X_{XOC}$	Cowan *et al.* (1993)
D1	Pseudo first order	$-k_2 \cdot X_{VSS} \cdot S_{XOC}$	Melcer *et al.* (1994)
D2		$-k_2 \cdot X_{TSS} \cdot S_{XOC}$	Poseidon (2005)
D3		$-k_2 \cdot X_{B,H} \cdot S_{XOC}$	Jacobsen *et al.* (1996)
D4		$-k_2 \cdot X_{B,XOC} \cdot S_{XOC}$	Govind *et al.*(1991)

The pseudo first order expressions in Process D1 and D2 take into account the suspended solids concentration and thus distinguish between e.g. an activated sludge

reactor (high X_{TSS}) and an aerated lagoon (low X_{TSS}). On the other hand the removal rate increases linearly with the suspended solids concentration independently of the sludge activity (a plant operated at a very long sludge age and a resulting high but "dead" X_{VSS} could be predicted to be more effective than in reality). This is solved by the formulation in D3 and D4 which requires estimates of actual active biomass concentrations.

In growth based models, such as the ASM models, different biomass fractions responsible for different reactions are modelled explicitly as dynamic state variables. A "general" process model for aerobic growth of specific XOC degrading biomass is shown in matrix notation in Table 3. The growth rate of specific biomass with S_{XOC} as substrate (Process 1) is given by the maximum specific growth rate of specific biomass on XOC $\hat{\mu}_{XOC}$ [T^{-1}] and the half saturation constants K_{XOC} [M COD·L^{-3}] and $K_{O,XOC}$ [M -COD·L^{-3}]. The ratio between the mass of formed biomass and degraded XOC is given by the yield Y_{XOC}. The specific biomass decay (Process 3), is characterised by the decay rate parameter b_{XOC} [T^{-1}]. Complicating things quite a lot, most bacteria can use many different organic compounds to satisfy their energy needs (McCarty, 2000) and it is logic to in a general approach assume that the specific biomass growth on "normal" mixed substrate as well. In Table 4.2 this is seen as Process 2, which conceptually has corresponding but numerically different, parameter values as process 1.

Processes 1-3 were recently used by Peev *et al*. (2004) to model biodegradation (not sorption) of linear alkylbenzene sulphonates (LAS). In Jacobsen and Arvin (1996) it is assumed that the removal of S_{XOC} does not result in an increase of specific biomass and $\hat{\mu}_{XOC}$ is treated as a degradation rate k_{bio} rather than a growth rate. By replacing $\hat{\mu}_{XOC}$ with $k_{bio}\cdot Y_{XOC}$ in Process 1, and by replacing the 1 in matrix element (1,5) with 0, the matrix is identical their proposed model. Siegrist *et al.,* (1989) noted that the specialists may preferably degrade other substrates than the XOC, e.g. that growth on easily degradable substrate might compete with degradation of their studied micropollutant, nitrilotriacetate (NTA). Therefore they multiply Process 1 with a switching function $K_{I,XOC}/(K_{I,XOC}+S_S)$ to switch off growth on XOC when S_S is high.

Table 4.2 shows a possible XOC process add-in to the ASM models, not the entire resulting integrated process model. If the additional processes were to be included with e.g. ASM1, several processes not shown would affect the S_O and S_S variables as well. This is illustrated in Figure 4.2 (left), where the XOC state variables are integrated with the carbonaceous components of ASM1. It can be seen that in this case the specific XOC degrading biomass has to compete for the "normal" active heterotrophic biomass $X_{B,H}$ [M COD L^{-3}] of ASM1 (which cannot be seen from Table 4.2).

Table 4.2. A general matrix representation for aerobic growth of XOC degrading biomass (assuming that nitrogen and phosphorus are present at sufficient concentrations). S_{VSS} is calculated from the particulate COD components of ASM1 assuming an average COD/VSS ratio of 0.75. [(1)]Decay of specific XOC degraders produces slowly degradable substrate (X_S) and particulate products arising from biomass decay (X_P) in ASM1. [(2)]Other processes affecting S_S and S_O are not shown.

i	**Component →**	1	2	3	4	5	**Process Rate [M COD L^{-3} T^{-1}]**
j	**Process ↓**	S_O[(2)]	S_S[(2)]	S_{XOC}	X_{XOC}	$X_{B,XOC}$	↓
1	Aerobic growth of specific organisms on soluble XOC	$-\frac{1-Y_{XOC}}{Y_{XOC}}$		$-\frac{1}{Y_{XOC}}$		1	$\hat{\mu}_{XOC}\cdot\left(\frac{S_{XOC}}{K_{XOC}+S_{XOC}}\right)\cdot\left(\frac{S_O}{K_{O,XOC}+S_O}\right)\cdot X_{B,XOC}$
2	Aerobic growth of specific organisms on readily biodegradable substrate	$-\frac{1-Y_{XOC,SS}}{Y_{XOC,SS}}$	$-\frac{1}{Y_{XOC,SS}}$			1	$\hat{\mu}_{XOC,SS}\cdot\left(\frac{S_S}{K_{S,XOC}+S_{XOC}}\right)\cdot\left(\frac{S_O}{K_{O,XOC}+S_O}\right)\cdot X_{B,XOC}$
3	Decay of specific organisms					-1[(1)]	$b_{XOC}\cdot X_{B,XOC}$
4	Sorption of XOC			-1	1		$k_{sor}\cdot S_{XOC}\cdot S_{VSS}$
5	Desorption of XOC			1	-1		$k_{des}\cdot X_{XOC}$
		Oxygen [M (-COD) L^{-3}]	Readily bio-degradable substrate [M (COD) L^{-3}]	Soluble XOC [M COD L^{-3}]	Sorbed XOC [M COD L^{-3}]	Specific XOC degraders [M COD L^{-3}]	*Kinetic parameters:* μ_{XOC}, $\mu_{XOC,SS}$, K_{XOC}, $K_{O,XOC}$, $K_{S,XOC}$, b_{XOC}, k_{sor}, k_{des} *Stoichiometric parameters:* Y_{XOC}, $Y_{XOC,SS}$

Figure 4.2 (right) shows the evolution of the XOC concentration with time following addition of a hypothetical non-volatile XOC at t=0 d to an aerated vessel (operating in batch mode) with the processes of Table 4.2 extended with the above-mentioned switching function of Siegrist *et al.* (1989). The simulation can be seen as a continuation of the hypothetical sorption experiment in Figure 4.1, but now with variable X_{VSS} and biodegradation as well. Immediately after addition, some soluble XOC rapidly attaches to the initially present VSS and forms sorbed XOC (Processes 4-5). During the first day, readily degradable substrate (S_S) is removed by aerobic growth of heterotrophs (not shown in the matrix) and aerobic growth of XOC degraders (Process 2). The associated biomass growth involves a continuation of the sorption process. At t≈1.2 d, the primary substrate is depleted and the starving competent biomass substitutes S_{XOC} for S_S as substrate, and the process aerobic growth of XOC degraders with S_{XOC} (Process 1) takes over. When degradation of S_{XOC} has begun, sorbed XOC is released to solution and eventually degraded.

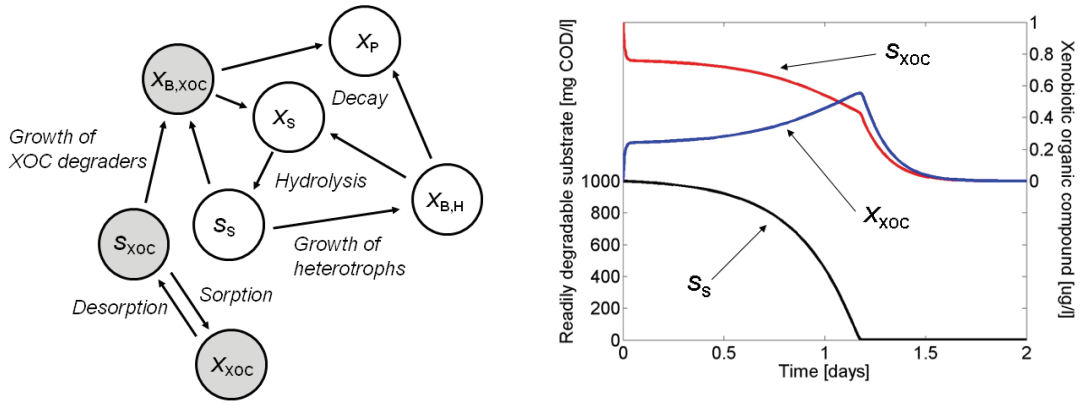

Figure 4.2. (Left) Illustration of the new state variables (shaded) and their pathways while applied to the carbonaceous components of ASM1. (Right) A simulation showing the fate of a hypothetical non-volatile XOC in an aerated vessel following a pulse addition at t = 0.

It is worth noting that all parameters in growth based models like the one in Table 4.2 usually cannot be determined from available experimental observations. For example, Siegrist *et al.* (1989) neglect processes 2 and 3 in their parameter estimation procedure and choose the inhibition constant high so that the switching function is close to 1.

4.2 Flow, storage and transport modelling

4.2.1 Flow routing

Compared to WWTPs, where compartments with constant and completely mixed volumes most often can be defined, the hydraulic properties of the upstream system can be very complex. Two relatively simple methods to model the formation of stormwater flow at the catchment outlet have been applied in the thesis. They describe the following phenomena in a similar manner:

1. The rainfall is converted to so-called effective rain P_{eff} [$L \cdot T^{-1}$] by the subtraction of initial loss [L] at the beginning of the rainfall. In addition to abstracting the first part of the rainfall, this results in a time-delay between the first recorded raindrops and the generated hydrograph.

2. The effective rain is multiplied with the total impervious area A_{tot} [L^2] and the runoff coefficient ϕ [-]. The latter parameter is a factor taking into account that only part of the impervious area is directly connected to the sewer system; in this thesis it is not distinguished from the hydrologic reduction factor.

The subsequent shaping of the hydrographs distinguishes the two methods. In the first, in the sequel referred to as the *time-area method* (e.g. Butler and Davies, 2004), a catchment-specific concentration time is used to model the time required for transport through the catchment and the resulting smoothening on the runoff hydrograph. In the second method, referred to as the *non-linear reservoir method*, the stormwater runoff Q [$L^3 \cdot T^{-1}$] is calculated as $Q=A_{tot} \cdot K \cdot h^{5/3}$, where K is a catchment-specific so-called reservoir coefficient [$L^{3/5} \cdot T^{-1}$] and h [L] is the depth of the hypothetical reservoir, which is given from the following mass balance equation:

$$\frac{dh}{dt} = \phi \cdot p_{eff} - K \cdot h^{5/3} \tag{4.6}$$

The hydraulic routing effects of the sewers are not described mechanistically in the models above but can be conceptually included through the choice of parameter values (initial loss, ϕ , K).

As described below, one attempt to model *part-full pipe flow* in a more physical manner has been made. The pipes of the sewer are divided into a number of segments i, each being built up of n identical cylinder stretches numbered 1,..,j-1,j,j+1,..,n. The segments are characterised by a flow $Q_{\text{full},i}$ [$L^3 \cdot T^{-1}$] obtained when the pipe is flowing full, an inner pipe diameter d_i [L] and a total segment length L_i [L], see Figure 4.3. The number of stretches within each segment will determine the degree of "plug-flow" for the segment. Various pipe segments can then be combined to form a network.

