Ministry of Environment and Energy
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Fate Modelling Based on Measured Concentrations in Wastewater and Sludge

*NERI Technical Report No. 354*

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Fate Modelling Based on Measured Concentrations in Wastewater and Sludge

***NERI Technical Report No. 354***
***2001***

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# Data sheet


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Abstract: The steady-state compartment description of the biological reactors and settlers in wastewater treatment plants that is used in SimpleTreat has been evaluated with respect to an alternately operated WWTP situated in Roskilde, Denmark. The effect of substituting a complex discontinuous operation, involving alternating degradation and flow conditions between two reactors, with one single biological reactor with continuos flow (SimpleTreat) has been investigated by setting-up two models representing the respective operation schemes.
An experimental series was performed where inlet, outlet, primary sludge and secondary sludge samples were taken and analysed for phthalates, nonylphenols and LAS. Generally the modelled half-lives for the phthalates were low and the removal efficiencies of the nonylphenols and phthalates were high compared to literature values.
The results from the modelling work concludes that it is possible to substitute a complex alternating operation with a system containing one single biological reactor, corresponding to SimpleTreat, when a suggested empirical aggregate 1$^{st}$ order degradation rate is employed.



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|---|---|
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# Contents

# Summary


**General overview**
The present work comprises an emission survey of LAS, six different phthalates, nonylphenol and nonylphenol-diethoxylate and a model set-up of Roskilde wastewater treatment plant. They are a part of an investigation constituting the emission and fate of the substances in Roskilde municipality in a system comprising the wastewater treatment plant (WWTP), Roskilde Fjord and sludge amended fields.

The emission survey supplies input values to the sewer and WWTP which in turn defines the substance concentrations in the effluent water that is disposed to the Fjord (*Vikelsøe et al., 2000*) and the sludge that is stored on the field adjacent to the Fjord (*Sørensen et al., 2000*).

**Emission survey**
The result from the emission survey comprises annual mean inlet concentrations to Roskilde WWTP of LAS, total phthalates and nonylphenol ethoxylates derived from import/export data, manufacturers, previous investigations and estimates concerning the fate of the substances in the different environmental compartments.

$$C_{LAS} = 20 \pm 20 \ \frac{\text{mg LAS}}{\text{liter}}$$

$$C_{phthalates} = 150 \pm 128 \ \frac{\text{mg phthalates}}{\text{liter}}$$

$$C_{NPnE} = 2 \ \frac{\text{mg NPnE}}{\text{liter}}$$ (no deviation is stated due to insufficient data)

These figures are inserted in the WWTP model to estimate the sensitivity of the outlet concentrations towards variations in inlet and process parameters.

**Wastewater treatment plant**
In the EUSES risk assessment system for chemicals *(TGD, 1996)* the description of the processes in the wastewater treatment facility is central. The compartment description paradigm is used to calculate the partitioning between different phases in the wastewater treatment combined with an assumed first order degradation. As a part of EUSES the SimpleTreat model assumes continuos flow through the system where different reactors are connected in series.

However, in Denmark it is often the case that the sewage is not treated in a continuous process but rather in a discontinuous operation, where the redox potential changes discontinuously during alternation between aeration and no aeration respectively. Furthermore the outlet is taken from different reactors during time. Thus, it is not obviously true that the

continuous operation approach used in SimpleTreat is sufficient for risk assessment when alternating operation treatment facilities are considered. A central issue in this work is therefore to investigate the importance of the actual mode of operation (continuous/discontinuous) in order to identify the need for adjustments in SimpleTreat if the alternating operation needs to be covered by the conclusions from the model.

As a model plant Bjergmarken WWTP in Roskilde, Denmark, treating the waste water from 80,000 PE in an alternately operated BIO-DENIPHO activated sludge operation, is regarded. Furthermore, the model set-up for Bjergmarken WWTP is used to calculate a mass balance for 9 different substances, cf. Table **19**.

**Continuous vs. discontinuous model set-up**

The complex system functionalities associated with the WWTP are incorporated into 2 models of varying complexity according to the general modelling paradigm described in *Sørensen et al. (2000)*.

Model 1 comprises the alternating operation cycle and includes aerobic and anoxic degradation respectively, expressed through the corresponding pseudo 1$^{st}$ order degradation rates $k_{1N}$ and $k_{1D}$ respectively. Furthermore adsorption is described through the retention factor, $R = 1 + K_d \cdot X_B$, where $K_d$ is the partition coefficient and $X_B$ is the concentration of particulate matter.

In model 2 the biological treatment cycle is aggregated into one reactor with a continuous flow equal to the daily mean flow. Different from SimpleTreat model 1 and 2 do not include volatilisation, stripping, acid/base dissociation, temperature dependencies and diffusion in settled particulate matter thus reducing the uncertainties related to the large number of input variables. The consequence of the omitted processes have been discussed.

The reactor hydraulics of model 2 thus resembles SimpleTreat and the deviations between the more complex model 1 and model 2 are used to evaluate the uncertainties in using SimpleTreat in the simulation of an alternately operated WWTP.

The dissolved outlet concentration calculated in model 1 reveals the dynamic alterations in the plant. After a period of constant inlet concentrations and flow steady-state occurs and the outlet concentration curve fluctuates around a mean “cycle steady-state” value, cf. Figure **1**. The amplitude can be calculated from

$$\text{Amplitude} = 1.6 \cdot 10^{4} \cdot \frac{k_{1N}}{R} + 2 \cdot 10^{-2} \quad [\%] \qquad (\mathbf{1})$$

and reaches approximately 3% for a hydrophobic and easily degradable substance such as linear alkylbenzene sulfonate (LAS).

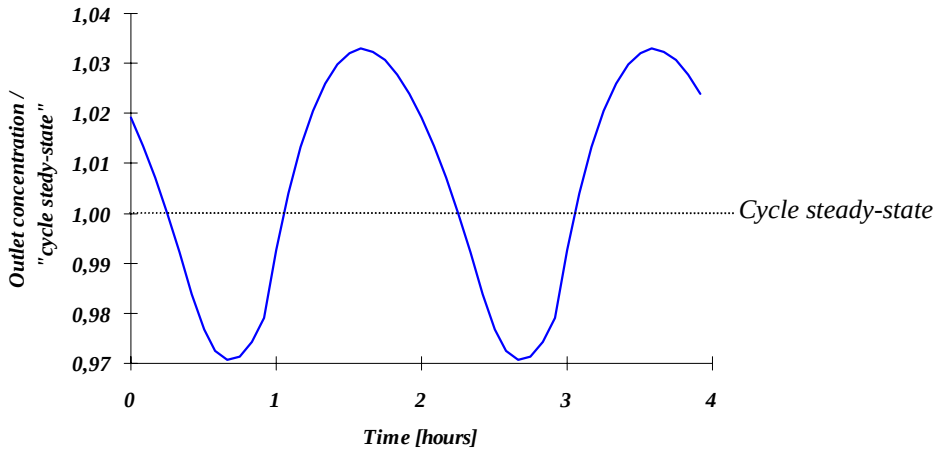



***Figure 1.*** *Calculated steady-state fluctuations of outlet concentration from Bjergmarken WWTP during one operation cycle (4 hours). Simulated with model 1.*

If the same process parameters are used in model 2 the deviation between the steady-state outlet concentration in model 2 and the mean "cycle steady-state" concentration in model 1 lies in the interval from 2 to 35%, with the largest values for easily degradable, hydrophilic substances.

A calibrated empirical 1st order degradation rate for model 2, $k_1$(model 2), can be calculated from

$$\frac{k_1(\text{model 2})}{R} = \frac{2279 \cdot \left(\frac{k_{1N}}{R}\right)^2 + 0.963 \cdot \left(\frac{k_{1N}}{R}\right)}{\left(0.275 \cdot \left(\frac{k_{1D}}{k_{1N}}\right)^2 - 0.822 \cdot \frac{k_{1D}}{k_{1N}} + 1.55\right)} \qquad \textbf{(2)}$$

If this value is inserted in model 2 (Equation **46**) the deviations are no more than 2% between the outlet concentrations in model 1 and 2. However, for substances with aerobic half lives longer than approximately 2 hours $k_1$(model 2) can be set equal to $k_{1N}$.

An integrated sensitivity analysis and 1st order uncertainty analysis approach concludes that the uncertainties related to the input parameters in model 2 results in uncertainties in the outlet concentrations that are much larger than the periodic fluctuations in model 1. Thus, the complex operation cycle in model 1 can be reduced to a single biological reactor, analogous to SimpleTreat, with continuous flow when the 1st order degradation rates, $k_{1N}$ and $k_{1D}$ are substituted with the empirical degradation rate in Equation **2**.

## Using model 2

An experimental series was performed during 8 days in May 1999. Each day one composite inlet sample and one outlet grab sample was collected from Bjergmarken WWTP. One grab sample from the primary sludge and one from the secondary sludge was collected.

The experimental concentrations are used to calibrate model 2 with respect to $K_d$ and $k_{1N}$ for the 9 investigated substances.

***Table 1.*** Calibration parameters based on model 2 and experimental data.

| | ***Mean aerobic half life*** $t_{½} = \frac{ln\ 2}{k_{1N} / R}$ ***[hours]*** | ***Mean partition coefficient*** $K_d$ ***[litre · kg$^{-1}$]*** |
|---|---|---|
| Linear alkylbenzene sulfonate, **LAS** | 1.3 | 2,760 |
| Di-(2ethylhexyl)-phthalate, **DEHP** | 21.6 | 13,060 |
| Dibutylphthalate, **DBP** | insufficient data | insufficient data |
| Dipentylphthalate, **DPP** | 19.0 | 2,570 |
| Benzylbutylphthalate, **BBP** | 79.1 | 3,530 |
| Di-(n-octyl)-phthalate, **DnOP** | 29.0 | 19,200 |
| Di-(n-nonyl)-phthalate **DnNP** | 32.8 | 28,600 |
| Nonylphenol **NP** | 7.2 | 2,080 |
| Nonylphenol-diethoxylate, **NPDE** | 6.3 | 3,640 |

In table **19** the results are presented. The calculated aerobic half lives are generally low for the phthalates compared to literature values, typically found for soil experiments, but it is important to notice that the experimental conditions are never coherent with the highly favourable conditions in the WWTP where the high concentration of micro-organisms are adapted to the prevailing conditions in terms of temperature, flow, substance concentrations etc.

The mean values in Table **1** and mean experimental inlet concentrations and flows are used in model 2 to calculate a mass balance for the investigated substances, i.e. the fraction of the influent mass that can be found in the outlet, degraded fraction, primary sludge and secondary sludge respectively. A further differentiation into dissolved and adsorbed fractions is performed.

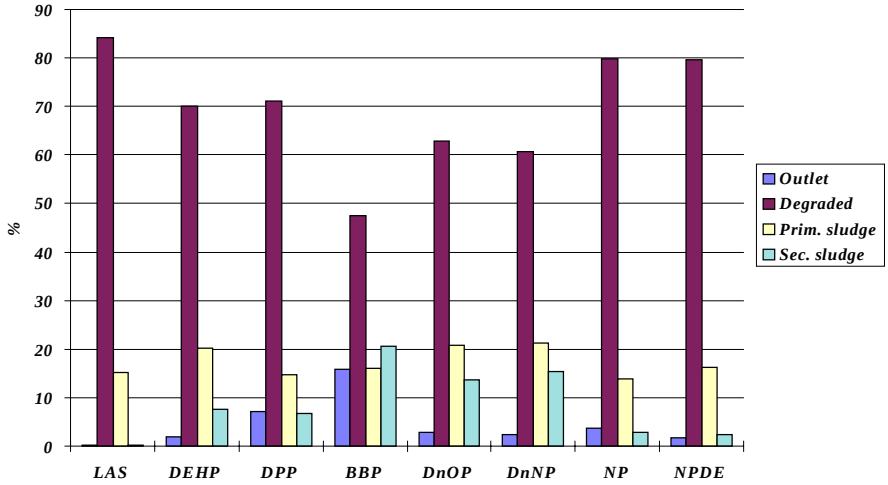



***Figure 2.*** *Fate of investigated substances in the alternately operated WWTP. Calculations are performed with model 2.*

From the experimental and model results it can be concluded that the alternate plant operation is very efficient with respect to degradation of hydrophilic as well as hydrophobic substances.