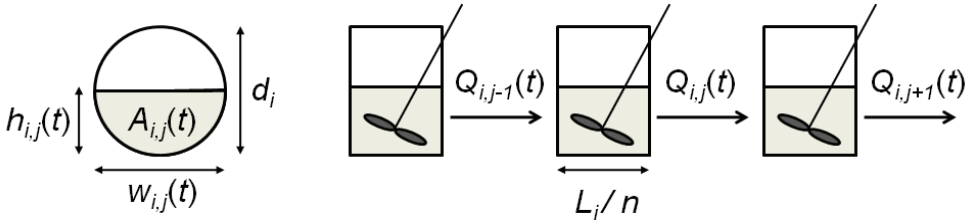

Figure 4.3. Illustration of one pipe segment including notation for geometrical properties.

The volumetric mass balance for one pipe segment stretch is:

$$\frac{\mathrm{d}A_{i,j}}{\mathrm{d}t} = \frac{1}{L_i / n}\left(Q_{i,j\text{-}1} - Q_{i,j}\right) \tag{4.7}$$

where $A_{i,j}$ [L^2] is the water filled cross-sectional area of stretch *i,j* and $Q_{i,j\text{-}1}$ [$L^3 \cdot T^{-1}$] and $Q_{i,j}$ are the influent and effluent flow rates of stretch *i,j* respectively. The outflow is calculated according to an empirical equation originally derived by Bretting (1941):

$$\frac{Q_{i,j}}{Q_{\mathrm{full},i}} = 0.46 \cdot 0.5\cos\left(\pi \frac{h_{i,j}}{\mathrm{d}_i}\right) + 0.04 \cdot \cos\left(2\pi \frac{h_{i,j}}{\mathrm{d}_i}\right) \tag{4.8}$$

where $h_{i,j}$ is the water level relative to the bottom of the pipe and $Q_{\mathrm{full},i}$ is the flow rate when the pipe is completely full. The aim of Equation 4.8 is to take into account that in part-full pipes, the maximum flow velocity Q/A occurs when the pipe is slightly less than full. From Equation 4.7 it is seen that the wetted cross sectional area is the actual state variable. When this state variable changes a new effluent flow rate (given by the new water level height) needs to be calculated according to Equation 4.8. The wetted cross section area (see Figure 4.3 for notation) is correlated with the water level height according to the geometry of circle segments (e.g. Råde and Westergren, 1998):

$$A(t) = \left(\frac{d}{2}\right)^2 \cdot \cos^{-1}\left(\frac{\frac{d}{2} - h(t)}{\frac{d}{2}}\right) - \left(\frac{d}{2} - h(t)\right) \cdot \sqrt{\left(2 \cdot \frac{d}{2} \cdot h(t) - h(t)^2\right)} \tag{4.9}$$

The hydraulic modelling approach keeps track of water level height and velocity.

4.2.2 Storage in detention structures

Detention is in this thesis modelled as equalisation basins following the theory of a linear reservoir:

$$Q = \frac{Q_{\max}}{V_{\max}} \cdot V \tag{4.10}$$

where Q is the basin effluent, $Q_{\max}$ denotes the capacity of the downstream system unit and $V_{\max}$ is the volume capacity. If this is exceeded, the maximum flow rate is passed on downstream while the remainder is discharged via a combined sewer overflow structure.

$$\begin{aligned} Q_{\mathrm{overflow}} &= Q_{\mathrm{in}} - Q \quad \text{if } V = V_{\max} \text{ and } Q_{\mathrm{in}} > Q \\ Q_{\mathrm{overflow}} &= 0 \qquad\qquad\quad \text{else} \end{aligned} \tag{4.11}$$

where Q_{in} and Q_{overflow} is the influent and overflow flow rate respectively. The hydraulic mass balance for the detention basin becomes:

$$\frac{dV}{dt} = Q_{\text{in}} - Q - Q_{\text{overflow}} \tag{4.12}$$

4.2.3 Pollutant accumulation-washout

Often, high pollutant stormwater runoff concentrations are seen in the beginning of rain events, a fact that is thought to depend on flushing of pollutants accumulated in the system during preceding dry weather periods. This feature influence e.g. how a monitoring program is designed optimally (when do we measure?) and subsequently how a mitigation strategy is implemented (type of treatment and location?). In this thesis two types of pollutant accumulation-washout processes are considered.

The model for *sediment storage and depletion* was originally formulated as part of the dynamic influent data generation model of Gernaey *et al.*, (2005, 2006) as a "first flush effect generation model block". It is a good example of a highly conceptual model (actually, the level of conceptualisation is so extreme that it is referred to as 'phenomenological' in the cited reference). A constant user-defined fraction i_{TSS} [-] of the influent TSS is assumed to settle and deposit by sedimentation during dry weather to form deposited solids M_{sed} [M], which are re-suspended during periods of increased flow:

$$\frac{dM_{\text{sed}}}{dt} = i_{\text{TSS}} \cdot Q \cdot X_{\text{TSS}} \cdot \left(1 - \frac{M_{\text{sed}}}{\gamma_1}\right) - \left(\frac{Q^{\gamma_2}}{\gamma_3^{\gamma_2} + Q^{\gamma_2}}\right) \cdot M_{\text{sed}} \cdot \gamma_4 \tag{4.13}$$

The general notation γ_i is here used to compartmentalise the i=1,…,4 conceptual model parameters. In the first term on the right hand side γ_1 [M] is interpreted as the maximum amount of solids that can deposit in the sewer. γ_2 [-] and γ_3 [L^3/T] are parameters used to shape a hill-shaped function, which determines at what flow, and how sudden, re-suspension is activated. γ_4 [-] is similarly to γ_2 a dimensionless parameter used to tune the strength of the first flush. In a more mechanistic formulation of the phenomena in Equation 4.13 the parameters would be variables dependent on e.g. physical properties such as sewer system dimension, slope and roughness etc.

The intention of the *surface accumulation-washout* model is to represent the building up of various pollutants on the impervious surfaces (e.g. roofs, roads) of the catchment. Pollutants are accumulated in dry periods and washed off during rainfall, processes described with classical build-up and washout functions (Overton and Meadows, 1976):

$$\frac{dM_{\text{surf}}}{dt} = A_{\text{tot}} \cdot \theta_1 - \left(\theta_2 + \theta_3 \cdot p_{\text{eff}}\right) \cdot M_{\text{surf}} \tag{4.14}$$

where M_{surf} [M] is the stored pollutant on the surfaces and θ_i i=1,2,3 represent parameters depending on compound- and catchment-specific properties; the dry

deposition load θ_1 [$M \cdot T^{-1} \cdot L^{-2}$] (representing different sources of pollution e.g. traffic activities, surface corrosion and atmospheric deposition), the rate coefficient for pollutant dry removal θ_2 [T^{-1}] (representing removal by wind and other means) and finally the rate constant for wet removal by wash-off θ_3 [L^{-1}].

Note the similarities between the sediment storage model above and the accumulation washout model**:** Instead of the Hill function switching depletion on when the flow is high, the surface model assumes that wash-off is first order with regard to the effective rainfall, else they are similar in structure: θ_1 corresponds to $i_{TSS} \cdot Q \cdot TSS / A_{tot}$, θ_2 to $i_{TSS} \cdot Q \cdot TSS / \gamma_1$ and θ_3 to γ_4.

4.3 Model configuration building and process selection

4.3.1 The integrated model

Every urban catchment, sewer system and WWTP are unique and show different behaviour. Therefore it is difficult to define a "general" or "global" integrated model. Many integrated urban wastewater systems however encounter the same type of problems, which could be studied with the help of benchmarking a model that is capable of capturing these.

The chosen layout of the integrated combined urban wastewater system is inspired by the Harrestrup river catchment located in the south-western part of the city of Copenhagen, which is used as physical system in the DTU Environment course "Integrated Urban Water Quality Management" (Grum *et al*., 2000). The model of the combined integrated wastewater system (Figure 4.4) is composed of models of the following sub-systems: an urban catchment, two equalisation basins with associated overflows, a trunk sewer, and a WWTP.

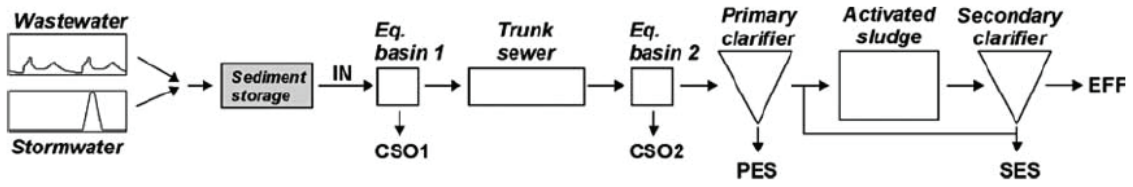

Figure 4.4. The simulated integrated urban wastewater system of focus area 1 with stream notation. CSO: combined sewer overflow, EFF: effluent, PES: primary excess sludge, SES: secondary excess sludge. From **Paper 1**.

Although a very simple representation of an integrated system, it was developed so that it can be used to elucidate integrated scale problems often seen and reported in the literature e.g.: (1) induced re-suspension during wet weather, which increases the pollutant load on the downstream system, (2) overflow from basin structures, which involves that urban wastewater is discharged to the recipient without treatment and (3) effects of operational conditions on the WWTP performance.

Rain falling on the urban catchment is converted to stormwater through the time-area method (Section 4.2). Typical daily concentrations and flow profiles of wastewater from households and industry are created according to the influent wastewater generation model of Gernaey *et al.* (2005, 2006), here slightly extended to generate the original 13 ASM1 component concentrations as well as the 3 additional XOC specific components S_{XOC}, X_{XOC} and $X_{B,XOC}$ as defined in Table 4.2. It is assumed that the total concentrations of pyrene in stormwater and BPA in wastewater are constant and that sorption equilibrium with the dynamic suspended solids concentration is established at generation. BPA, which partly is attached to the suspended solids of the wastewater settle during dry weather and re-suspend during increased flow according to Equation 4.13, in the hypothetical sediment storage tank, which is placed at the outlet of the catchment. The generated runoff and possibly depleted sediments are then routed through the trunk sewer model (Section 4.2.1). The associated retention and smoothening of the runoff profile depends upon the dimensions of the trunk sewer and make possible for the modeller to study possible un-equally distributed overflows of the two surrounding equalisation basins, which are defined by Equations 4.10-4.12 (Section 4.2.2). A series of five activated sludge reactors followed by a secondary settling tank, according to the Benchmark Simulation No. 1 (BSM1) system description developed within the European COST action 624 collaboration (see Copp, 2002), is used to simulate a common WWTP configuration, a continuous activated sludge system with internal recirculation designed for COD and nitrogen removal. The implemented primary clarifier model is described in Jeppsson *et al*. (2006).

Processes 1-5 in Table 4.2 are used to model the physico-chemical and biological processes of the two XOCs. Sorption and desorption (Processes 4-5) is assumed to occur in the entire system and for both compounds. This is required to simulate removal with the primary and secondary excess sludge streams as well as the accumulation in the catchment during dry weather and it is also practical in the view of possible future work, which could include separate models for transport of soluble and particulate material in the equalisation basins and trunk sewer. Biodegradation by specific BPA degrading biomass is only considered in the WWTP where Processes 1-3 are integrated with the BSM1 default ASM1 process model. Only BPA is affected by biodegradation. Volatilisation is not considered since this process is not relevant for the case-study compounds.

It is clear from the specification in Chapter 3 that the aim of FA1 is not to produce exact numerical numbers of the mass-flows, but rather to elucidate important phenomena, and the selection of the type of physically interpretable but conceptual sub-model formulations are thus motivated. The equalisation basin model is formulated both to be simple and to be general. Settling is not described and no distinctions are made between dissolved and suspended components (this would require the definition of a specific basin geometry, location of weirs etc). The reasons for formulating the seemingly complex trunk sewer model are found by again having a glance at the original problem specification. The perspective is to provide a general simulation tool for micropollutants

in the integrated system, many micropollutants are volatile and (models for) this process depends on the flow velocity and air/water contact area. Thus, the model needs to describe these variables as a function of time.

In general, the parameter values of the case study in **Paper 1**, although believed to be realistic, have been chosen subjectively. For example the growth and decay rates of the specific biomass are chosen to equal the ones of autotrophic biomass in ASM1. The influent concentration of $X_{B,XOC}$ are manipulated to adjust the steady state removal by biodegradation. These assumptions result in a model where the WWTP remove approximately 70% of the BPA by biodegradation as well as one that is sensitive to the sludge age, a fact that is supported by literature (Clara *et al.,* 2005). Models like this, developed for enhancing process understanding, can support a statement like "why do we find the typical stormwater pollutant pyrene in a wastewater treatment plant also after long periods of dry weather conditions?", whereas the results can not be used directly for engineering design (e.g. dimensioning).

Figure 4.5 shows the total mass of pyrene in the WWTP following the simulated storm event (12 mm during 5 h) of **Paper 1**. Initially it is zero since the wastewater is assumed not to contain pyrene. When the stormwater reaches the WWTP, pyrene attaches to the activated sludge since pyrene has a high K_d value and as it is not easily degraded it stays in the WWTP during several sludge ages. The diurnal variation is an effect of the suspended solids concentration dynamics caused by the dynamic influent generation model. The highly different time constants of the integrated system here become clear. Although the studied rain event lasts for only a couple of hours, the stormwater pollutant is found in the biological reactors of the WWTP during 3-4 weeks.

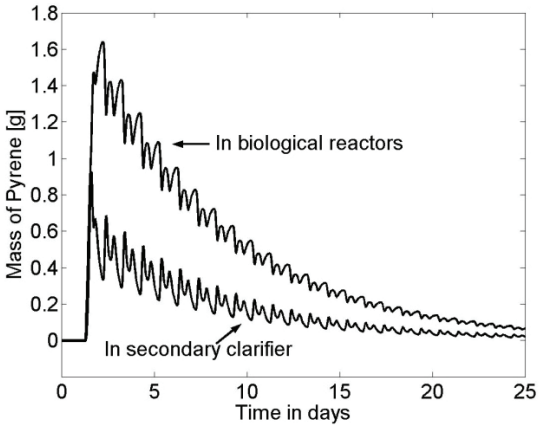

Figure 4.5. Accumulated mass of pyrene in the WWTP (from **Paper 1**).

Figure 4.6 (top left) shows how the stored sediments are resuspended during the high flow rate induced by the rain event. The increased contribution of stormwater in the runoff involves a dilution of the BPA concentration (Figure 4.6, bottom left), with the exception of the peak caused by the first flush. Despite the general dilution, the first flush phenomenon results in an increased load of BPA in the WWTP effluent (Figure

4.6, right). The wastewater generation model is the reason for the (on a daily scale) dynamic BPA mass flow profile.

Due to the detention implemented in the model through the trunk sewer model the two equalisation basins overflow at different times. In the specific case of **Paper 1** equalisation basin 1 happen to overflow when BPA concentrations are high and the BPA overflow load is thus higher here. This exemplifies that the developed model takes into account effects like the distribution of overflow pollutant loads depending on the dynamics of the pollutant mass routing process and location of CSO structures in the system.

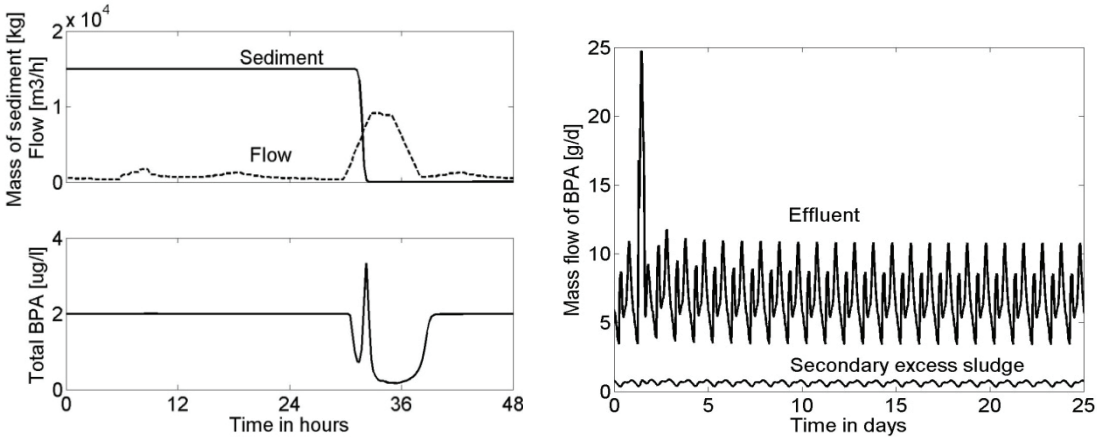

Figure 4.6. Top left: Resuspension of stored suspended solids due to the increased flow rate of the rain event. Bottom left: Concentration of total BPA in the sewer trunk. Right: Mass flow of BPA from the WWTP. From **Paper 1**.

4.3.2 The stormwater quality model

The starting point for the model used in FA2 is the SEWSYS model of Ahlman (2006). SEWSYS is a conceptual stormwater model developed for simulations of substance flows in urban drainage systems. It was developed with the objective of being a tool for testing various source control options by scenario analysis and for summarizing knowledge about the distribution of surfaces as pollution sources within a catchment. Rain is converted to stormwater through the non-linear reservoir hypothesis shown in Equation 4.6. Pollutants are accumulated on and washed out from three different types of surfaces: roofs, roads and other impervious areas, according to the accumulation-washout process model shown in Equation 4.14. In SEWSYS each modelled substance is linked to different source parameters which are combined with catchment specific attribute data to give emission factors, a feature which is however not used in this thesis. Summed up these contribute to the build up of pollutants, which are washed off and mixed with the stormwater during rain.

Combining Equations 4.6 and 4.14 gives the model shown in Figure 4.7, where the stormwater concentration C [M·L^{-3}] has been obtained by assuming complete mix of the rain and the washout pollution:

$$\frac{d(V \cdot C)}{dt} = V \cdot \frac{dC}{dt} + C \cdot \frac{dV}{dt} \tag{4.15}$$

and dV/dt is given from Equation 4.6:

$$\frac{dC}{dt} = \frac{p_{eff}}{h \cdot A_{tot}} \cdot \left(\theta_3 \cdot M_{Surf} + \phi \cdot A \cdot (C_{rain} - C)\right) \tag{4.16}$$

All parameters and variables in Equation 4.16 except the rainwater concentration C_{rain} [M·L^{-3}] have been defined above.

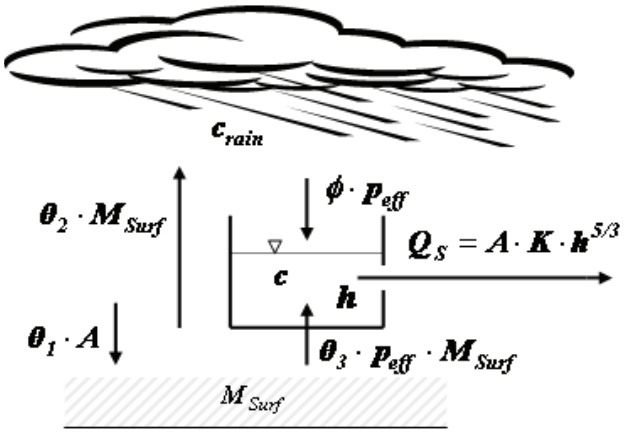

Figure 4.7. The conceptual stormwater rainfall-runoff and accumulation-washout model. From **Paper 3**.

Figure 4.8 shows the performance of the applied stormwater model. The rain (5 events in 4 days) and runoff are shown in the upper panel (left and right). In the lower panel (left) the variable mass of stored pollutant on the surface is shown whereas the right plot shows the stormwater pollutant concentration. As will be further discussed in Chapter 6, neither of these two state variables (M_{surf} and C) are directly observed.

It must be mentioned that although the stormwater model used in this thesis was implemented by the author, it was not developed as a part of this thesis. There are many proposed urban stormwater quality models in the literature (Elliot and Trowsdale, 2007) and it is not evident that the use of a conceptual process-based model is the best choice for load estimation. Vaze and Chiew (2003) for example conclude that if only estimates of event loads are of interest, regression models should be used because they are simpler and require less data compared to process-based models. However, dynamic models are needed to study e.g. the implications of first flush phenomena on the removal processes in stormwater treatment systems such as ponds.

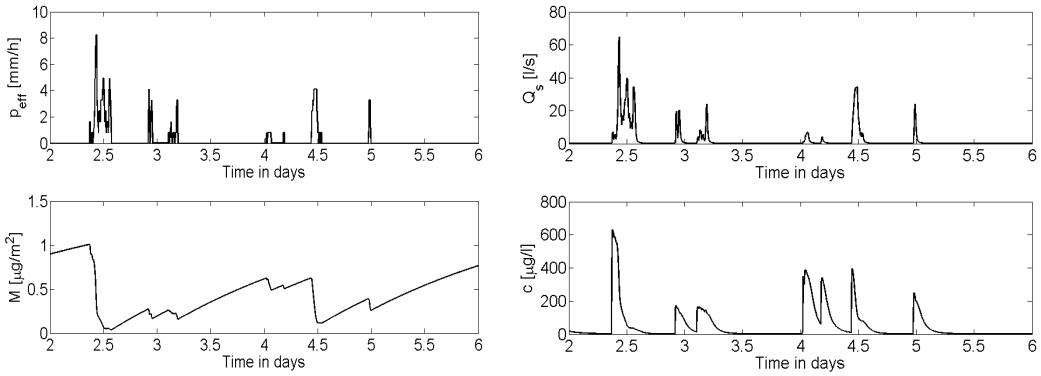

Figure 4.8. A 4 day simulation with the stormwater quality model used in focus area 2. Effective rainfall (top left), stored pollutant on the surfaces (bottom left), stormwater runoff (top right) and stormwater concentration (bottom right).

4.3.3 The Lynetten WWTP model

In contrast to the recirculating WWTP configuration modelled in FA1, the WWTP model of FA3 was formulated based on experiments conducted at a plant equipped with the more specific Bio-Denitro configuration (Henze *et al.*, 2002). In this, the internal recirculation is replaced by controlling the aeration and flow directions in an alternating manner. Figure 4.9 shows a simulation of typical concentration profiles in the process.

The model configuration (Figure 4.10) follows the layout of the physical plant where pre-settled wastewater enters the biological treatment with 3 completely mixed activated sludge reactors (1 anaerobic, 2 aerobic/anoxic) and 1 secondary settler modelled with the Takács 10-layer model (Takács *at al.,* 1991). ASM1 was chosen as a basis for the process model and calibrated to fit online measurements of suspended solids, ammonia, nitrate and phosphate in the two aeration tanks. The calibration was conducted "heuristically", mainly through the fractionation of the influent wastewater into ASM1 concentrations.