# Resumé


**Oversigt**
Rapporten indeholder en emissionsoversigt for LAS, seks phthalater, nonylphenol og nonylphenol-diethoxylat samt et model set-up af Roskilde rensningsanlæg (Bjergmarken). De indgår i en undersøgelse af emissioner og skæbne af stofferne i Roskilde by og omegn. Undersøgelsen omfatter rensningsanlægget, Roskilde fjord og slamgødskede marker.

Emissionsoversigten giver input til rensningsanlægget, som efterfølgende giver stofkoncentrationer i det rensede vand som udledes til fjorden *(Vikelsøe et al., 2000)*. Det producerede slam lagres på en mark i nærheden af fjorden *(Sørensen et al., 2000)*.

**Emissionsoversigt**
Resultatet fra emissionsoversigten er opgivet som årsmiddel indløbskoncentrationer til Roskilde rensningsanlæg for LAS, total phthalater og nonylphenol ethoxylater. De er beregnet ud fra import/eksport data, samtaler med producenter, tidligere undersøgelser og estimater for skæbnen af stofferne i miljøet.

$$C_{LAS} = 20 \pm 20 \ \frac{\text{mg LAS}}{\text{liter}}$$

$$C_{\text{phthalates}} = 150 \pm 128 \ \frac{\text{mg phthalates}}{\text{liter}}$$

$$C_{NPnE} = 2 \ \frac{\text{mg NPnE}}{\text{liter}}$$ (ingen standardafvigelse pga. få data)

Tallene anvendes i rensningsanlægsmodellen til at estimere følsomheden af de beregnede udløbskoncentrationer med hensyn til variationer i inløbet og anlæggets procesparametre.

**Rensningsanlægget**
I EUSES risikovurderingssystemet for kemiske stoffer, er beskrivelsen af processerne og dynamikken i rensningsanlægsmodulet (SimpleTreat) væsentligt. Disse generiske compartment modeller, der er udviklet og brugt som beskrevet af f.eks. *Mackay (1991)* og *Mackay et al. (1992)*, kan blandt andet anvendes til at beregne fordelingen af stof mellem de forskellige faser i anlægget. I EUSES antages et kontinuert flow gennem systemet som består af en række serieforbundne reaktorer.

I Danmark bliver spildevandet imidlertid ofte behandlet i anlæg hvor flowet gennem hver enkelt reaktor er diskontinuert, samtidig med at der kun luftes i perioder, hvilket giver skiftende redox potentialer i de enkelte reaktorer. Derudover kommer udløbsvandet fra skiftende reaktorer som funktion af tid. Det er derfor ikke givet, at den kontinuerte flow tilgang der anvendes i SimpleTreat er acceptabel til risikovurdering af

stoffer i alternerende rensningsanlæg. Et centralt emne i denne rapport er således at undersøge vigtigheden af anlæggets driftscykus med henblik på at indføre justeringer i SimpleTreat, hvis alternerende anlæg skal kunne beskrives tilfredsstillende.

Som model anlæg er rensningsanlægget Bjergmarken i Roskilde valgt. Det modtager spildevand fra 80,000 PE i et alternerende BIO-DENIPHO aktiv-slam anlæg. Rensningsanlægsmodellen anvendes til at beregne en massebalance for 9 forskellige stoffer.

**Kontinuert vs. diskontinuert model set-up**

De komplekse processer og dynamiske forhold i rensningsanlægget er indarbejdet i 2 modeller med forskellig kompleksitet, i henhold til det generelle modelparadigme, der er beskrevet i *Sørensen et al. (2000)*.

Model 1 beskriver den alternerende cyklus og inkluderer aerob såvel som anoxisk nedbrydning, beskrevet ved pseudo $1^{ste}$ ordens nedbrydningsraterne $k_{1N}$ og $k_{1D}$, respektive. Desuden er adsorptionen beskrevet gennem retentionsfaktoren, $R = 1 + K_d \cdot X_B$, hvor $K_d$ er fordelingskoefficienten og $X_B$ er koncentrationen af partikulært materiale.

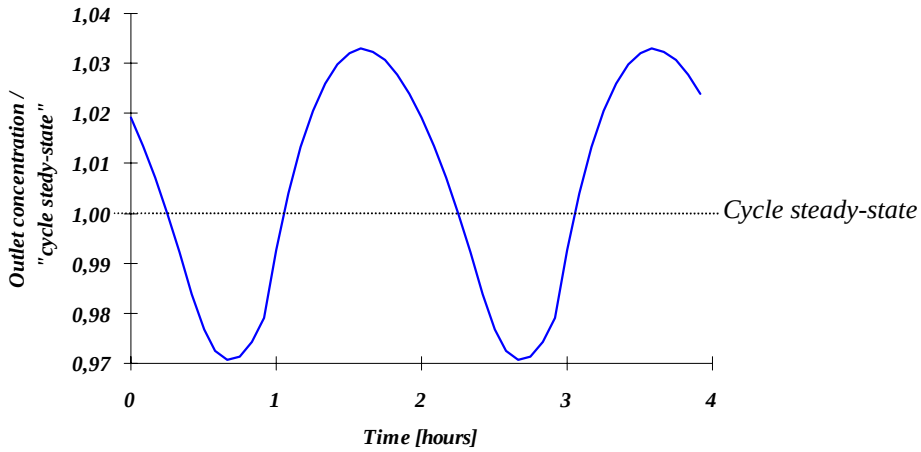
I model 2 er de mikrobiologiske nedbrydningsprocesser samlet i én bioreaktor med et kontinuert flow svarende til det målte døgnmiddelflow. Til forskel fra SimpleTreat inkluderer model 1 og 2 ikke afdampning, stripning, syre/base dissociation, temperatur afhængigheder og diffusion i sedimenteret partikulært materiale, hvilket reducerer usikkerheden der er relateret til de mange input variable. Konsekvenserne af at udelade processerne er diskuteret.

Reaktorhydraulikken i model 2 ligner SimpleTreat og afvigelsen mellem den mere komplekse model 1 og model 2 er brugt til at evaluere usikkerhederne ved at anvende SimpleTreat til at simulere alternerende anlæg.

Koncentrationen af opløst stof i udløbet afspejler de dynamiske skift i anlægget. Efter en periode med konstante indløbskoncentrationer og –flow opstår der steady-state og udløbskoncentrationen vil svinge omkring en middel ”cyklus steady-state” værdi, cf. Figur 1. Amplituden kan beregnes af:

$$\text{Amplitude} = 1.6 \cdot 10^{4} \cdot \frac{k_{1N}}{R} + 2 \cdot 10^{-2} \quad [\%]$$

Amplituden er ca. 3% af middelkoncentrationen for et hydrofobt og letnedbrydeligt stof som lineær alkylbenzen sulfonat (LAS).




***Figur 1.*** *Beregnet steady-state forløb af udløbskoncentration fra det alternerende anlæg i løbet af én driftcyklus. Model 1 er anvendt.*

Hvis de samme procesparametre anvendes i model 1 og 2, vil afvigelsen mellem "cyklus steady-state" koncentrationen i model 1 og steady-state koncentrationen i model 2 ligge i intervallet mellem 2 til 35%, med de største værdier for letnedbrydelige, hydrofile stoffer.

En kalibreret empirisk 1ste ordens nedbrydningsrate for model 2, $k_1$(model 2), kan beregnes af:

$$\frac{k_1(\text{model 2})}{R} = \frac{2279 \cdot \left(\frac{k_{1N}}{R}\right)^2 + 0.963 \cdot \left(\frac{k_{1N}}{R}\right)}{\left(0.275 \cdot \left(\frac{k_{1D}}{k_{1N}}\right)^2 - 0.822 \cdot \frac{k_{1D}}{k_{1N}} + 1.55\right)}$$

Hvis denne beregnede værdi indsættes i model 2 bliver afvigelserne ikke større end 2% mellem udløbskoncentrationerne i model 1 og 2, henholdsvis. For stoffer med aerobe halveringstider der er større end ca. 2 timer, kan $k_1$(model 2) direkte sættes lig med $k_{1N}$.

En integreret følsomhedsanalyse og 1ste ordens usikkerhedsanalyse konkluderer, at usikkerhederne relateret til inputparametrene i model 2 resulterer i usikkerheder i udløbskoncentrationerne der er meget større end de periodiske fluktuationer i model 1. Det er altså ikke nødvendigt at beskrive de komplekse skift i flowet gennem reaktorerne. Driftscyklen i model 1 kan derfor reduceres til én enkelt bio-reaktor med kontinuert flow svarende til model 2 og SimpleTreat under forudsætning af 1ste ordens nedbrydningsraterne $k_{1N}$ og $k_{1D}$ erstattes med den empiriske nedbrydningsrate $k_1$(model 2) i ovenstående ligning.

## Anvendelse af model 2

En eksperimentel serie blev udført i løbet af 8 dage i maj 1999. Hver dag blev en blandet indløbsprøve og en stikprøve fra udløbet taget fra Bjergmarken rensningsanlæg. En stikprøve fra primær slammet og en fra sekundær slammet blev desuden taget i løbet af perioden.

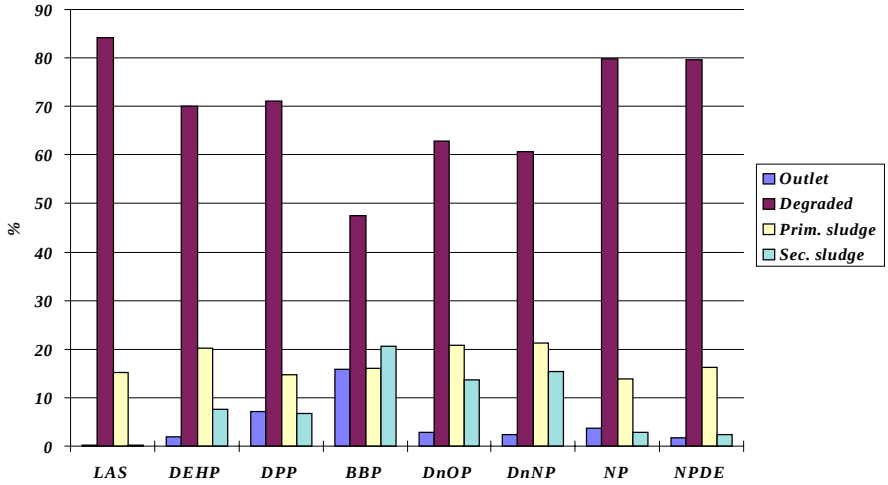
De eksperimentelt målte koncentrationer blev anvendt til at kalibrere model 2 med hensyn til $K_d$ og $k_{1N}$ for de 9 undersøgte stoffer. I Tabel 1 er de beregnede resultater vist.

***Tabel 1.*** Kalibreringsparametre fra model 2 og eksperimentelle data.

| | ***Middel aerob halve-ringstid $t_{½}$ [timer]*** | ***Middel fordelings koefficient $K_d$ [litre · $kg^{-1}$]*** |
|---|---|---|
| Linear alkylbenzene sulfonate, **LAS** | 1.3 | 2,760 |
| Di-(2ethylhexyl)-phthalate, **DEHP** | 21.6 | 13,060 |
| Dibutylphthalate, **DBP** | manglende data | manglende data |
| Dipentylphthalate, **DPP** | 19.0 | 2,570 |
| Benzylbutylphthalate, **BBP** | 79.1 | 3,530 |
| Di-(n-octyl)-phthalate, **DnOP** | 29.0 | 19,200 |
| Di-(n-nonyl)-phthalate **DnNP** | 32.8 | 28,600 |
| Nonylphenol **NP** | 7.2 | 2,080 |
| Nonylphenol-diethoxylate, **NPDE** | 6.3 | 3,640 |

De beregnede aerobe halveringstider er generelt lave for phthalaterne sammenlignet med litteraturværdier, der typisk er fundet i jordforsøg. Det er derfor vigtigt at bemærke, at de eksperimentelle forhold sjældent er ens, da mikroorganismerne er tilpasset de gunstige forhold med hensyn til temperatur, flow og stofkoncentrationer i rensningsanlægget.

Middelværdierne i tabellen og middelværdierne af de eksperimentelle indløbskoncentrationer er anvendt i model 2 til at beregne en massebalance for stofferne i anlægget, det vil sige andelen af indløbsmængden der kan findes i udløbet, nedbrudt, i primærslammet og i sekundærslammet, henholdsvis, se Figur 2. En inddeling i opløst og adsorberet stof er desuden udført.




***Figur 2.*** *Skæbnen af 9 undersøgte stoffer i det alternerende anlæg i procent af indløbsmængden. Beregnet med model 2. Indløb = 100%.*

Af de eksperimentelle data og af modelberegningerne kan det konkluderes, at det alternerende anlæg er meget effektivt til at nedbryde såvel hydrofile som hydrofobe stoffer.

# 1 Emission survey

## 1.1 Introduction to emission survey

When environmental hazards of substances are investigated it is of fundamental interest to determine the major sources of emission, i.e. to identify the major products, consumption figures and the quantities of the investigated chemicals used in these products. It is essential to understand in which way the products are used and if the chemicals are "lost" to the atmospheric, aquatic or terrestrial compartment. Some chemicals, such as the surfactants, are almost completely disposed in the wastewater, while others, such as the phthalates, enter the environment in a more complex way, e.g. through waste.

An updated and revised paradigm for the general framework of a mass flow analysis or substance flow analysis (SFA) has been developed by the Danish Environmental Protection Agency (EPA, 2000). The SFA is used as a standard tool in the process of identifying important sources and flows of hazardous substances in a given system defined in space and time.

In the future a potential field for application of SFA is for providing input to risk assessments for chemical substances carried out according to EU regulations. In fact a SFA is a basic part of the exposure assessment according to the EU technical guidance document for risk assessment (*TGD, 1996*).

The SFA thus summarises information regarding consumption and flow in emission factors that easily can be used in risk assessment modelling. However, the substance emission is often the weak link in the sense that it is very uncertain with respect to emitted mass and transport mechanisms and therefore the overall fate model becomes associated with considerable uncertainties that makes decision making doubtful.

The present emission survey is a simplified and schematic form of a SFA where only annual mean consumption figures are taken into account. It is a part of an investigation determining the fate of LAS, six different phthalates, nonylphenol and nonylphenol-diethoxylate in Roskilde municipality comprising a wastewater treatment plant (WWTP), Roskilde Fjord and a sludge amended field. The emission survey supplies input values to the sewer and WWTP which in turn defines the substance concentrations in the effluent water that is disposed to the Fjord and the sludge that is stored on the field adjacent to the Fjord.

The starting point to this overall fate model is thus the emission survey and the reliability, or uncertainty, of the combined model will depend strongly on the uncertainties associated with the survey. However, consumption can not be standardised and will always display local variations. Disclosure of the consumption pattern of the individual consumer or industry is, however, beyond the scope of this project.

## 1.2 General definitions

An estimate of the emission of a specific chemical to the different environmental compartments can be performed by deriving emission factors. The first step is to determine the concentrations of the chemical in consumer products and the consumption figures for these products, as exemplified in Table **2**. Such data can be obtained from e.g. Statistics Denmark, the Danish Product Register, manufacturers, importers and from the literature.

***Table 2.*** Concentration of chemical X in consumer product P and consumption of product P.

| **Product** | **Concentration of chemical X [mg chemical · kg product$^{-1}$]** | **Consumption of product [tons · day$^{-1}$]** |
|---|---|---|
| **P** | $C_X$ | $K_P$ |

The emission factors are defined according to product, activity and recipient, as exemplified in Table **3**. The factors in Table **3** state the concentrations of chemical X in the respective recipients or media, through emission of product P, during specific activities.

***Table 3.*** Emission factors for chemical X originating from various activities of product P.

| **Activity** | **Emission to sewage [mg · litre$^{-1}$]** | **Emission to soil [mg·kg soil$^{-1}$]** | **Emission to air [µg · m$^{-3}$gas]** | **Emission to waste [mg · kg$^{-1}$]** |
|---|---|---|---|---|
| **Production** | | | | |
| **Compounding** | | | | |
| **Processing** | | | | |
| **Use** | | | | |
| **Disposal** | | | | |
| **Incineration** | | | | |

An illustrative example: The emission of chemical X, present in product P, to recipient R, caused by activity A, yields the following emission factor

$$\begin{gathered}\text{Concentration of X in P [g X} \cdot \text{tons P}^{-1}] \cdot \\ \text{Consumption of P [tons P} \cdot \text{day}^{-1}] \ / \\ \text{Flow of recipient R [weight or volume} \cdot \text{day}^{-1}] \\ = \text{g X} \cdot (\text{weight or volume})^{-1}\end{gathered}$$

$$\Downarrow$$

$$\frac{C_X \cdot K_P}{F_R} = \frac{\text{gX}}{\text{weight or volume}}$$

From this example it is seen, that the flow of recipient, or carrier medium, $F_R$, is required, e.g. the sewage flow rate per capita or person equivalent (PE) when washing activities are considered or the waste gas production per Giga Joule when electricity production from a power plant is considered. For this purpose the population and/or industrial equivalents together with other catchment area data are often needed as inputs to quantify the recipient flow.
In this work the emission survey for substance concentrations in the sewage inlet to Roskilde WWTP is performed. The survey is designed to be a

part of the emission, WWTP, soil, inlet system and in conjunction with the WWTP analysis hourly inlet flow data are obtained, that can be used as recipient flow data in the emission survey, when precipitation and infiltration are taken into account.

The catchment area is Roskilde municipality, where the following general data can be used to estimate the substance concentrations in the sewer.

- Person equivalents: 80,000 PE (Denmark in total: 5.3 mio PE).
- Mean hourly inlet flow to Roskilde WWTP: $492 \pm 356$ $m^3 \cdot hour^{-1}$.
- Industrial load based on water consumption: 20 - 25%.

The substances that are considered here are six different phthalates that are present in a variety of products that are disposed to different environmental compartments, linear alkylbenzene sulfonate (LAS) an anionic surfactant, used in laundry and cleaning detergents, nonylphenol (NP) and nonylphenol-dietoxylate (NPDE) that primarily are decomposition products from the non-ionic surfactants nonylphenol ethoxylates.

Two of the phthalates and NP are investigated on account of their suspected hormone-disrupting effects and LAS is included due to the toxicity towards aquatic organisms. Furthermore LAS is included as a model substance due to the well documented physico-chemical properties that have been determined extensively in previous investigations and the relatively simple emission pathway that predominantly is through the sewage system, which reduces the uncertainties in the model calculations that are related to the emission survey.

## 1.3 Linear alkylbenzene sulfonate, LAS

LAS is a highly water soluble surface active agent widely used in laundry, cleaning, dishwashing formulations and personal care products (*e.g. Børglum et al., 1994*). It also appears as additive in agrochemicals and in the production of textiles. When sodium is replaced by calcium both linear and branched isomers are suitable for use as emulsifier in pesticide formulations (*Painter, 1992*). The commercial products are mixtures of various phenyl substituted alkyl homologues, typically C10 to C13, with an average carbon chain length of approximately 11.8 (*Matthijs et al., 1987*). The proportions differ depending on the alkylation process used. The chemical structure is illustrated in Figure **3**.

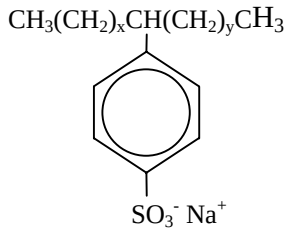



***Figure 3.*** *Chemical structure of LAS.*
*Where x + y = n and n = 7 - 11 carbon units (McAvoy et al., 1993).*

LAS has been the major anionic surfactant used in laundry and cleaning products world wide since its introduction about 25 years ago. The estimated annual consumption of LAS in 1987 was 1.8 million metric tons on a global scale and 485 thousand metric tons in Western Europe (*Berth et al., 1989*). In Denmark the consumption was approximately 7000 tons per year in 1987 (*Børglum et al., 1994*). An average growth rate of 1 - 2% per year was expected in 1989 (*Berth et al., 1989*).

1997 annual import, export and production figures for the raw material groups that are relevant to LAS emissions are stated in Table **4** *(Statistics Denmark, 1999; Børglum et al., 1994 for 1986 figures; Berth et al., 1989; personal communication with manufacturers, 1999).*

***Table 4.*** Concentrations and consumption of LAS containing raw material. Consumption = production + import - export *(Statistics Denmark, 1999).*

| **Raw material** | **LAS concentration wt-%** | **Annual consumption of product [tons per year]** |
|---|---|---|
| Aqueous solutions containing disodium alkyl benzene sulfonate (LAS) in amounts between 30 and 50 wt-% | 30 - 50 | 1,316 |
| Anionic organic surfactants, incl. retail, excl. disodium alkylbenzene sulfonate (LAS) in amounts between 30 and 50 wt-% | ~ 40 | 15,908 |
| Surfactant preparations, retail | 0 - 20 | 5,456 |
| Surfactant preparations, excl. retail | 0 - 20 | 9,876 |
| Prepared laundry and cleaning formulations, retail | 1 - 10 | 57,146 |
| Prepared laundry and cleaning formulations, excl. retail | 1 - 10 | 46,847 |

The total annual consumption of LAS, based on Table **4**, is approximately 13,500 ± 5,000 tons LAS · $year^{-1}$.

For further differentiation into more specific consumer products the following key figures can be considered for the content of LAS.

| | |
|---|---|
| Liquid laundry detergents | 10 - 20% LAS |
| Powder laundry detergents | 5 - 10% LAS |
| Liquid dishwashing detergents | 5 - 20% LAS |
| Liquid cleaning detergents | 5 - 10% LAS |
| Other products (retail) | 5 - 10% LAS |

Once used the products are almost exclusively discharged into the sewage system and led to the wastewater treatment plants. In some cases domestic or even industrial raw sewage is discharged directly into the surrounding waters without any previous chemical or biological treatment but these situations do not to occur in the considered area. In the case of flooding the sewage is stored in 3 reactors placed on different locations in the catchment area and subsequently led to the WWTP.

It is therefore assumed that the emission of LAS occurs only during use, without any significant loss at the production, compounding or processing stages. Furthermore all of the used chemical will enter the sewage system and will be led to the WWTP before being discharged into the environment.

Thus, the emission factor for LAS is rather simple, cf. Table **5**.

***Table 5***. Emission factor for LAS containing consumer products.

| **Emission factor for LAS products** | **Emission to sewage system [tons per year]** |
|---|---|
| Use | $13{,}500 \pm 5{,}000$ |

The degradation in the sewage system is approximately 10 - 68% ($0.39 \pm 0.29$) (*AISE Workshop, 1995*) of the emitted mass.

Assuming a proportional distribution with respect to person equivalents and sewage flow, the total LAS concentration to the WWTP inlet, is

$$C_{inlet,LAS} = \frac{13{,}500 \pm 5{,}000 \ \frac{\text{tons LAS}}{\text{year}} \cdot 0.39 \pm 0.29 \cdot \frac{80{,}000}{5{,}300{,}000}}{(492 \pm 356) \cdot 10^3 \cdot 24 \cdot 365 \ \frac{\text{liter}}{\text{year}}} \approx 20 \pm 20 \ \frac{\text{mg LAS}}{\text{liter}}$$

These figures are in excellent agreement with other investigations (e.g. Feijtel, 1995) stating concentrations in the inlet to WWTP's around 15 mg LAS $\cdot$ litre$^{-1}$.