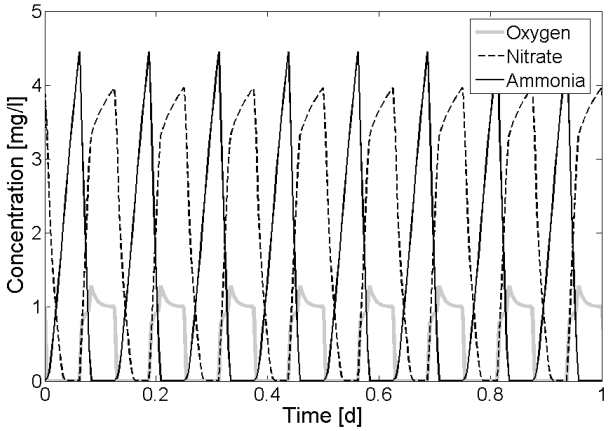

Figure 4.9. Alternating concentration profiles in one of the aerobic/anoxic reactors of the Bio-Denitro process.

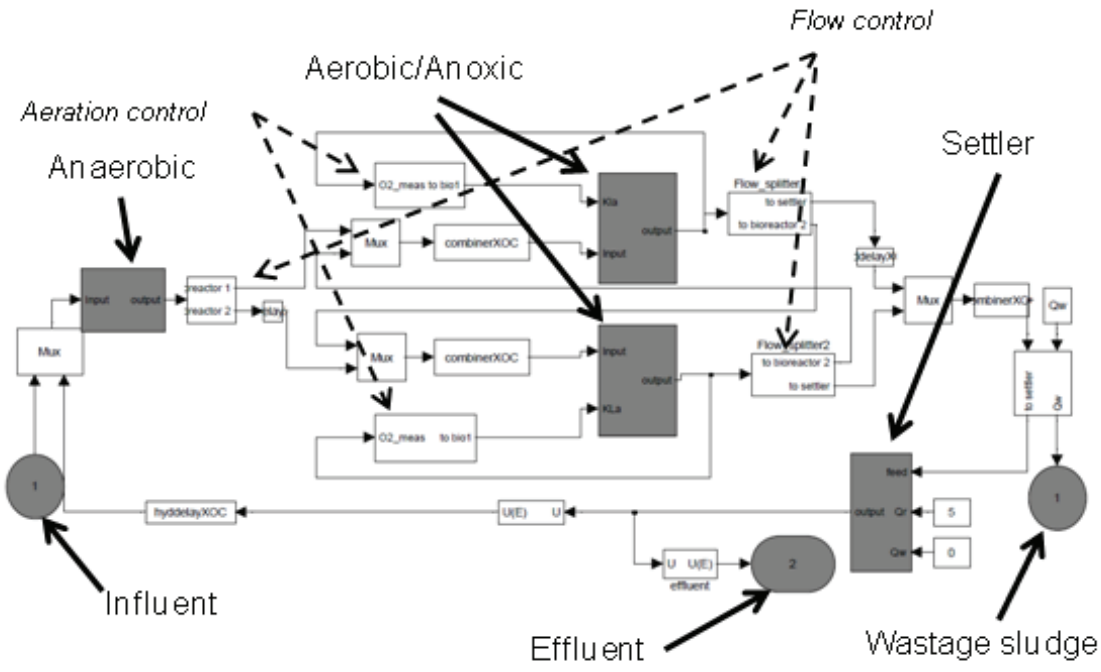

Figure 4.10. A SIMULINK screen print of the Lynetten WWTP model. Dimensions and typical flow rates are shown in **Paper 5** (Figure 1).

The proposed add-in to ASM1 includes 3 additional components (2,3,4) and 4 additional processes (1,3,4,5) as defined in Table 4.2. The process model is thus similar in structure to the one of the integrated model. The reason for dismissing process 2 in FA3 is that the experimental data is believed not to be sufficient for establishing growth of specific biomass on natural substrate. This is further discussed in Chapter 5.

5 Parameter estimation of the BPA biodegradation model

In this chapter it is discussed how experimental data collected at the Lynetten pilot-scale WWTP are used together with the hypothesised WWTP model (Section 4.3.3) to estimate a number of biodegradation model parameters and to establish the presence of a separate BPA degrading microorganism.

5.1 Description of experimental data

For analysis four groups of data from various experimental occasions are exhaustively considered:

1. *Background:* No active experiment was conducted. Data consists of influent and effluent samples collected during normal operation and analysed for total BPA concentration.

2. *Dosage 1:* The influent wastewater (15 °C) was spiked with 10 g BPA/d during 46 days, which corresponded to a total influent concentration of 842 µg/l. Data consists of effluent grab samples analysed for total BPA concentration.

3. *Dosage 2:* The influent wastewater (20 °C) was spiked with 10 g BPA/d during 34 days, which corresponded to an influent concentration of 1009 µg/l. The experiment had been preceded by dosage of 1 g BPA/d during 60 days, corresponding to a total influent BPA concentration of 109 µg/l. The data set consists of grab- and flow-proportional effluent samples analysed for total BPA concentration.

4. *Operational:* The plant was first operated normally (50% aeration time), which was followed by a change in the operational settings (70% aeration time). The data set consists of influent and effluent samples from both periods (**Paper 6**). The samples were analysed for total BPA concentration.

The *Background* data set shows that during normal operating conditions, the total concentration of BPA is lowered from 9 µg/l in the influent to 4 µg BPA/l in the effluent (**Paper 5**). In the same paper it is also shown that this removal probably is caused by biodegradation under aerobic conditions.

The two data sets *Background 1* and *Background 2* are plotted in Figures 5.1-5.2. Figure 5.1 shows that the measured effluent BPA concentration converges towards the influent concentration (833 µg BPA/l) after approximately 5 days. The subsequent BPA removal increased during 40 days until the measured effluent concentrations were at the same level as during the *Background* experiment.

5.2 Model simplification and preparation for calibration

The hypothesised process model, which is shown in Table 4.2, is the most simple explanation for the observed behaviour. To facilitate the calibration procedure, a number of model simplifications were done:

- The Bio-Denitro configuration was mathematically simplified to a chemostat.
- Immediate sorption equilibrium was assumed.
- The maximum specific growth rate of specific biomass on "natural" substrate was assumed to be zero, thus this process was neglected (process 2 in Table 4.2).
- The numerical values of the decay rate (b_{XOC}) and yield (Y_{XOC}) were assumed and not included in the calibration.

Motivations for these simplifications can be found in **Paper 7**. Note that replacing the Takács settler model with a perfect settler model (chemostat) do not imply that we say that e.g. secondary settling should never be modelled or that the replacement of the two alternating Lynetten tanks with a single tank assumes that a BioDenitro plant behaves similar to a standard recycling plant. The simplifications are for this specific case and the available data, where they do not seem to have a significant effect on the estimation of the selected model parameters.

5.3 Calibration procedure

The data from the *Background* and *Dosage 1* experiments were used for calibration of the parameters of the hypothesised BPA degradation model. The *Dosage 2* data were subsequently used for model validation.

Regarding the sorption parameters k_{des}=1000 d^{-1} and k_{sor}=0.5 l mg $VSS^{-1}\cdot d^{-1}$, which correspond to a K_d of 0.5 l· g VSS^{-1}, were used. These values are in accordance with the data (during the first 5 days in Figure 5.1, biological growth has not started and sorption/desorption is the only active process) and with values reported in literature. In principle, this choice of sorption parameters affects the subsequent estimation of biodegradation parameters but in the case of BPA sorption is not very important: although the highest K_d value found in literature is selected (1 l·g SS^{-1}, Clara *et al.*, 2004), less than 7% of the influent BPA load is removed via sorption.

The calibration protocol developed and shown in **Paper 7** suggests a method to give the parameters $\hat{\mu}_{XOC}$, K_{XOC} and $X^0_{B,XOC}$ (the initial concentration of specific XOC degrading biomass) numerical values. In short, the developed estimation method proceeds as follows: Starting from steady state, a dynamic simulation mimicking the *Dosage 1* experiment is performed. An optimisation algorithm (*fmincon* in Matlab) is used to find the value of $\hat{\mu}_{XOC}$ that minimises the sum of squared errors (Equation 2.4) between simulated and measured effluent BPA concentrations. K_{XOC} is constrained by being replaced with a function depending on $\hat{\mu}_{XOC}$ and the effluent steady state BPA concentration. The initial steady state specific biomass concentration is constrained by

being replaced with a function depending on $\hat{\mu}_{XOC}$ and the influent and effluent BPA concentration. This is to allow for including information from the *Background* experiment in the dynamic estimation.

Following the methodology, two attempts (*i*) and (*ii*) to estimate the parameters are done. The results of these are shown in Figure 5.1 below. In (*i*) the steady state removal is respected, while in (*ii*) this is only partially true. The steady state effluent concentration is indeed respected but instead of calculating the initial biomass concentration from the steady state removal, it is in case (*ii*) estimated together with $\hat{\mu}_{XOC}$ from the step-response data.

5.4 Results

The simulated effluent BPA concentrations shows a reasonable fit to the experimental concentration data for both estimations. The steeper slope of the simulation in (*i*) compared to the data depends on the initial low concentration of specific biomass which requires a high estimate of $\hat{\mu}_{XOC}$ to simulate the time required to reach a new steady state effluent. In estimation (*ii*) an improvement of the fit is obtained by estimating the initial biomass concentration as well. Note however that the results of (*ii*) are not in accordance with the hypothesized model and experimental observations. A 10 times higher influent BPA concentration would be required to cultivate the high estimate of initial specific biomass. Attempt (*ii*) should here thus be seen as a guide for future model development, where a plausible new hypothesis could be that part of the "normal" heterotrophs are capable of metabolising BPA as well.

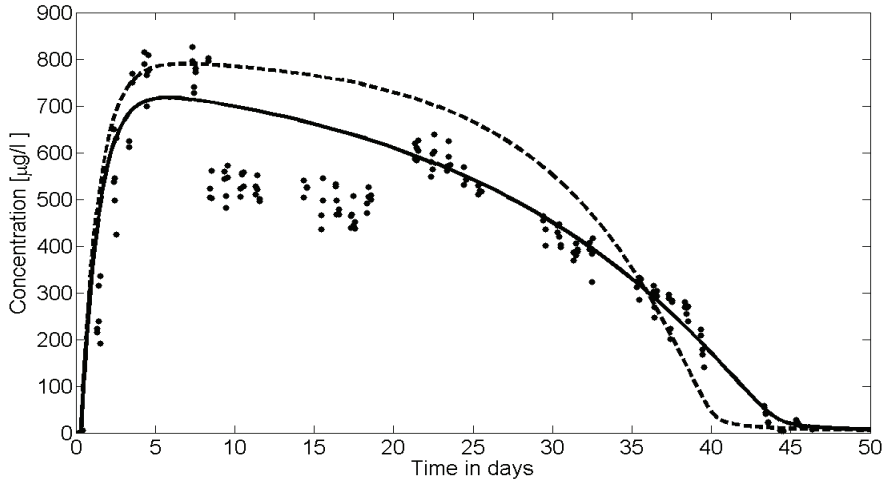

Figure 5.1. Calibration of the BPA model based on the *Background* and *Dosage 1* experiments (from **Paper 7**). Dots: Measured effluent BPA concentrations. Dashed line: Estimation (*i*). Solid line: Estimation (*ii*).