Large uncertainties are related to the emission figures as well as the degradation estimates in the sewers and the storm tanks.

## 1.4 Phthalates

The phthalates were introduced in the 1920's as softeners in plastic materials and are among the most important chemicals in various industrial products. The predominant use is as additives in polyvinylchlorid (PVC) where the presence of phthalates gives rise to products that are soft and workable *(e.g. Plastindustrien, 1996)*. They are generally non-reactive and are therefore not chemically bound in the plastic matrix which enables them to migrate to the surface of the material where they can be transported to the surrounding environment, e.g. air, water, soil etc *(Furtmann, 1996)*. The migration within the material increases with increasing temperature and branching of the alkyl chains, see Figure **4**.

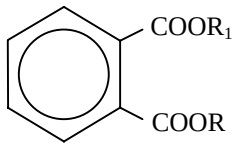



***Figure 4.*** *General chemical structure of phthalates. $R_1$ and $R_2$ are alkyl groups.*

The phthalates are diesters of phthalic acids and are produced from a reaction between phthalic acid and appropriate alcohols. The structure thus contains a rigid planar aromatic ring with two flexible (straight or branched) alkyl chains, $R_1$ and $R_2$. The polar carboxyl groups, C = O, are buried within the molecule thus having an insignificant influence on the physical properties of the molecule, with the exception when $R_1$ or $R_2$ are small alkyl chains such as methyl and ethyl (*Helweg, 1996*).

Phthalates with short side chains have properties that are very different from those with longer side chains, such as the intensively studied and widespread Di-(2 ethylhexyl)-phthalate (DEHP). The smaller phthalates are rapidly degraded aerobically and anaerobically *(Shelton et al., 1984)* and have a lower tendency to adsorb, whereas long chain phthalates, such as DEHP, are predominantly degraded aerobically. Even though specific phthalates are easily degradable, constant concentrations can be found in surface waters. Some investigators state, that the micro-organisms do not degrade the substances below a certain threshold concentration of a few µg per litre, possibly due to energy considerations (*Furtmann, 1996*). This phenomenon has been studied in *Sørensen et al., 2000* where an alternative irreversible 1$^{st}$ order adsorption kinetic model has been suggested that fits the data more satisfactorily.

The phthalates that are considered in the present study comprise (*cf. Vikelsøe et al., 1999*)

| | |
|---|---|
| Di-(2ethylhexyl)-phthalate | DEHP |
| Dibutylphthalate | DBP |
| Dipentylphthalate | DPP |
| Benzylbutylphthalate | BBP |
| Di-(n-octyl)-phthalate | DnOP |
| Di-(n-nonyl)-phthalate | DnNP |

The emission factors for the Danish marked are based on an extensive investigation performed for 1992 sales and consumption figures for various products and activities (*Hoffmann, 1996*).

The import of phthalates in pure form, phthalates in compounded PVC and phthalates in semi-manufactures for product manufacturing in Denmark, is estimated to be 6,500 tons, 3,000 – 5,000 tons and 2,000 – 2,500 tons, respectively, giving a total of 11,500 – 14,000 tons per year in 1992 *(Hoffmann, 1996)*. In addition to this is an unknown amount of raw material and semi-manufactures for the production of lacquer, paint, varnish, adhesives, fillers and denaturants that is small compared to the main products. In comparison with this *Axelsen et al., (1984)* state a total consumption of phthalates of 7,000 tons for 1982.

In Table **6** the phthalate containing products are stated. The consumption figures for production and use, the used phthalates and annual emissions to air, water, soil, recycling, toxic waste and waste treatment are also stated.

***Table 6.*** Consumption and emission figures for phthalates in Denmark, 1992 (*Hoffmann, 1996*).

| **Product** | **Consumption [tons phth. · year$^{-1}$]** | **Main phthalates in product** | **Emissions [tons phthalates · year$^{-1}$]** | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Air | Water | Soil | Recycling | Toxic waste | Waste treat. |
| **PVC** | | DEHP | | | | | | |
| - Production | 7,700 – 11,900 | BBP | 1 - 12 | <1 | - | 350-550 | 20 - 110 | 350 - 550 |
| - Use | 9,200 – 9,500 | | 0.4 - 5.5 | 0.1 - 16 | - | 250 | - | 2,500 – 7,800 |
| **Lacquer, paint, varnish** | 130 - 500 | DBP Diisodecylph. | | | | | | |
| - Production | | DEHP | - | - | - | - | 1.5 - 7.5 | - |
| - Use | | BBP | 0.01 - 0.05 | 1.5 - 15 | - | - | 3 - 45 | 130 - 500 |
| **Adhesives** | 160 - 220 | DBP | | | | | | |
| - Production | | DEHP | - | 0.2 - 2.2 | - | - | ? | - |
| - Use | | BBP | - | 1.2 - 38 | - | - | - | 160 - 220 |
| **Fillers** | < 400 | Diisooctylph. | | | | | | |
| - Production | | | ? | ? | - | - | ? | - |
| - Use | | Diisodecylph. DBP | ? | ? | - | - | - | < 400 |
| **Denaturants** | < 5 | | | | | | | |
| - Production | | | - | - | - | - | ? | - |
| - Use | | | < 2.5 | < 1.3 | - | - | - | < 1.3 |
| **Insulation material** | < 50 | Diisooctylph. | | | | | | |
| - Production | | DEHP | - | - | - | - | ? | - |
| - Use | | | - | - | - | - | - | ? |
| **Total** | | | 1.4 - 20 | **3 - 77** | - | 600 - 800 | 25 - 163 | 3,150 – 8,850 |
| - Production | 8,000 – 13,000 | | 1 - 12 | 0.2 - 3.2 | | 350 - 550 | 22 - 118 | 350 - 550 |
| - Use | 9,500 – 10,700 | | 0.4 - 8 | 3 - 74 | | 250 | 3 - 45 | 2,800 – 8,300 |

*-: No emissions estimated.*
*?: Emission unknown.*

Assuming that the total amount of phthalates emitted to water from production and use is transported to the sewer and that the degradation in the sewage system is negligible, the mass in the inlet to the Danish waste water treatment plants is 3 - 77 tons phthalates · year$^{-1}$ or expressed as a mean value and standard deviation: 43 ± 19 tons phthalates · year$^{-1}$ (*Hoffmann, 1996*). The value, updated with consumption figures received from Statistics Denmark, representing 1998 is virtually identical.

Assuming a proportional distribution with respect to person equivalents and sewage flow, the mass flow to the Roskilde WWTP inlet, is

$$M_{inlet,prod+use} =$$

$$43 \pm 19 \ \frac{\text{tons phthalates}}{\text{year}} \cdot \frac{80{,}000}{5{,}300{,}000} = 640 \pm 286 \ \frac{\text{kg phthalates}}{\text{year}}$$

In addition to this there is a contribution from the atmospheric wet and dry deposition which will transport gaseous and particulate bound phthalates to the target area, approximately 16 $km^2$, and then further on to the sewage system. *Vikelsøe et al., (1998)* have found a DEHP dry deposition rate of 140 - 540 μg DEHP $\cdot$ $(m^2 \cdot year)^{-1}$ from field studies in Roskilde municipality. The total mass of all investigated phthalates will be approximately a factor of 2 higher.

The annual mean mass flow of deposited phthalates that are transported to the waste water treatment plant in Roskilde is thus

$$M_{inlet,deposition} =$$

$$(140 - 540)\frac{\mu\text{g phthalates}}{m^2 \cdot \text{year}} \cdot 2 \cdot 16 \cdot 10^6 \ m^2 = 4.5 - 17.3 \ \frac{\text{kg phthalates}}{\text{year}}$$

This figure is only about 1% of the mass derived from production and use and will be neglected in the following. However, it should be considered in relation to observed concentrations in agricultural soils without sludge amendment. The hourly mean inlet flow to the WWTP has been measured to be 492 ± 356 $m^3 \cdot hour^{-1}$ during 8 days in May 1999, leading to the following inlet concentration

$$C_{inlet,phthalate} =$$

$$\frac{640 \pm 286 \ \frac{\text{kg phthalates}}{\text{year}}}{(492 \pm 356) \cdot 10^3 \cdot 52 \cdot 7 \cdot 24 \ \frac{\text{liter}}{\text{year}}} = 150 \pm 128 \ \frac{\mu\text{g phthalates}}{\text{liter}}$$

*Hoffmann (1996)* emphasises that the consumption figures are underestimated since the amount of raw material and semi-manufactures containing phthalates meant for lacquer, paint, varnish, adhesives, fillers and denaturants are not known. The smallest relative uncertainties are found for the PVC products due to more accessible sales and product information.

The consumption figures are decreasing in the 90'ies for PVC and lacquer etc. products while other products such as sanitary foils, clothing and toys and others are expected to increase due to lacking substitution possibilities and increasing import (*Hoffmann, 1996*).

*Vikelsøe et al. (1998)* calculated a mass balance for the above mentioned phthalates for the sources: car wash centres, a hospital, a kindergarten, an adhesive industry and an industrial laundry in relation to the total phthalate mass flow into the Roskilde WWTP. The investigated sources accounted for approximately 12% of the influx of DEHP. The order of importance of sources were laundries, deposition, car washes and hospital. The deposition rates showed a seasonal variation with a minimum in the winter.

Phthalate concentrations at the WWTP inlet were measured to be in the range 30 - 270 µg phthalates · litre$^{-1}$, with the most abundant substances being DBP, DEHP, DnOP and DnNP. This interval is in good agreement with 150 ± 128 µg phthalates · litre$^{-1}$ that is found from the emission survey.

## 1.5 Nonylphenol (NP) and nonylphenol-diethoxylate (NPDE)

Nonylphenol-polyethoxylates (NPnE) are synthetic surface active substances that are used in the industry as tensides, emulgators and surfactants in paints, lacquers, soaps, cosmetics, pesticides, detergents and insulating materials (*Pallesen et al., 1996*). They comprise a hydrophobic branched C9 alkyl-group and a hydrophilic alcohol polyethoxylate group in para-position, cf. Figure **5**.

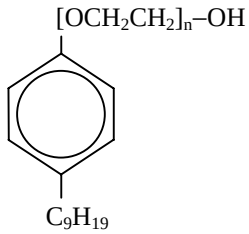



***Figure 5.*** *Chemical structure of nonylphenol-polyethoxylate (NPnE).*

The oligomer distribution in a commercial NPnE mixture, which is most commonly used in laundry detergents is found by *Ahel et al. (1994)* to consist of 3 to 20 ethoxy moieties per molecule.

Following use the NPnE's are primarily disposed to the sewer and led to WWTP's where the parent oligomers are efficiently eliminated during biological treatment. The degradation products predominantly comprise nonylphenol (NP), nonylphenol-monoethoxylate (NPME), nonylphenol-diethoxylate (NPDE) and nonylphenoxy carboxylic acids (NPEC) where the abundance of the particular metabolite is dependent on the treatment conditions and influence of physicochemical processes (*Ahel et al., 1994*).

NP, NPME and NPDE are more lipophilic than their parent substances and are therefore more susceptible to bioaccumulation. NP is found to be toxic towards aquatic organisms and furthermore to exhibit hormone disrupting effects (*TemaNord, 1996*).

NP itself is only used in limited amounts as plastic softener, in paint and laquer, in spermatocidals, cleaning agents, pesticide formulations and in orimulsions. NP is on the list of unwanted substances and is being substituted in these products with the exception of pesticide formulations.

The production of NP and NPnE in Western Europe was in 1987 estimated to be approximately 70,000 tons · year$^{-1}$ of which 56,000 tons · year$^{-1}$ was used in Western Europe and 14,000 tons · year$^{-1}$ was exported. In Table **7** the numbers of products in different applications and the annual consumption figures for NPnE for these applications are stated. The figures are for Denmark in 1995.

***Table 7.*** Consumption figures for NPnE for Denmark in 1995, *(Nordisk Ministerråd, 1996).*

| | **Number of products** | **Annual consumption [tons · year$^{-1}$]** |
|---|---|---|
| **Paint/laquer** | 168 | 63 |
| **Pesticides** | 53 | 175 |
| **Cleaning materials** | 663 | 1,066 |
| **Detergents** | 51 | 115 |
| **tensides** | 22 | 293 |
| **Insulating materials** | 74 | 77 |
| **Fillers** | 159 | 66 |
| **Lubricants** | 33 | 33 |
| **Building materials** | 30 | 28 |
| **Cosmetics** | 31 | 20 |
| **Total** | 1,284 | 1,936 |

Assuming that the consumption is reduced with 50% in 1999 and that 50% is disposed via the sewer the inlet concentration to the WWTP is

$$C_{inlet,NPnE} =$$

$$\frac{480\ \frac{\text{tons NPnE}}{\text{year}} \cdot \frac{80{,}000}{5{,}300{,}000}}{(492 \pm 356) \cdot 10^3 \cdot 24 \cdot 365\ \frac{\text{liter}}{\text{year}}} \approx 2\ \frac{\text{mg NPnE}}{\text{liter}}$$

Measurements from the inlet to Roskilde WWTP showed concentrations of approximately 5 and 100 µg · litre$^{-1}$ for NP and NPDE respectively which is the same order of magnitude as WWTP inlet measurements performed by *Ahel et al., (1994)*. In comparison the NP concentration in the inlet to a WWTP was found to be 0.7 mg · litre$^{-1}$ (*TemaNord, 1996*).

# 2 Introduction to wastewater treatment plant

The wastewater treatment plant (WWTP) application in EUSES, SimpleTreat, is designed for a single bio-reactor with continuous flow. The possibility of using this set-up in the description of an alternately operated WWTP needs to be investigated.

The necessary systemic and model complexities for simulating the fate of 9 different substances in an alternately operated BIO-DENIPHO activated sludge waste water treatment plant situated in Roskilde municipality, Denmark, are determined. Two models are set up according to the general modelling paradigm described by *Sørensen et al., (2000)*. The complex system functionalities associated with the WWTP are incorporated into two models of varying complexity thus investigating the influence of the two conceptually different uncertainty sources, i.e. uncertainties arising from model structure and uncertainties due to input values, respectively.

The primary objective is to set up a model that simulates the concentration levels in the plant in terms of dynamic fluctuations as well as mean steady state concentrations. When dealing with a BIO-DENIPHO WWTP the model inputs, such as flow, influent concentrations, sludge recycling, reactor volumes etc., are highly determining for the variability of the effluent concentrations and to a lesser degree of the sludge concentrations. The model parameters, e.g., degradation rate, adsorption coefficient, hydrolysis rate etc., also play an important role in determining the overall removal of the chemicals in question.

An important point is to reduce the model description to a limited set of independent input parameters. These must contain the necessary information needed to perform a parameter study that will deal with the essential problems of the actual system. For each chemical the significance of the physico-chemical processes must be evaluated and only the most predominant are to be included.

Values for the model input parameters must be obtained and when the structural uncertainties associated with the input parameters and the uncertainties related to model are mutually optimised the optimum model complexity is reached. The total model uncertainties associated with the simulations are calculated by using first order analysis and sensitivity analysis where an approximation of the mean value and standard deviation of the state variables (concentrations) are found on basis of the variations in the model input parameters. To evaluate the influence of model structure on the calculations, different model formulations are developed for the same application. By comparing the calibration parameters and sensitivity toward variations in field conditions an estimate of the most appropriate model structure can be obtained.

The model is calibrated with experimental data by adjusting two model parameters, i.e. the pseudo 1$^{st}$ order degradation rate constant and the sorption equilibrium constant respectively. If the adjusted calibration parameter values are within the range of experimentally determined values reported in the literature the model is considered to be realistic.

# 3 Plant description

The considered activated sludge WWTP (Figure **6**) is situated in Roskilde municipality (Figure **7**), Denmark, and has the following capacity

| | |
|---|---|
| Person equivalents: | 80,000 PE. |
| $BOD_5$: | 4,800 kg per day. |
| Total nitrogen: | 712 kg. per day. |
| Total phosphorous: | 260 kg. per day. |
| Dry weather flow*: | 50,400 $m^3$ per day. |
| | *:sewage + infiltration |
| Rain water flow: | 79,500 $m^3$ per day. |

Discharge criteria:

| | |
|---|---|
| $BOD_5$ (modified): | 15.0 mg per litre. |
| Total-N (nitrogen), all year: | 5.5 mg per litre. |
| Total-N (nitrogen), 01.05-31.10: | 6.0 mg per litre. |
| Total-P (phosphorous): | 1.5 mg per litre. |
| pH: | 6.5 - 8.5 |
| Suspended matter: | 30.0 mg per litre. |
| Precipitate: | 0.5 mg per litre. |

The sewage is pumped through a grating where larger objects such as cloths, pebbles, wood parts etc. are removed. In the aerated sand and fat trap sand and gravel is settled whereupon it is loaded into containers along with the grating material. Fat and oil etc. is separated and pumped to the digestion reactor where it is degraded anaerobically under production of methane. The gas is stored and used for heating of bouldings and digestion reactor.

After this initial separation approximately 30% of the sewage flow is led through the primary settlers where the suspended particulate matter is deposited by gravitation and pumped to the anaerobic digestion reactor via a concentration reactor. The digested sludge is centrifuged to reach a dry matter content of 30%.

It is difficult to estimate the sludge flow that is scraped from the primary settler. As a rough estimate 15% of the flow to the primary settler is removed as primary sludge, which gives a mean flow of $q_{PS} = 0.15 \cdot 0.3 \cdot Q$.

The settler is assumed to consist of two totally mixed volumes, i.e. a volume of clarified liquid $(1 - f_{PS}) \cdot V_{PS}$, and a volume of settled suspended matter $f_{PS} \cdot V_{PS}$, where $f_{PS}$ is the sludge volume fraction in the settler. This constant is assumed to be 0.25 and constant in time. Approximately 75% of the suspended matter entering the primary settler is removed as primary sludge, which is considered to be a conservative estimate with respect to substances adsorbed to primary sludge (*Mikkelsen, 1995*).

Due to the low active microbial concentration in the influent sewage the degradation is negligible in the primary settler and sludge.

The presettled water is mixed with the remaining raw influent water (70% of Q) and the recycled sludge from the secondary settler. It is pumped to the first biological reactor designed for biological nitrogen and phosphorous removal (BIO-DENIPHO) combined with chemical precipitation of phosphorous. The reactor is anaerobic and the adapted micro-organisms do not degrade persistent substances such as phthalates and nonylphenols.

The following biological reactors are alternately aerobic and anoxic (no oxygen) and will remove nitrogen and organic substance through nitrification and denitrification, respectively, according to the operation cycle described in Figure **9**. The mean hydraulic retention time in the biological reactors is approximately 19 hours. The concentration of micro-organisms (sludge) increases in the biological reactors and the conditions will be optimised with respect to degradation of slowly degradable organic substances.

Following the biological reactors the sewage and produced sludge is led to the secondary settlers where water and suspended matter is separated. Again the settler is assumed to consist of two totally mixed volumes. The recycling flow to the biological reactors, is approximately 60% of the influent wastewater flow and the sludge circulates approximately one time per day. It is estimated that 5% of the recycled sludge flow is led to dewatering in concentration tanks and centrifuges and when a dry matter content of about 25% is reached it is brought to sludge storage tanks.

The hydraulic retention time in the total plant is approximately 46 hours. The sludge age is approximately 20 days.

In Figure **8** a schematic sewage and sludge flow-sheet for the modelled WWTP is shown.