For validation (see **Paper 7** for details), the estimates from (*i*) are used in a simulation of the *Dosage 2* experiment (Figure 5.2). Compared to the calibration scenario, this validation scenario is identical with regards to inputs (step increase in influent BPA load). However, the initial state of the process is expected to be different (*Dosage 2* was preceded by an additional dosage period whereas *Dosage 1* was conducted with "fresh" sludge) and the operational and environmental conditions are significantly different. In summary one can say that the calibrated model is exposed to a difficult validation scenario, especially regarding the varying temperatures. Temperature is well known to have a high influence on the rate parameters of biological degradation models and the correction factors used to describe it could not be calibrated before validation.

The validation shown in Figure 5.2 does not give a perfect fit but the model predicts the correct general structure of the data. The results show that biodegradation of BPA is sensitive to operational conditions before and during the experiment and that the proposed model structure is capable of capturing important characteristics of the observed BPA removal.

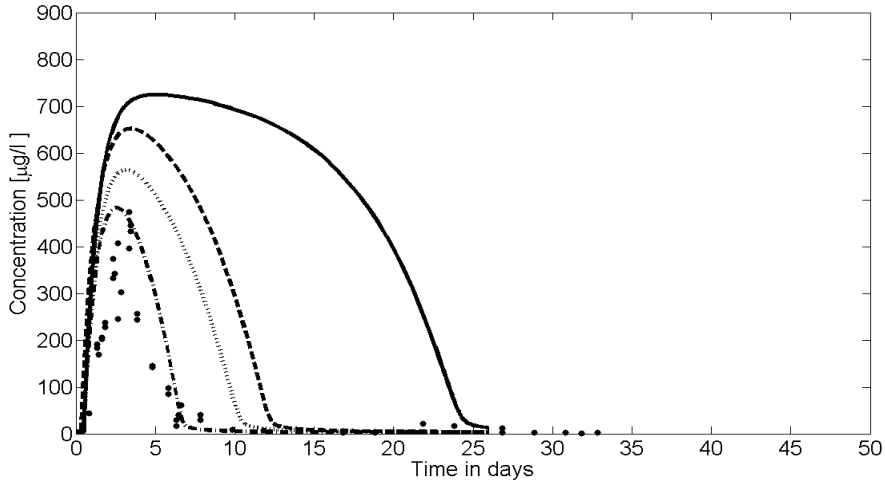

Figure 5.2 Evaluation of BPA model by simulating the *Dosage 2* experiment (from **Paper 7**). Dots: Measured effluent BPA concentrations. Solid line: No preceding BPA dosage. Temperature corrections according to $X_{B,H}$ of ASM1. Dashed line: Temperature corrections according to the heterotrophs ($X_{B,H}$) of ASM1. Dotted line: Temperature corrections according to the autotrophs ($X_{B,A}$) of ASM1. Dashed-dotted line: Fitted temperature corrections. For details, see **Paper 7**.

For application of the proposed model and parameter estimates to natural wastewater environments, with low BPA concentrations, the results must be extrapolated. It should then be considered that the BPA concentrations during the dosage experiment were significantly higher than during normal WWTP operation and that some parameter values have been assumed fixed in the calibration.

6 Uncertainty-based calibration of the accumulation-washout model

In this chapter it is discussed how experimental data (rain intensities, stormwater flow and concentrations) from a sampling campaign are used together with a model (the SEWSYS model, Section 4.3.2) to estimate the uncertainty related with model predictions of stormwater pollutant loads. The chapter is based on **Papers 2**, **3** and **4**.

6.1 Description of experimental data

For the total period of the sampling campaign (five weeks), there are continuous (1-minute resolution) measurements of the stormwater flow, y_Q [$L^3 \cdot T^{-1}$], at the catchment outlet as well as (1-minute resolution) rain intensity measurements. The rain intensity measurements had been averaged to 5-minute resolution data before they were used as a model input in this thesis. For 13 of the in total 18 identified rain events, 57 flow proportional samples were collected during the sampling intervals t_k, k=1,2,...,57, having typical durations of 20-80 minutes. The samples were analysed for Zn, Cu, Pb and Cd concentrations. These measurements are denoted $y_{C,k}$ [$M \cdot L^{-3}$]. In Figure 6.1 the characteristics and notation of the available experimental data for event #3 are shown. The coloured areas in the upper panel (light and dark grey) represent the, for this event, 14 sampled stormwater volumes. The entire event was not sampled, which is seen as the non-coloured area during the last hour of the event. In the following the event volumes are therefore sometimes referred to as the "partial" sampled event volume etc.

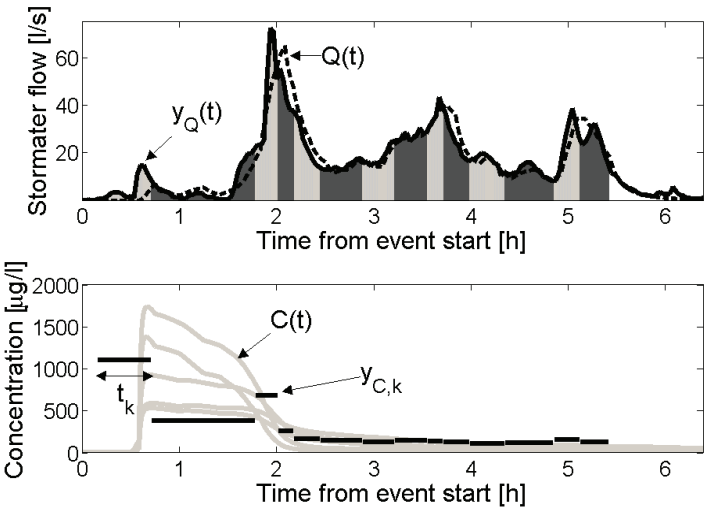

Figure 6.1. Available data and main model outputs exemplified for event #3. *Upper panel*: Recorded stormwater flow (y_Q, solid line), sampled stormwater volumes (light and dark grey coloured areas) and simulated stormwater flow (Q, dashed line). *Lower panel*: 5 simulations of the stormwater concentration (C, grey lines) for various values of parameters θ and flow proportional concentration measurements collected during the time periods t_k (y_C, horizontal lines). From **Paper 4**.

Table 6.1 shows a summary of the experimental results for each of the j =1,2,...,18 events. Furthest to the left the event id:s with associated number of sub-samples in parenthesis are shown. The event durations (t_j) and volumes (V_j), including the percentage of actually sampled volumes in parenthesis, are listed to the right. The antecedent dry weather periods (t_{dry}) and maximum rain intensities with a 5-minute resolution (P_5) for each event are given as well. The event mean concentrations (*EMC*s) shown furthest to the right have been calculated as flow-weighted averages of the concentration measurements within each event. Because the entire events were not sampled, they represent "partial" event mean concentrations. At the bottom, the observed "partial" site mean concentrations (*SMC*s) are shown. These have been calculated as flow weighted averages of all 57 samples.

Table 6.1. A summary of the experimental data on an event-basis. See the text and Ahlman (2006) for details. *The shown EMCs have been estimated based on partly sampled event volumes. From **Paper 4**.

Event j		t_j [h]	V_j [m^3]		t_{dry} [d]	P_5 [mm·h^{-1}]	*EMC** [µg·l^{-1}]			
							Zn	*Cu*	*Pb*	*Cd*
1	(-)	13.1	145	(-)	-	2.5	-	-	-	-
2	(-)	2.6	11	(-)	1.1	0.8	-	-	-	-
3	(*14*)	6.4	351	(*96%*)	0.6	8.2	343	254	23.4	0.40
4	(*3*)	7.5	108	(*88%*)	0.3	4.1	370	258	16.0	0.43
5	(-)	6.7	30	(-)	0.8	0.8	-	-	-	-
6	(*6*)	3.1	159	(*85%*)	0.2	4.1	292	181	9.9	0.33
7	(*2*)	1.1	35	(*77%*)	0.4	3.3	288	219	10.5	0.28
8	(*1*)	3.5	58	(*81%*)	6.9	9.9	752	887	103.2	1.01
9	(*1*)	2.5	28	(*72%*)	0.6	3.3	1050	600	35.5	1.72
10	(*1*)	1.5	40	(*61%*)	2.8	5.8	951	736	44.4	1.66
11	(*3*)	3.0	85	(*86%*)	2.2	6.6	798	334	23.2	1.01
12	(*3*)	3.4	72	(*94%*)	1.7	2.5	619	344	11.3	0.67
13	(*2*)	1.3	21	(*83%*)	3.6	1.6	1436	632	17.1	1.71
14	(*8*)	7.9	195	(*85%*)	4.4	4.1	688	345	18.3	0.85
15	(*2*)	2.3	40	(*82%*)	0.6	3.3	428	233	8.8	0.82
16	(*11*)	14.9	420	(*55%*)	1.4	4.1	294	169	4.9	0.37
17	(-)	4.4	75	(-)	1.3	1.6	-	-	-	-
18	(-)	15.7	295	(-)	0.4	3.3	-	-	-	-
						SMC*	**470**	**295**	**19.5**	**0.59**

6.2 Model reformulation and preparation for uncertainty analysis

To facilitate the calibration and uncertainty analysis of SEWSYS the original model (cf. section 4.3.2) was slightly reformulated and simplified. The two main assumptions, which are done in both **Papers 2**,**3** and **4** are summarised below and further motivated in **Paper 4**.

1. After calibration against the observed stormwater event volumes, the hydrological parameters K, ϕ and $LOSS$ were kept fixed. The pollutant concentrations of the pure rain water (C_{rain}) were assumed fixed as well.

The basic assumption here is that for pollutant load modelling the accumulation-washout process is significantly more uncertain than the rainfall-runoff process. Results of a sensitivity analysis also showed that simulation of the SMC is not sensitive to the hydrological sub-model. With the calibrated parameters (K=0.4, ϕ=0.62 and $LOSS$=0.36 mm) the hydrological model moreover simulate the observed event volumes well.

2. No attempts to model the origins of the four heavy metals were done. The various surfaces (roofs, roads, etc) of SEWSYS were combined to one total impervious area A_{tot} and the included emission factors were lumped into one dry deposition load parameter θ_1 [$M \cdot T^{-1} \cdot L^{-2}$] representing several sources of pollution (e.g. traffic activities and surface corrosion), depositing pollutants uniformly on A_{tot}.

The motivation for this simplification is that the model assumes uniform rainfall and no spatial dimensions, and because samples were collected at the catchment outlet only. The emission factors can thus not be identified from the results of the sampling campaign. The model reformulation is an action aimed at reducing the problem of equifinality, a concept which was introduced in Section 2.3.4. Various sets of e.g. "the emission factor for Cu surface corrosion" and "the emission factor for Cu in brake wear" give identical Cu loads in the catchment outlet.

An important outcome of the reformulation and simplification is that the dry deposition load θ_1, the rate coefficient for pollutant dry removal (θ_2) and finally the rate constant for wet removal by wash-off (θ_3) alone are used to describe the uncertainty related with pollutant load modelling. In the sequel of the chapter, θ refers to the random accumulation-washout parameter vector $\theta=(\theta_1\ \theta_2\ \theta_3)$ of Equations 4.14 and 4.16; all other model parameters and input data are considered to be fixed.

6.3 Specification of the prior parameter distribution

For now it is sufficient to note that uniform uncorrelated prior parameter distributions have consistently been used for θ_1, θ_2 and θ_3. This is the common choice in the case of limited prior knowledge. The upper and lower limits (the ranges) for the distributions vary slightly between **Papers 2**, **3** and **4**. This reflects that the prior used in **Paper 3** unavoidably is affected by the results of **Paper 2** and that, in the same manner, the prior of **Paper 4** depends on the results from both **Paper 2** and **Paper 3**. The applied prior ranges are motivated in the running text below and are finally summarised in Table 6.2.