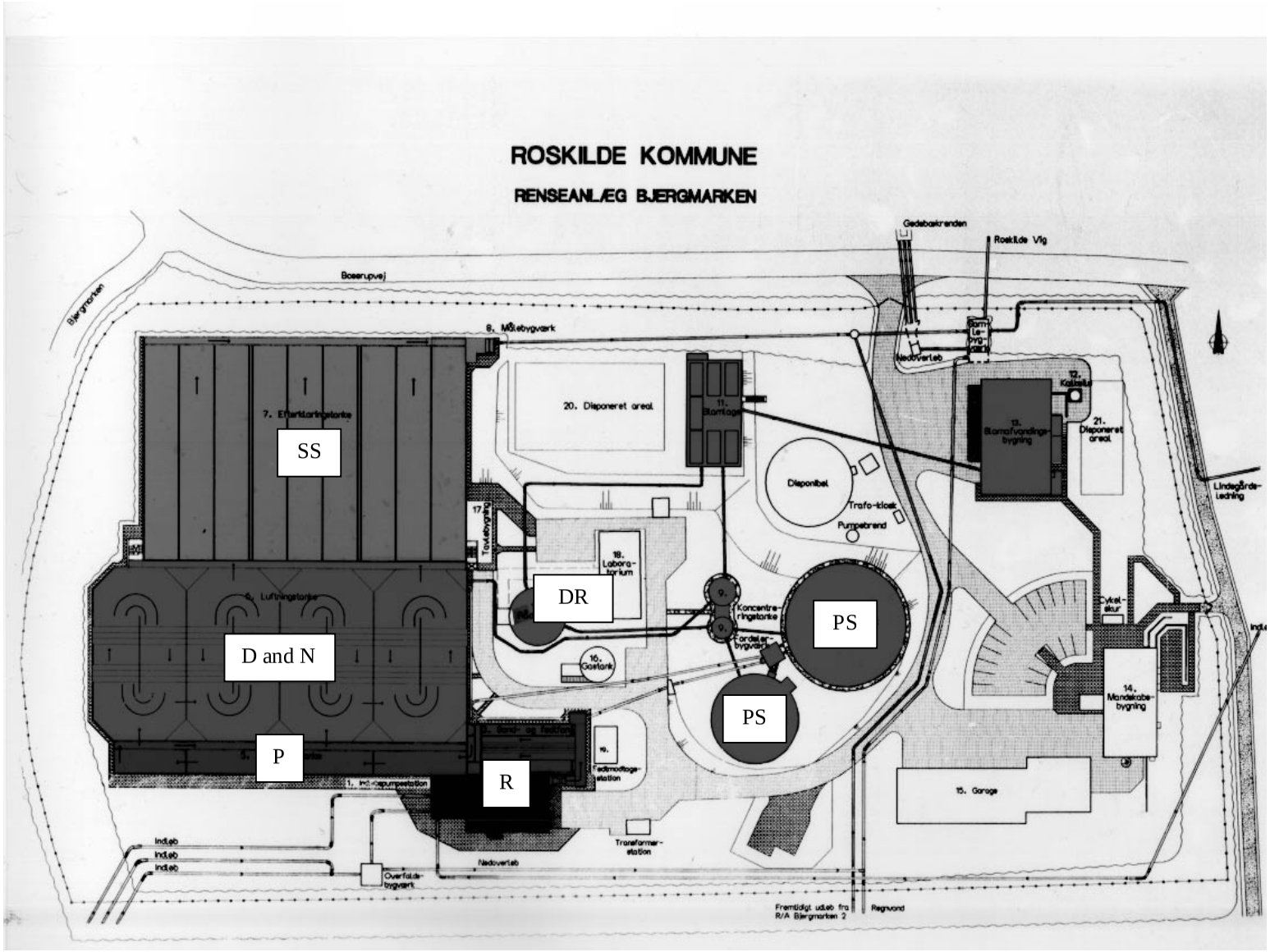



***Figure 6.*** *Alternately operated, activated sludge WWTP.Abbreviations see Figure 8.*

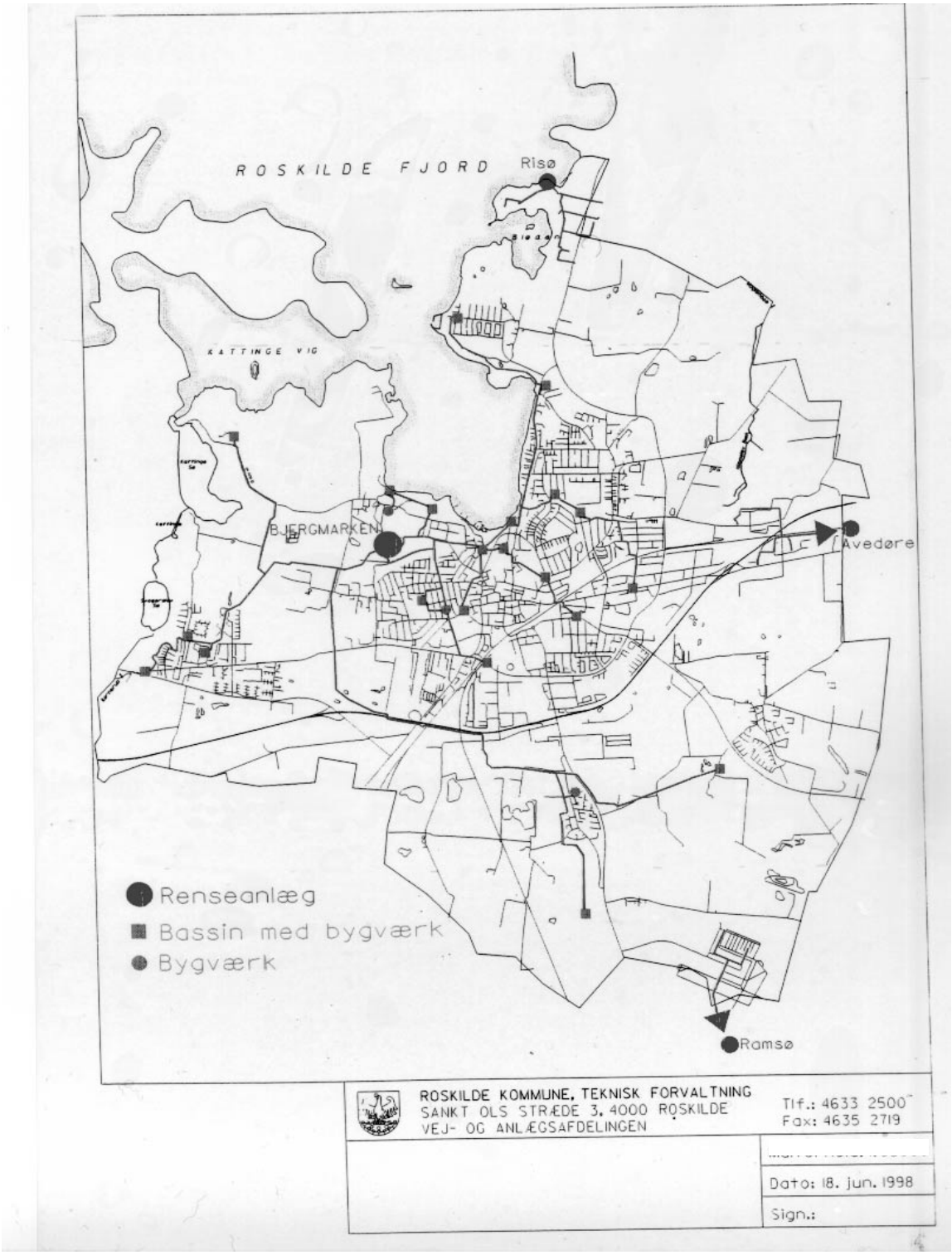



***Figure 7.*** *Catchment area in Roskilde municipality.*

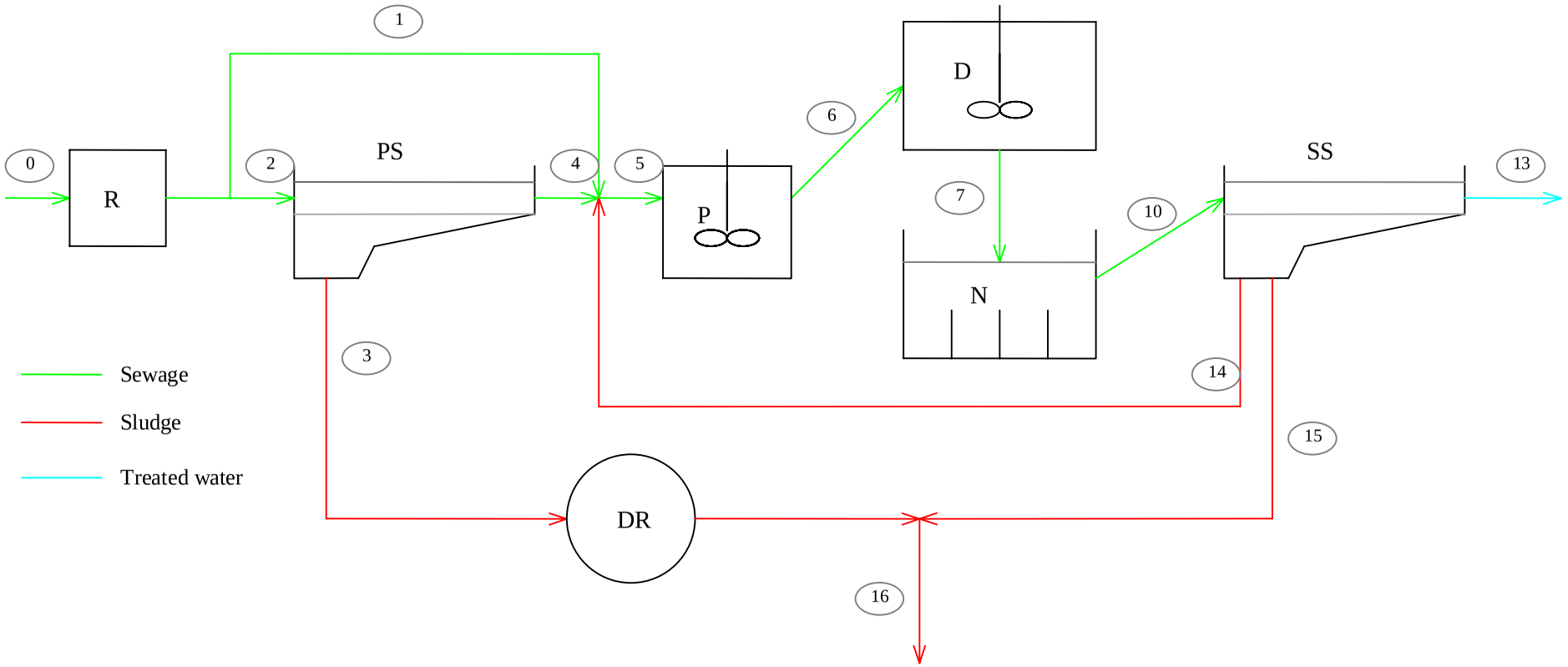



***Figure 8.*** *Sewage and sludge flow-sheet of BIO-DENIPHO waste water treatment plant in Roskilde.*
*Each number denotes a concentration that is calculated in the model.*

R = Pump, rough grating, sand and fat separation. Grid material and sand is loaded into containers and fat is pumped to the digestion reactor (DR).
PS = Primary settler. Approximately 30% of the influent sewage is led to the PS. Settled primary sludge is pumped to DR.
DR = Sludge digestion reactor.
P = Anaerobic reactors for propagation of phosphorus assimilating bacteria. Additionally chemical precipitation of phosphorus with $FeCl_2$ is performed.
D = Anoxic denitrifying reactors. Nitrate is converted into $N_2$ and dissolved organic matter is degraded.
N = Aerobic nitrifying reactors. Ammonium is converted into nitrate and dissolved organic matter is degraded.
SS = Secondary settler. Settled sludge is recycled to biological reactors or is dehydrated and together with the digested primary sludge is disposed, e.g. on agricultural fields.

The alternate operation cycle consists of 6 phases, as illustrated in Figure **9**.

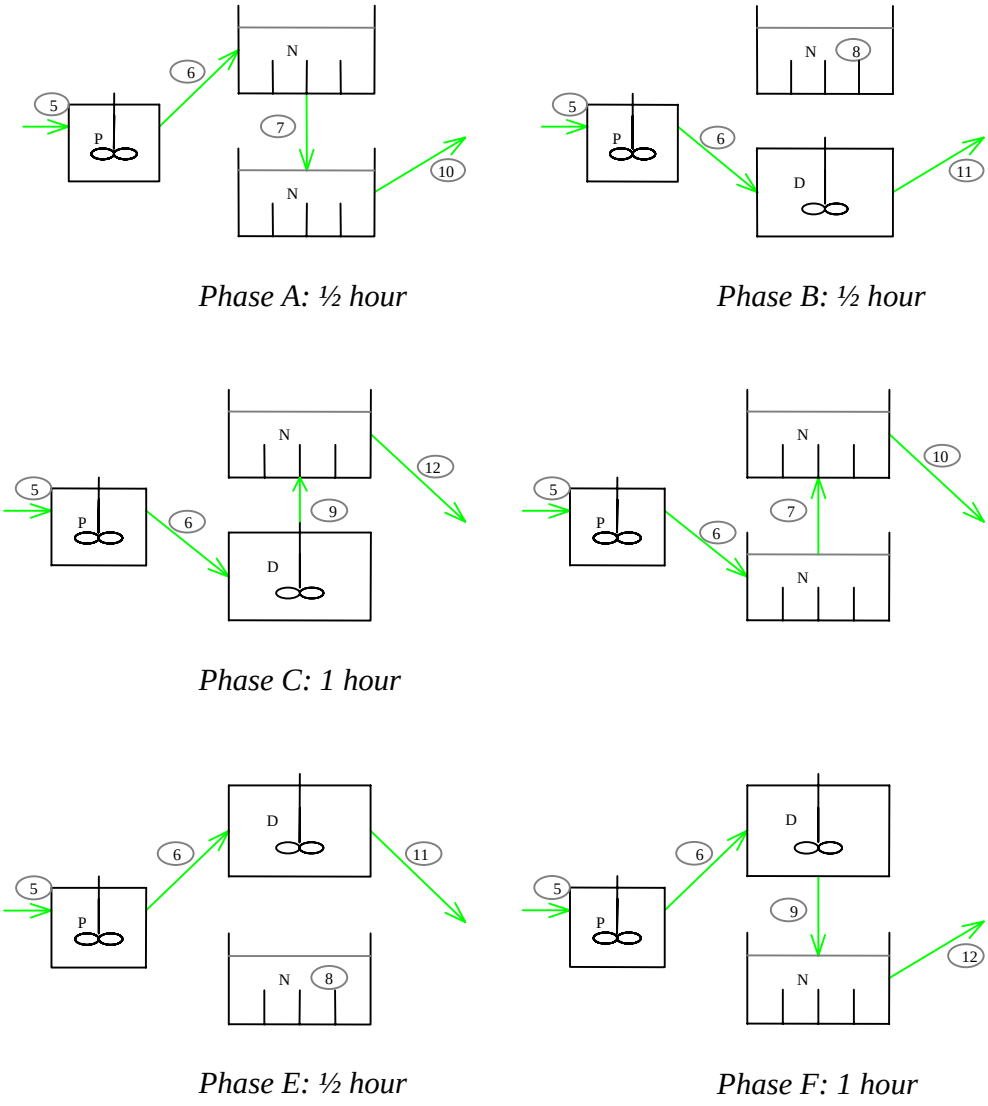



***Figure 9.*** *Alternate operation cycle. Each number denotes a concentration that is calculated in the model.*

# 4 Processes

A number of factors are important when the removal of organic substances in a waste water treatment plant is considered. The following processes occurring in the different reactors are used and commented in this work