6.4 Specification of the likelihood function

To specify the likelihood function two questions have been considered. The first is related to how to compare the "goodness" of various parameter sets e.g. how to grade simulations $m(\theta)$ as compared to experimental data y. The second question is related to

the information content of the available observed data and to what model output variable that should be evaluated.

6.4.1 Structure of the likelihood function

While the chosen "flat" structure of the prior parameter distribution is quite obvious, there are numerous available likelihood functions proposed in literature (see Beven and Freer, 2001) and the choice is subjective. Often the model errors are assumed to be independent and normally distributed. This was done in Kanso *et al*. (2005) where suspended solid concentrations in stormwater runoff with a model similar to the one presented here were studied. In Freni *et al*. (2008) the (also frequently applied) Nash and Sutcliffe efficiency criterion was used to analyse the model predictive uncertainty of maximum peak flow, flow volume, maximum peak BOD concentration, BOD load and maximum oxygen depletion in a down-stream river cross-section. It has been shown (perhaps not surprisingly) in the literature that the selection of likelihood function influence the results of the uncertainty analysis. Some of the proposed likelihood measures do not let the modeller control the extent with which the observations are covered by the simulations, an issue treated systematically in this thesis as explained in section 2.3.4. However, the choice is only one of several subjective choices that have to be made and in this thesis the following likelihood function has consistently been applied:

$$L(y \mid \theta) = \exp\{-SSE(\theta, y)/T\} \tag{6.1}$$

Here, exp denotes the exponential function and *SSE* is the sum of squared errors, as defined in Equation 2.4. The parameter set minimising the sum of squared errors is given the highest likelihood while the decrease in likelihood due to larger errors will depend on the value of the scaling factor *T*. This is further discussed in Section 6.5.1.

6.4.2 Model output variables

The experiments were designed to provide information about the pollution load and the available concentration measurements $y_{C,k}$ do not say anything about the pollutant behaviour within the sample periods, thus they cannot directly be compared with the continuous simulation $C(t)$ of Equation 4.16. The basic model output variable of interest for all three papers of FA2 is the 57 simulated individual intra-event sample masses $m_{M,k}$ [M]:

$$m_{M,k} = \int_{t_k} C(t) \cdot Q(t)\, dt \tag{6.2}$$

which are to be compared with the corresponding observed intra-event sample mass $y_{M,k}$ [M]:

$$y_{M,k} = y_{C,k} \cdot \int_{t_k} y_Q\, dt \tag{6.3}$$

The sample masses were combined in various ways in the three papers. This is shown and motivated below.

In **Paper 2**, the model was calibrated by inserting the observed individual sample masses $y_{M,k}$ [M] in the objective function:

$$SSE(\theta, y) = \sum_{k=1}^{57} \left(y_{M,k} - m_{M,k} \right)^2 \tag{6.4}$$

In **Paper 3**, the cumulative sum of the observed masses was instead used:

$$SSE(\theta, y) = \sum_{k=1}^{57} \left(\sum_{w=1}^{k} \left(y_{M,w} - m_{M,w} \right) \right)^2 \tag{6.5}$$

In **Paper 4**, the masses were evaluated on an event basis.

$$SSE(\theta, y) = \sum_{\substack{j=3,4,\\ 6,..,16}} \left(\sum_{\substack{\text{All } k \\ \in \text{Event } j}} y_{M,k} - \sum_{\substack{\text{All } k \\ \in \text{Event } j}} m_{M,k} \right)^2 \tag{6.6}$$

From Equation 6.2 it is clear that the prediction of these sampled intra-event volumes have an impact on the prediction of the sampled mass. As the hydrological model parameters are kept fixed the predicted intra-event volumes depend only on the time series input data, i.e. the effective rain. This data is also fixed within each study but differ slightly in **Papers 2**, **3** and **4**. In **Papers 2** and **3** the effective rain data were obtained from calibration of a continuous time initial loss model proposed by Vezzaro (2006). In **Paper 4**, the following (default in SEWSYS) relationship between rainfall and runoff was used to estimate the hydrological parameters *LOSS* and ϕ :

$$RUNOFF_j = \phi \cdot \left(RAIN_j - LOSS \right), \qquad \left(RAIN_j - LOSS \right) \geq 0 \tag{6.7}$$

where $RUNOFF_j$ denotes the measured stormwater runoff volume [L] for event j and $RAIN_j$ [L] the corresponding rain volume. Both time series provides good estimates of the total stormwater event volumes. However, the one of **Paper 4** (see Figure 5 in this paper) shows quite bad performance considering prediction of the sampled intra-event volumes. This is the main reason for why in **Paper 4**, the 13 partial event masses are considered in the likelihood function whereas in **Paper 2**, the analysed model outputs are the 57 individually sampled copper masses.

Consider for example the first sample of event #3 (Figure 6.1, upper panel). The observed sample volume is 10 m^3 and the measured concentration of Zn in the sample is 1100 $\mu g \cdot l^{-1}$, which corresponds to a mass of 11 g Zn in the runoff. Although the

hydrological model simulates the total event volume well (351 m^3), the predicted volume of the considered individual sample is far too low (1.4 m^3). This involves that, to predict the observed mass, the three accumulation-washout parameters must be chosen to give an average concentration of around 8 $mg \cdot l^{-1}$, i.e. a significantly higher concentration compared to the measured one. The consequence of such a procedure is that the uncertainty in predicting the hydrograph is projected on the accumulation-washout parameters. The main reason for calibrating against the sampled event masses in **Paper 4**, is to reduce this type of effect.

In **Paper 3**, the cumulative sum of the sampled masses is studied. The reason for this "inconsistency" lies in the framework of the CTSM parameter estimation tool where you by default calibrate against a discrete "grab sample" and not a discrete "time-averaged sample".

6.5 Application

The stormwater flow and loads of copper were simulated in all three papers, whereas in **Paper 4** the loads of zinc, lead and cadmium were simulated as well.

With the chosen uniform prior distribution and structure of the likelihood function (Equation 6.1), Equation 2.7 states the following for the posterior parameter distribution:

$$g(\theta \mid y) \propto \exp\{-SSE(\theta, y)/T\} \tag{6.8}$$

This resulting expression of the model parameter uncertainty has previously been used by Mailhot *et al*. (1997) to investigate the uncertainty related to stormwater quality model calibration (using artificial data).

Two different methods for approximating the posterior parameter distribution are used in the thesis: importance sampling and the metropolis algorithm. In **Paper 2** and **3** importance sampling (e.g. Robert and Casella, 2004) was used. In **Paper 4** the metropolis algorithm (Metropolis, 1953) was used. In **Paper 2** a specific metropolis algorithm named SCEM-UA (Vrugt *et al*., 2003), was applied and compared with the importance sampling methodology. A description of the theories behind these is behind the scope of this summary. Importance sampling is briefly introduced in **Paper 2** while the basic ideas of the metropolis algorithm are given in **Paper 4**. For more dense descriptions one can refer to statistical literature such as Robert and Casella (2004) and Tanner (1996). Although a few comments are made below, the idea of this thesis has not been to grade the two methods against each other. They are simply two alternative simulation-based ways of coping with Equations 2.8 and 2.9.

6.5.1 Deciding when the uncertainty is adequately described

The parameter T in Equation 6.8 can be seen as a scaling factor whose value depends upon the confidence the modeller has on measurements compared to the model. A small

value of T will result in narrow posterior distribution prediction bounds while a larger value will widen the posterior and the uncertainty bounds. To exemplify this, consider the following Metropolis algorithm iteration (as it is implemented in **Paper 4**):

You have drawn a parameter set $\theta^{(1)}$ and propose a second set $\theta^{(*)} = \theta^{(1)} + \varepsilon$, where ε is a normally distributed (symmetric) multivariate with mean 0 and spread defined by the covariance matrix $\sum$ and a scaling factor s, $\varepsilon \sim N(0, s \cdot \sum)$. The proposal is accepted with the acceptance probability α:

$$\alpha\left(\theta^{(1)}, \theta^{(*)}\right) = \max\left(1, \frac{g\left(\theta^{(*)} \mid y\right)}{g\left(\theta^{(1)} \mid y\right)} = \frac{L\left(y \mid \theta^{(*)}\right) \cdot \pi\left(\theta^{(*)}\right)}{L\left(y \mid \theta^{(1)}\right) \cdot \pi\left(\theta^{(1)}\right)} = \frac{\exp\left\{-SSE\left(\theta^{(*)} / T\right)\right\}}{\exp\left\{-SSE\left(\theta^{(1)} / T\right)\right\}}\right) \quad (6.9)$$

If $SSE\left(\theta^{(*)}\right) < SSE\left(\theta^{(1)}\right)$ the acceptance probability is 1, e.g. moves to areas with higher posterior probability is always accepted. Now assume the example illustrated in Figure 6.2 where the first parameter set gives a "good" simulation with $SSE\left(\theta^{(1)}\right)$ = 75 and that the proposed set is not as good and yields $SSE\left(\theta^{(*)}\right)$ = 275. If the two sets are evaluated with T=100, the acceptance probability is 0.06/0.47=0.14 (solid arrows) whereas if T=300 is applied, we accept the proposal with probability 0.40/0.78=0.51 (dashed arrows). Thus, by changing the value of T you "choose" to what degree "bad" simulations will be accepted.

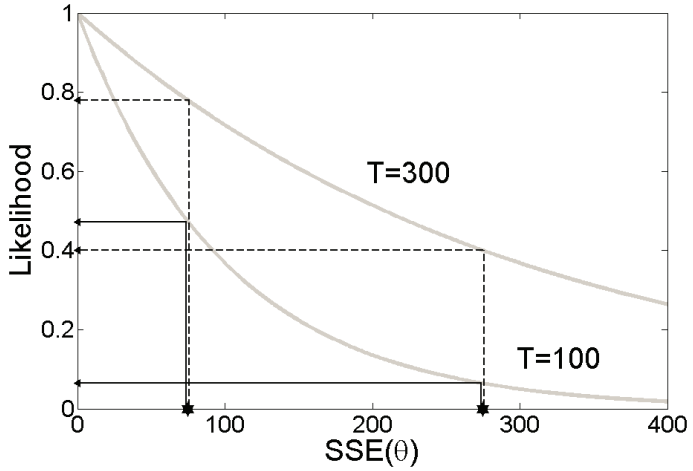

Figure 6.2. Illustration of the metropolis algorithm and the function of the scaling factor T. With T=100, the move $\theta^{(1)} \rightarrow \theta^{(*)}$ is accepted with probability 0.06/0.47=0.14 whereas with T=300 the acceptance probability is 0.40/0.78=0.67 cf. Equation 6.9. From **Paper 4**.

In all following applications, a small value of T was initially selected. This was then increased until a significant number of the observations were covered by the 95% empirical prediction quantiles.

6.6 Results

Figure 6.3 shows the resulting modelled empirical prediction quantiles of the observed Cu masses while using the individually sampled masses in the likelihood function. Among the 57 measurements, 6 (encircled) are not within the 95% quantiles.