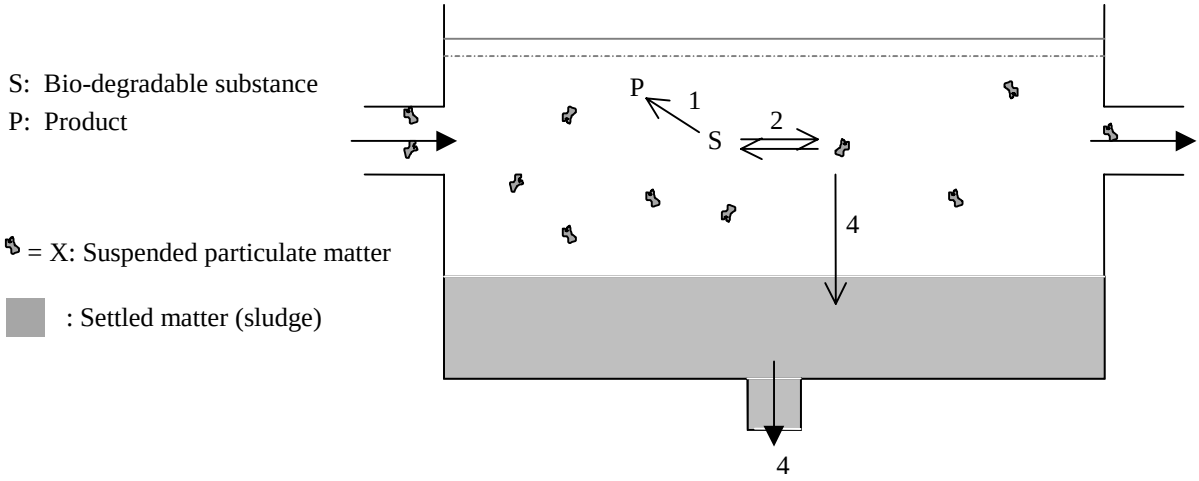



***Figure 10.*** *Overview of processes involving substances in a WWTP reactor.*

1: Microbial and abiotic *degradation* (photolysis, oxidation, volatilisation, precipitation)
2: *Adsorption* to particulate matter and/or complex or micelle formation
3: *Hydrolysis*
4: *Sedimentation* of suspended particulate matter and removal of sludge

*Stripping* from the aereation reactors and evaporation from the settlers are believed to be negligible for LAS and nonylphenols. For the phthalates some substances have considerable vapour pressures, which will be commented in section 6.6.1. Bio-degradation is the predominant removal process in a WWTP and in the model set-ups volatilisation is neglected.

The influence of *temperature* on the degradation of LAS and other surfactants has been summarised by *Feijtel (1995)* into the following important facts. The references are cited by *AISE (1995)*.

- Temperature has little or no effect on condition and degradative capacity of sludge. Phosphate is main driver for growth, (*Painter et al., 1978*).
- In-situ experiments measuring heterotrophic activity of microorganisms in Antarctic waters (0°C) indicate that the activity of indigeneous microflora is similar to microflora of temperate regions, (*Morita et al., 1975*).
- Microorganisms present in Arctic and other cold water bodies are uniquely adapted to extremely low temperatures, (*Morita et al., 1975*).

- Aerobic bio-degradation rates measured for $^{14}C$ toluene in sediments of 5°C are similar to the rates determined at 20 and 30°C, (*Bradley and Chapelle, 1995*).
- In-situ measurements of bio-degradation rate and extent for alcohol ethoxylate (AE) and alcohol ethoxy sulphate (AES) indicated no effect of temperature during the season - i.e. change over 9 degrees C down to 12$^{o}$C, (*Guckert et al., 1995*).
- Removal of alkylphenol ethoxylates is reduced at lower temperatures. This effect was not reported for LAS *(Painter et al., 1978, Stiff et al., 1973*), AE (*Kravetz et al., 1991*) or less pronounced for LAS/AE (*Birch, 1991*).
- LAS/AE degradation rates are not correlated with overall microbial activity, (*Knaebel et al., 1990*).
- Seasonal fluctuations in removal and mineralisation rates of LAS over a temperature range of 4 to 30°C, (e.g. *Palmisano et al., 1991, Takada et al., 1992, Quiroga and Sales, 1989*).

Based on the above stated fact it is reasonable to suggest that seasonal temperature variability does not affect the surfactant removal efficiency. Even more so in relation to this study, where the monitoring program runs over one week and in this way only includes daily variations. The temperature will influence the solubility of the phthalates but again in the present study this can be neglected.

## 4.1 Microbial and abiotic degradation

The microbial degradability is depending on a number of factors. In Table **8** a summary is shown with respect to chemical properties of the substance, environmental conditions and biomass.

***Table 8.*** Important properties with respect to microbial degradation.

| ***Chemical properties*** | ***Environmental conditions*** | ***Biomass*** |
|---|---|---|
| Molecular weight | Oxygen concentration | Inoculum source |
| Molecular size | Substance concentration | Lag phase |
| Polymerisation | Nutrient salts, mineral tracers, | Degradation of specific |
| Aromacity | | substance as |
| Substitution | vitamins | only carbon source |
| Branching | (Temperature, see above) pH | Degradation of specific |
| Solubility | | substance in |
| | Suspended matter, surface area | mixtures |
| | Other organic substances | |

Only the free dissolved substance is assumed to be degraded by the action of the viable biomass. The dissolved phase of the phthalates comprises molecular aggregates or micro droplets and free molecules, where the latter is very low due to the low solubility, *Hvidt et al., (2000)* cf. section 3.2.2. The bio-degradation rate is based on the Monod-expression (e.g. *Schnoor, 1996*)

$$\frac{dC_S(bio)}{dt} = - \frac{\mu}{Y} \cdot \frac{C_S}{C_S + K_S} \cdot \frac{C_{ox.}}{C_{ox.} + K_{ox.}} \cdot C_{X_B} \quad \left[ \frac{\text{mg S}}{\text{liter} \cdot \text{sec.}} \right] \qquad (3)$$

The predominant removal process is microbial transformation occurring under aerobic or anoxic conditions performed by bacteria, algae or fungi. In the primary settler the concentration of active biomass is too low for bio-degradation to occur, and in the secondary settler the electron acceptor concentrations are negligible.

The following assumptions are made

Under all conditions, aerobic as well as anoxic, the concentration of the electron acceptor is much larger than the corresponding half saturation constant ($C_{ox.} >> K_{ox.}$). This approximation is appropriate since on-line measurements of oxygen and nitrate enable variations of sewage volumes in the N and D reactors respectively that optimise the degradation conditions.

The concentration of the dissolved degradable substance is much smaller than the half saturation constant ($C_S << K_S$), which is true for most substances in WWTP's.

The biomass specific to the actual substance is assumed to be active at all times and the concentration is constantly low in time and equal in all the bio-reactors.

The ratio $\mu/Y$ is constant regardless of the biomass and substance concentrations. This approximation is very rough and is only true within narrow concentration limits *(Mikkelsen, 1994)*.

On basis of these approximations Equation **3** can be transformed to Equation **4** by introducing a pseudo 1st order bio-degradation rate constant, $k_{1bio}$.

$$\frac{dC_S(bio)}{dt} = - k_{1bio} \cdot C_S \quad \left[\frac{mg\ S}{liter \cdot sec.}\right] \qquad (\mathbf{4})$$

where

$$k_{1bio} = \frac{\mu}{Y} \cdot \frac{1}{K_S} \cdot C_{X_B} \quad \left[\frac{1}{sec.}\right] \qquad (\mathbf{5})$$

The abiotic degradation is assumed to be negligible in activated sludge plants for the considered substances. In principle, however, it can be included by assuming 1st order rate constants equivalent to Equation **4**

$$\frac{dC_S(abio)}{dt} = - (k_{1ph} + k_{1ox} + k_{1vol} + k_{1pr}) \cdot C_S \quad \left[\frac{mg\ S}{liter \cdot sec.}\right] \qquad (\mathbf{6})$$

Where $k_{1ph}$, $k_{1ox}$, $k_{1vol}$ and $k_{1pr}$ are the pseudo 1.order rate constants for photolysis, oxidation, volatilisation and precipitation respectively. The constants are defined for the dissolved bio-degradable substance S, see Figure **10**.

## 4.2 Sorption and solvation

Sorption is an important process when predicted environmental concentrations (PEC) are determined due to the many kinds of surfaces that are present in the different environmental compartments and in other highly heterogeneous systems such as WWTP's.

It is assumed that removal processes such as bio- and abiotic degradation and hydrolysis occur only in the dissolved phase but for hydrophobic substances such as LAS and DEHP adsorption to particulate matter (sludge) and sedimentation is a very significant removal mechanism. Combined with the high bio-degradation rate the overall removal of LAS from WWTP's is around 98% *(e.g. Painter et al., 1989)*. The phthalates are highly hydrophobic and are therefore only sparingly soluble *(Hvidt et al., 2000)*. The low saturation concentrations are dependant on the chemical "environment", i.e. complexing agents, particulate matter et al.

The substances can attach to surfaces in two ways. In physical adsorption there is a van der Waals interaction between the adsorbate and the substance forming bonds that have long ranges but are very weak. In chemical adsorption the substances form chemical bonds (usually covalent) to the surface resulting in strong adsorption. Generally the substances of interest are non-ionic and thus prefer the organic carbon phase of the particulates to the more polar aqueous phase. It is thus an adsorption phenomenon rather than a surface reaction. The adsorption process is assumed to leave the molecular structures of the substances virtually unaltered.

In the model set-up it is assumed that the adsorption-desorption processes are instantaneous, reversible and linear in concentrations. Sorption reactions usually reach chemical equilibrium rapidly compared to other processes in the system, and the kinetic relationships related to adsorption can be assumed to be steady-state. The reversibility is true in some cases but for highly hydrophobic substances, such as the phthalates, the adsorption will be very strong and reversibility is doubtful. 1$^{st}$ order irreversible adsorption has been shown to describe soil adsorption more satisfactorily *(Sørensen, 1999)*.

Different regimes for simulating adsorption capacities can be employed. The Langmuir adsorption model is defined by a maximum adsorption capacity that is related to a monolayer coverage of surface sites, which is representative of a wide range of equilibrium sorption isotherms for organic adsorbates in natural waters *(Schnoor, 1996)*.

In the following it is assumed that one mol of adsorbed substance occupies one mol of sites on the adsorbate. The equilibrium between a substance in solution, S, with concentration $C_S$ [mol · litre$^{-1}$], an adsorbate, X, with a concentration of available sites $C_X$ [mol · litre$^{-1}$], and the adsorption complex, S-X, which occupies sites corresponding to the concentration $C_{S\text{-}X}$ [mol · litre$^{-1}$], can be defined according to

$$S + X \leftrightarrow S\text{-}X \qquad (7)$$

When unit activity coefficients are assumed the equilibrium constant yields

$$K_L = \frac{C_{S\text{-}X}}{C_S \cdot C_X} \quad \left[\frac{\text{liter}}{\text{mol}}\right] \tag{8}$$

Combined with the mass balance for the total number of sites on the adsorbate

$$C_{X,total} = C_X + C_{S\text{-}X} \tag{9}$$

the concentration of adsorbed substance is

$$C_{S-X} = \frac{K_L \cdot C_S \cdot C_{X,\,total}}{\left(1 + K_L \cdot C_S\right)} \quad \left[\frac{\text{mol}}{\text{liter}}\right] \tag{10}$$

When the number of available sites is large compared to the number of occupied sites, i.e. $K_L \cdot C_S << 1$, there is a linear relationship between the concentration of dissolved substance and the concentration of adsorbed substance, cf. Equation **11**. This assumption is valid for a WWTP system where the particulate mass is high.

$$C_{S-X} = K_L \cdot C_S \cdot C_{X,total} \quad \left[\frac{\text{mol}}{\text{liter}}\right] \tag{11}$$

For a specific adsorbate the concentration of available sites can be expressed through the particulate dry matter concentration, $C_{XB}$. The adsorption constant specific for this adsorbate, is transformed into the coefficient $K_d$.

$$C_{S-X} = K_d \cdot C_S \cdot C_{X_B} \quad \left[\frac{\text{mg S}}{\text{liter}}\right] \tag{12}$$

$K_d$ [litre · (kg D.W.)$^{-1}$] is a measure of the actual partition in natural waters that can be empirically derived from $K_{ow}$, $f_{oc}$ and $K_{oc}$ in environmental matrices where the organic carbon content is larger than 0.05 - 0.1%. When the organic content is lower there is an increasing tendency for adsorption to the inorganic parts of the matrix. This phenomenon is more pronounced for polar organic substances.