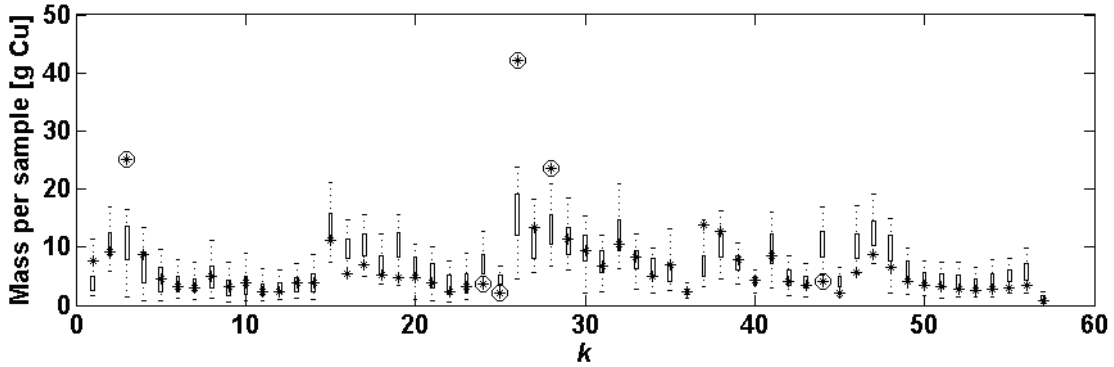

Figure 6.3. Measurements (stars) and model predictions (95 and 50% quantiles) of the intra-event sampled Cu masses. From **Paper 2**.

The empirical 50% and 95% quantiles were constructed as described in Section 2.3.4 with draws from the posterior, as illustrated in Figure 6.4. The structure of the model (Equation 4.14) implies that the ratio between the dry deposition rate (θ_1) and dry removal rate (θ_2), e.g. the horizontal axis, determines the maximum mass of pollutants that theoretically can accumulate on the surface during dry weather. The time required to achieve this equilibrium is given by the inverse of θ_2. The value of the wet removal rate (θ_3) on the vertical axis determines the rate at which the accumulated pollutants are depleted during wet weather.

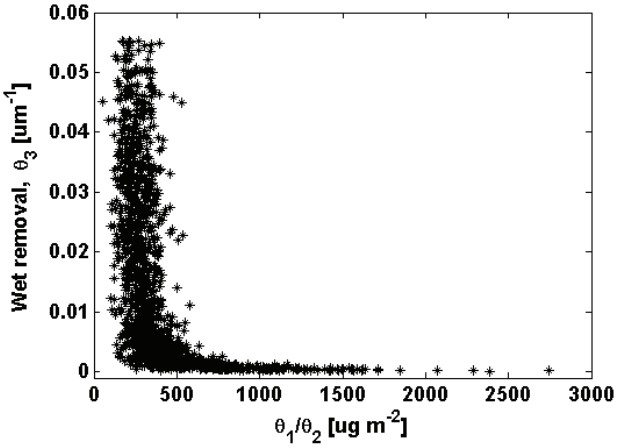

Figure 6.4. Draws from the posterior distribution used to construct the quantiles in Figure 6.3. From **Paper 2**.

As shown in Table 6.2 wide prior parameter distributions were assumed in **Paper 2**. The investigated time constants for the pollutant build up process are 1.8-18 hours. The relatively short time required to reach equilibrium, imposed by the a priori selected high values of the lower limit for θ_2 (1.3 d^{-1}) involves that the "pool of pollutant mass" on the surface at the end of a dry period will be in the same order of magnitude as $\theta_1/\ \theta_2$. As this mass is lowered, the model output is no longer sensitive to increasing values of the wet removal rate. In other words, as shown in Figure 6.4, conditionally on $\theta_1/\ \theta_2 < 400$ μg $Cu \cdot m^{-2}$, changing the value of θ_3 between 0.002 and 0.055 μm^{-1} does not have a large effect on the likelihood, all pollutants are washed off anyway.

From the study one can conclude that to simulate and bracket the observations, a wide range of parameter sets should be considered. The results also show that the applied upper limit in the prior for θ_1 (86 400 μg $Cu \cdot d^{-1} \cdot m^{-2}$) was unnecessarily high. In Figure 6.6 it is seen that posterior draws of θ_1 larger than 10 000 μg $Cu \cdot d^{-1} \cdot m^{-2}$ are not common. For the importance sampling methodology, which starts out with a large random sample from the prior distribution, this means that many unnecessary model runs with low likelihoods are conducted. If the metropolis algorithm is used this is in principle not a problem (compare **Paper 4**, where an open prior is used for θ_1) because it samples the parameter space according to the likelihood power.

Note that the posterior parameter distribution reflects the joint parameter probability, e.g. the probability of a parameter set. The conclusion above, that the upper limit of θ_1 was unnecessarily high, is conditional on the ranges for the other parameters. Figure 6.6 establishes a positive correlation between the dry deposition and dry removal and thus if higher values of θ_2 had been allowed, higher values of θ_1 would have appeared in the posterior.

In **Paper 3** the ranges for the prior distributions were modified based on the results of **Paper 2**. The maximum values for θ_1 and θ_3 and the minimum limit for θ_2 were significantly lowered. The resulting prediction quantiles (Figure 6.5) of the uncertainty-based calibration remained the same but less effort was spent on sampling "not relevant" parameters. The prediction quantiles obtained with the grey-box model (Figure 6.5) give rise to a lower uncertainty for prediction of total sampled mass (the 95% prediction bounds are ±30% of the mean for the grey box model compared to ±50% for the uncertainty-based model calibration methodology).

This difference is perhaps not surprising, since the two methods are based on different models. In the way the uncertainty-based model calibration has been applied the method cannot always handle errors in inputs. E.g. if there is no rain, the deterministic model will not simulate a load, no matter the values of the parameters. The grey-box model on the other hand can handle this by either of the two additional stochastic terms.

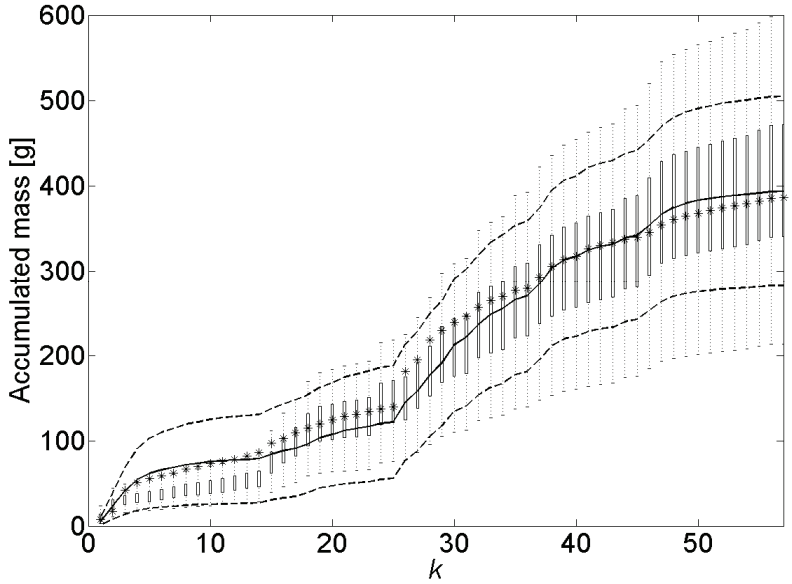

Figure 6.5. Predictions of the accumulated sampled copper loads with uncertainty-based calibration (quantiles) and grey-box modelling. From **Paper 3**.

The maximum likelihood estimates of the grey-box model parameters showed that the noise term σ of the differential equation was significant compared to the residual variance, i.e. the deviation between measured and simulated data cannot be solely explained by measurement errors.

In **Paper 4** the ranges for θ_3 were furthered narrowed. They were established by arguing that the time constant for pollutant depletion due to a (hypothetical, rectangular) rain with moderate-high intensity (2 $\mu m \cdot s^{-1}$) should not be smaller than 8 minutes whereas for a lower rain intensity of (0.2 $\mu m \cdot s^{-1}$) it should not be longer than 1 day. Table 6.1 shows that the length of the dry weather periods for the sampling campaign were 0.2-6.9 days. The ranges for θ_2 was established by assuming that the time constant for establishing pollutant equilibrium during dry weather ranges between 10 hours and 10 days. A faster pollutant build up would mean that we move towards a different model structure where the equilibrium is obtained instantaneously. A slower build up rate would be possible but since the available experimental data is limited the above-mentioned upper limit was chosen. With the new restrictions on the rate parameters it was possible to have an open uniform prior for the dry deposition parameter.

Table 6.2. The prior ranges used in **Papers 2, 3** and **4** for Cu.

	$\boldsymbol{\theta}_{1,Cu}$ [$\mu g \cdot d^{-1} \cdot m^{-2}$]		$\boldsymbol{\theta}_2$ [d^{-1}]		$\boldsymbol{\theta}_3$ [mm^{-1}]	
	min	*max*	*min*	*max*	*min*	*max*
Paper 2	0.0	86400	1.3	13.0	0.00	56
Paper 3	86.4	8640	0.0	13.0	0.00	10
Paper 4	0.0	∞	0.1	2.5	0.05	2

In Figure 6.6 draws of the dry removal versus the dry deposition rate posterior parameter distributions from **Paper 2** (circles) and **Paper 4** (stars) are shown. Although the model was calibrated against all sampled masses in **Paper 2** and the partial event masses in **Paper 4,** the results show that it is possible to cover the experimental observations with both a large and a smaller parameter space. The reason is obviously the strong correlation between the model parameters, especially θ_1 and θ_2.

The parameter distributions resulting from the presented methodology should not be interpreted as "all parameter sets must be considered to bracket the observations" but rather that "if we want to bracket the observations *and given wide ranges of parameters with the same prior probability*, we might find equally good parameter sets in a very big parameter space.

Figure 6.7 shows the 13 simulated and partially observed EMCs that were included in the uncertainty based calibration as well as simulated EMCs for the 5 events for which concentrations were not measured. If the only available information is the model, input data and experimental observations the inherent presumption for the 5 events lacking experimental evidence is that the system will behave similarly here as in calibration. This is an important underlying presumption of the methodology; the only thing that is 100% sure is that with the applied model, input data and calibrated parameter, outputs that with 95% probability is consistent with the experimental evidence are generated.

The histograms of the SMCs, simulated with the posterior parameter distribution derived in **Paper 4**, are shown in Figure 6.8 together with the "partially" observed SMCs of the sampling campaign. The 95% prediction quantiles for the SMCs are in this case these observed values ±20%, ±40%, ±80% and ±35% for Zn, Cu, Pb and Cd, respectively. The uncertainty for Cu (±40%) is slightly lower than in **Paper 2** where the total sampled copper mass is predicted with a ±50% uncertainty. One reason for this is that in **Paper 2**, the model outputs were forced to cover the individual sample masses.

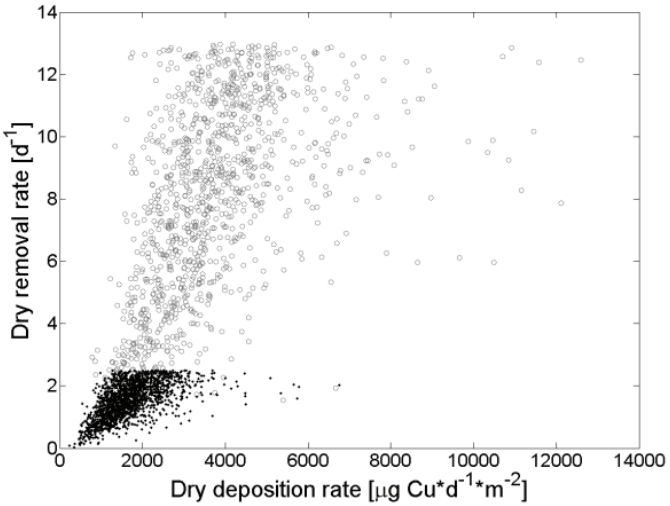

Fig 6.6. Draws from the posterior distribution from **Paper 2** (grey circles) and **Paper 4** (black dots).

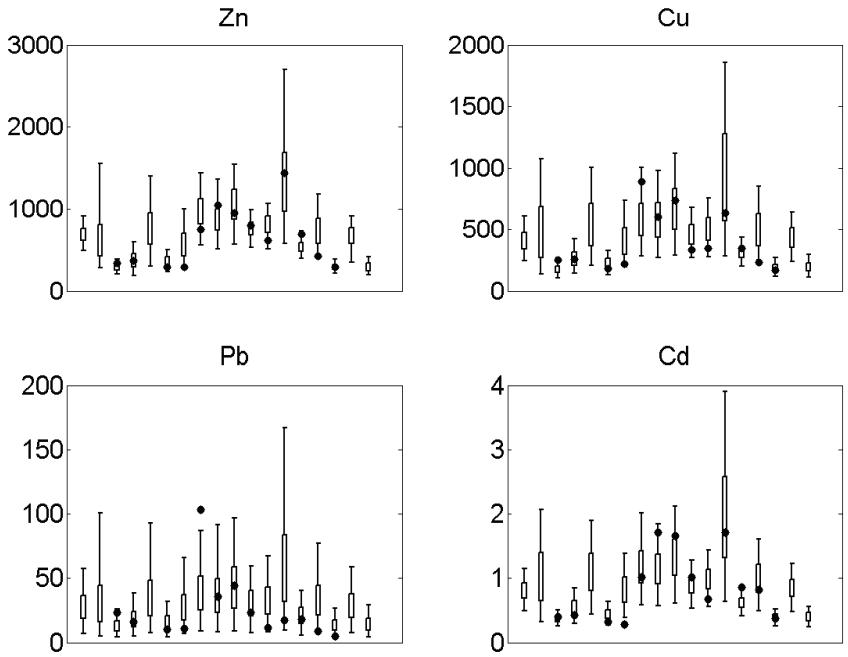

Figure 6.7. Simulated and "partially" observed EMCs [µg/l]. From **Paper 4**.

The uncertainties anticipated in Figure 6.8 are conditional on the experimental results and the concentration measurements are fairly high compared to other studies with mixed land use (see **Paper 4** for references), e.g. reality includes a site-to-site variation that is not considered in this study. Uncertainty in predicting pollutant loads from urban catchments without experimental data is therefore higher than the stated numbers.

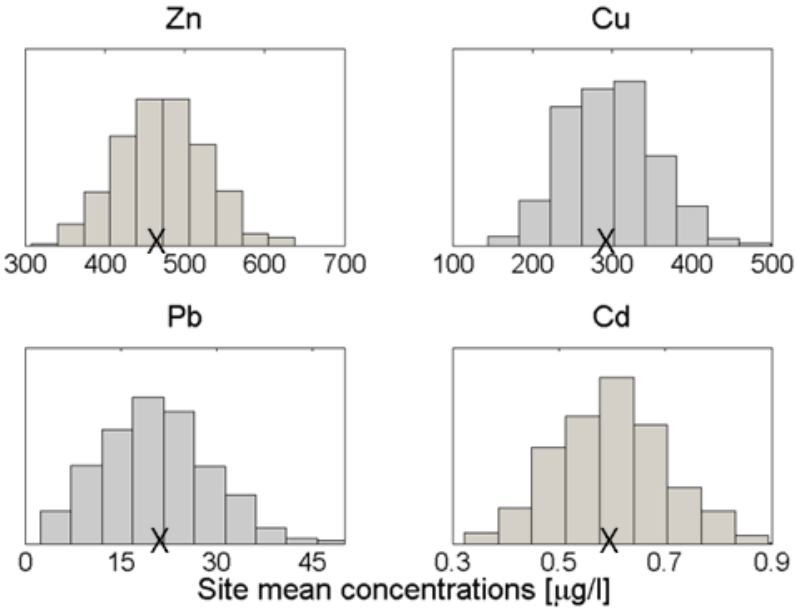

Figure 6.8. Histograms of the site mean concentrations for the four compounds with results of the measurement campaign indicated with crosses. From **Paper 4**.

7 Conclusions

In focus area 1 a dynamic mathematical model for the fate and transport of micropollutants in a simplified representation (few compartments) of the integrated urban wastewater system was formulated, implemented and used. The results of the conducted simulation study show the capability of the model to elucidate the following complex phenomena of importance to the fate of two xenobiotic organic compounds (XOCs), the wastewater pollutant bisphenol-A and the stormwater pollutant pyrene:

- Increased micropollutant loading on the downstream system during rain events due to re-suspension of wastewater pollutants accumulated by settling of particulate material in the sewer.
- Transient combined wastewater concentration profiles caused by such "first-flushes".
- The dependency of the dynamics of the pollutant mass routing process and the location of CSO structures in the system on the spatial distribution of overflow pollutant loads.
- The effect of both primary and secondary sludge production on the fate pathways of micropollutants in WWTPs.
- The effect of operational WWTP conditions (e.g. sludge age and hydraulic retention time) on the XOC removal capacity.
- The highly variable time constants of the integrated system.

Thereby, it can be concluded that lumped, conceptual, deterministic and dynamic models can be used to realistically simulate part of the fate-processes that affect micropollutants in the integrated urban wastewater system. The models do not need to include detailed hydraulic equations and can be formulated and implemented by extending well-established mathematical descriptions of the physical, chemical and biological processes that occur in the system.

While in focus area 1 the capability of the mentioned model types to elucidate various phenomena was established, methodologies to analyse the prediction uncertainty of the model outputs was highlighted in focus area 2. For the specific case of a conceptual stormwater surface accumulation-washout model and a relatively detailed measurement campaign the following conclusions can be drawn:

- The experimental observations do not contain information to calibrate various correlated source parameters of the original model, which therefore was re-formulated to yield a simpler structure involving fewer parameters.
- Wide posterior parameter distributions need to be considered to encompass a large share of the measurements with Monte Carlo simulations. The reason for this is uncertainties in input (rain) data, model structure and measurements of water quality

as well as correlation between model parameters, especially the dry deposition load and dry removal rate.

- Two ways of approximating the posterior model parameter distribution, a Markov Chain Monte Carlo algorithm and Importance Sampling, were applied and gave nearly identical distributions of the modelled outputs.
- With the uncertainty-based calibration methodology the total sampled mass of Zinc, Copper, Lead and Cadmium can be predicted with an uncertainty of approximately ±20%, ±40%, ±80% and ±35%, respectively. The results depend on the defined threshold value where the uncertainty is judged to be sufficiently described.
- By adding a stochastic noise terms to the deterministic model, the grey-box analysis show a prediction uncertainty of less than ± 30% for Copper.
- Even when conditioning dynamic stormwater quality models on on-site concentration data, relatively large uncertainties should still be acknowledged in connection with posting statements about heavy metal loads in stormwater.

In focus area 3 it is shown that BPA is degraded under strictly aerobic conditions and that biodegradation is the dominant part of the BPA removal. Experimental step-response data have been compared with a growth-based process model to conclude the following:

- Processes in the fast dynamic region, such as sorption and volatilisation, are not dominant for the fate of BPA. Instead, the data establish the presence and growth of BPA-degrading biomass.
- Although a simple biodegradation model is hypothesised, a number of parameters have to be kept fixed at values inspired by literature. Several other more complex biological degradation models are possible as well, but data does not contain enough information to establish those model structures.
- A tailor-made parameter estimation method was developed, which simultaneously utilizes steady state background concentrations and dynamic step response data, as well as conceptual simplifications of the plant configuration combined with both guided parameter value selection and numerical parameter estimation.
- After calibration the hypothesised BPA growth model showed a reasonable fit to the experimental data. The maximum specific growth rate for BPA degrading bacteria was estimated to be 0.47 d^{-1}, which means that an aerobic sludge retention time above 13 d is required to support growth.
- Validation results showed that biodegradation of BPA is sensitive to operational conditions before and during the experiment and that the proposed model structure is capable of capturing important characteristics of the observed BPA removal process.

8 Suggestions for future work

Unfortunate for any object sensitive to micropollutant exposure in urban society, but fortunate for urban water researchers all over the world, there's work left to do! Here are a few suggestions for future work that crossed my mind during the past years:

- Simulate the fate and behaviour of more pollutants (as a suggestion the EU water framework directive priority pollutants) in the integrated urban wastewater system to increase the understanding of their fate patterns. Volatilisation and stripping processes must be implemented in to the integrated model to study more types of micropollutants.

- Simulate more realistic and comprehensive long-term scenarios. Such scenarios could be used to e.g. study the efficiency of various BMP:s and treatment options towards reducing emissions from the integrated urban wastewater system. The applied uncertainty-based model calibration methodology generates results that easily can be used in more long-term predictions.

- To get more applicable insight in the behaviour of the specialised BPA degrading biomass in the Lynetten treatment plants further experiments at lower, more realistic BPA concentrations must be conducted.

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APPENDICES

7 papers, among which 5 have been published and 2 are submitted to international peer reviewed journals with ISI ranking, are enclosed as appendices to the printed version of thesis. The papers are however not included in the www-version. Copies of the papers may be obtained from the Library at the Department of Environmental Engineering, Technical University of Denmark (library@env.dtu.dk).

Paper 1: **Lindblom**, **E**., Gernaey, K.V., Henze, M. and Mikkelsen, P.S. (2006). Integrated modelling of two xenobiotic organic compounds. *Water Sci. Technol*., **54**(6-7), 213-221.

Paper 2: **Lindblom**, **E**., Ahlman, S. and Mikkelsen P.S. (2007). How uncertain is model-based prediction of copper loads in stormwater runoff? *Water Sci. Technol.,* **56**(11), 65-72.

Paper 3: **Lindblom**, **E**., Madsen, H. and Mikkelsen, P.S. (2007). Comparative uncertainty analysis of copper loads in stormwater systems using GLUE and grey-box modeling. *Water Sci. Technol*., **56**(6), 11–18.

Paper 4: **Lindblom**, **E**., Ahlman, S. and Mikkelsen P.S. (2008). Uncertainty-based calibration of a stormwater surface accumulation-washout model using sampled Zn, Cu, Pb and Cd field data. *Submitted.*

Paper 5: Press-Kristensen, K., **Lindblom**, **E**., Schmidt, J.E. and Henze, M. (2008). Examining the biodegradation of endocrine disrupting bisphenol A and nonylphenol in WWTPs. *Water Sci. Technol*., **57**(8), 1253-1256.

Paper 6: Press-Kristensen, K. **Lindblom**, **E**. and Henze, M. (2007). Modelling as a tool when interpreting biodegradation of micro pollutants in activated sludge systems. *Water Sci. Technol*., **56**(11), 11-16.

Paper 7: **Lindblom**, **E**., Press-Kristensen, K., Vanrolleghem, P.A., Mikkelsen, P.S. and Henze, M. (2008). Dynamic experiments with high bisphenol-A concentrations modelled with an ASM model extended to include a separate XOC degrading microorganism. *Submitted.*

The Department of Environmental Engineering (DTU Environment) conducts science-based engineering research within four themes:
Water Resource Engineering, Urban Water Engineering,
Residual Resource Engineering and Environmental Chemistry & Microbiology.
Each theme hosts two to five research groups.

The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

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