$K_{ow}$ and $K_{oc}$ values are given in the literature for a number of organic chemicals of environmental interest. Further details concerning the definitions of the coefficients can be found in e.g. *Schwartzenbach et al. (1993)* and *Schnoor (1996)*. In the present study $K_d$ values are found from calibration of the WWTP model with experimental data.

The $K_d$ value is characteristic for a specific biomass and in the modelled WWTP it is assumed that there exist two different “species” of suspended matter (sludge). In the inlet and in the primary settler the active biomass concentration is low and the amount of suspended organic matter is high. In the primary settler a large amount is settled out, after which the suspended matter in the biological reactors and the secondary settler

is predominantly consisting of active biomass formed during the aerobic, anoxic and anaerobic processes. Two different values, $K_{d,inlet}$ and $K_{d,reactor}$ respectively, can be assigned to the these suspended phases.

*Furtmann (1996)* found $K_d$ values for seven different phthalates in fresh sludge and activated sludge. They are calculated from measured dissolved and adsorbed concentrations and show higher $K_d$ values for activated sludge by a factor of approximately 10. The differences could, however, be a consequence of more pronounced degradation of dissolved substance in the activated sludge combined with negligible desorption, rather than different $K_d$ values

Characteristic $K_d$ values for substances such as LAS and DEHP in WWTP sewage are in the interval 1,000 – 20,000 litre · (kg D.W.)$^{-1}$. In soil and sediment the values are higher (*Furtmann, 1996*).

*Karichoff et al., (1979)* found that the adsorption of hydrophobic substances to sediments is linearly correlated to the organic content, given that the equilibrium concentration in the aquatic phase is below ½ the saturation concentration. In most cases linear relationships, according to Equation **11**, will describe the sorption processes satisfactorily (*Thomsen et al., 1998*).

For substances that are sparingly soluble, such as the phthalates, it is necessary to consider the solubility properties in relation to micelle formation or mechanisms that removes the substance from its molecular dissolved state to a state of non-degradability. Due to the hydrophobicity of the phthalates the dissolved state generally comprises molecular aggregates (or microdroplets) even at very low concentrations. With densities approximate to that of water these colloids will not form a separate phase but rather remain homogeneously distributed within the aqueous phase.

The solubility of phthalates is influenced by ionic strength, pH, temperature and the presence of co-solutes such as surfactants and other micelle formers that will increase the apparent solubility and mobility (*Thomsen et al., 1998*).

The solubility decreases with increasing molecular weight. The tendency for aggregate formation increases accordingly which results in an overestimation of the solubility of phthalates with alkyl chains longer than $C_6$ (*Howard et al., 1985 and Pedersen et al., 1996 and Hvidt et al., 2000*). However, In the present work, where the alkyl chains range between $C_4$ and $C_9$, the solubilities are approximated to follow the linear sorption isotherm in Equation **11**. Furthermore the total aqueous concentration is measured in the environmental samples and this comprises free as well as aggregated molecules.

## 4.3 Hydrolysis

Some substances entering the WWTP are not bio-degradable and in many cases the molecular sizes are determining for the accessibility to micro organisms. If such molecules are to be degraded they must first be divided into smaller substances. Chemical hydrolysis is a pathway by which an organic chemical reacts with water molecules or hydroxide ions and splits into smaller more polar products often with different chemical properties and environmental behaviour. The free energy related to such a process has a large negative value which implies that the reaction is irreversible.

Types of substances that are susceptible to chemical hydrolysis are

Alkyl halides, amides, amines, carbamates, carboxylic acid esters, epoxides, nitriles, phosphonic acid esters, phosphoric acid esters, sulfonic acid esters and sulfuric acid esters (*Schnoor, 1996*).

The hydrolysis rate is very sensitive to pH, but at a given pH and temperature the chemical hydrolysis rate can be reduced to a pseudo 1st order reaction rate constant analogous to Equation **4**.

Phthalates are carboxylic acid esters and nonylphenols are phenol esters and can therefore undergo chemical hydrolysis but more often enzymatically catalysed hydrolysis performed by extracellular enzymes synthesised by micro organisms is considered in WWTP's. In this type of hydrolysis structural rearrangements will occur for dissolved, adsorbed, degradable as well as non degradable substances. Since the process is often slower than the bio-degradation it is the rate determining step in WWTP's.

When organic particles, such as plant parts or soil particles, contain incorporated substances in their organic cluster, the breakdown of this cluster by hydrolysis mediates further bio-degradation of the dissolved substance. The removal rate is now dependant on the chemical structure and the surface area of the particles.

The hydrolysis step involves transformation of the original non degradable substance, O, into a smaller degradable substance, S.

If it is assumed that enzymatically catalysed hydrolysis only occurs in the aqueous phase and that it is dependant on the present electron acceptor (oxygen or nitrate), the rate can be described by the empirical Equation **13**.

$$\frac{dC_S}{dt} = \frac{-dC_O}{dt} =$$

$$k_h \cdot \frac{\frac{C_O}{C_{X_B}}}{K_X + \frac{C_O}{C_{X_B}}} \cdot \left( \left( \frac{C_{O_2}}{K_{O_2} + C_{O_2}} \right) + \eta \cdot \left( \frac{K_{O_2}}{K_{O_2} + C_{O_2}} \right) \cdot \left( \frac{C_{NO_3}}{K_{NO_3} + C_{NO_3}} \right) \right) \cdot C_{X_B} \quad \textbf{(13)}$$

Where $\eta$ is a correction factor for anoxic hydrolysis.

The expression

$$k_h \cdot \frac{\frac{C_O}{C_{X_B}}}{K_X + \frac{C_O}{C_{X_B}}} \cdot C_{X_B}$$

is a measure of the hydrolysis rate of a specific microbial species. When $C_O >> C_{XB}$ the rate is “saturated”.

The fractions in the brackets in Equation **13** describe the dependence on the concentration and type of electron acceptor.

The following assumptions are made

The concentration of hydrolysable substance is much smaller than the biomass concentration, $C_O << C_{XB}$.

Under aerobic conditions $C_{O2} >> K_{O2}$, $C_{O2} >> C_{NO3}$ and $C_O << C_{XB}$, giving

$$\frac{dC_O}{dt} = - k_{hy} \cdot \frac{C_O}{K_X} = - k_{1hy,O_2} \cdot C_O \quad \left[\frac{\text{mg O}}{\text{liter} \cdot \text{sec.}}\right] \qquad (\mathbf{14})$$

Under anoxic conditions $C_{NO3} >> K_{NO3}$, $C_{O2} = 0$ and $C_O << C_{XB}$, giving

$$\frac{dC_O}{dt} = - k_{hy} \cdot \frac{C_O}{K_X} \cdot \eta = - k_{1hy,NO_3} \cdot C_O \quad \left[\frac{\text{mg O}}{\text{liter} \cdot \text{sec.}}\right] \qquad (\mathbf{15})$$

Under anaerobic conditions $C_{NO3} = 0$, $C_{O2} = 0$ and $C_O << C_{XB}$, giving

$$\frac{dC_O}{dt} = 0 \qquad (\mathbf{16})$$

In the primary settler the biomass concentration is low and in the secondary settler the electron acceptor concentrations are low, resulting in negligible hydrolysis.

## 4.4 Overall substance removal

If the original substance is non degradable, hydrolysis is a necessary first step in substance removal. In this work no differentiation is made between removal caused by hydrolysis or bio-degradation. As soon as the original chemical structure of the substance is changed it is considered to be removed from the system.

Therefore the overall pseudo 1st order reaction rate constant, $k_1$, for a readily bio-degradable substance is described by Equation **17** while Equation **18** can be used when hydrolysis is necessary.

$$\frac{dC_S}{dt} = - (k_{1bio} + k_{1abio}) \cdot C_S = - k_1 \cdot C_S \quad \left[\frac{\text{mg S}}{\text{liter} \cdot \text{sec.}}\right] \qquad (\mathbf{17})$$

$$\frac{dC_O}{dt} = - k_{1hy} \cdot C_O = - k_1 \cdot C_O \quad \left[\frac{\text{mg O}}{\text{liter} \cdot \text{sec.}}\right] \qquad (\mathbf{18})$$

The substances that are considered in this work, LAS, phthalates and nonylphenols are estimated to be bio-degradable under aerobic as well as anoxic conditions and therefore Equation **17** is used in the following to define the pseudo 1st order removal rate in the biological reactors.

It is, however, more relevant to define the degradability in terms of a half-life, $t_{½}$, which is the time required to reduce the initial concentration by a factor of 2.

$$t_{½} = \frac{\ln(2)}{\frac{k_1}{R_{bio}}} \quad [\text{hours}] \qquad (\mathbf{19})$$

The concentration in Equation **19** is expressed as the *total* concentration, through the retention factor $R_{bio}$. $R_{bio}$ is commented further in Equation **29**.

## 4.5 Sedimentation and removal of sludge

Substances that are adsorbed on particulate matter can be removed from the sewage by sedimentation followed by sludge removal. The biological reactors are totally mixed and the sludge will therefore remain suspended and only be removed from the reactors with the advective flow. In the primary and secondary settlers the volumes are assumed to be divided into two totally mixed partitions, i.e. a sewage part and a settled sludge part.

The active biomass concentration at the inlet is low and accordingly the biomass in the reactors and the secondary settler originates from the biological growth processes. In this work the biomass production is not calculated analytically, but estimated on basis of dry weight measurements at the inlet, outlet and biological reactors.

It is estimated that 75 wt-% of the suspended matter entering the primary settler, $C_{XB,in}$, is removed as primary sludge, $C_{XB,PSsludge}$, thus

$$0.75 \cdot 0.3 \cdot Q \cdot C_{X_B,in} = q_{PS} \cdot C_{X_B,PSsludge} \Leftrightarrow$$

$$C_{X_B,PSsludge} = \frac{0.75 \cdot 0.3 \cdot Q \cdot C_{X_B,in}}{q_{PS}} = 5.0 \cdot C_{X_B,in} \quad \left[\frac{\text{kg } X_B}{\text{liter}}\right] \qquad (\mathbf{20})$$

The concentration of suspended matter leaving with the clarified water, $C_{XB,PSout}$, becomes

$$0.25 \cdot 0.3 \cdot Q \cdot C_{X_B,in} = (0.3 \cdot Q - q_{PS}) \cdot C_{X_B,PSout} \Leftrightarrow$$

$$C_{X_B,PSout} = \frac{0.25 \cdot 0.3 \cdot Q \cdot C_{X_B,in}}{(0.3 \cdot Q - q_{PS})} = 0.29 \cdot C_{X_B,in} \quad \left[\frac{kg\ X_B}{liter}\right] \qquad (21)$$

The biomass concentration entering the biological reactors, $C_{XB,bioin}$, and the biomass concentration in the sludge out take from the secondary settler, $C_{XB,SSsludge}$, can be calculated from mass balances around the primary and secondary settler respectively, yielding

$$Q \cdot C_{X_B,in} + q_R \cdot C_{X_B,SSsludge} =$$

$$q_{PS} \cdot C_{X_B,PSsludge} + (Q + q_R - q_{PS}) \cdot C_{X_B,bioin} \Leftrightarrow$$

$$C_{X_B,bioin} =$$

$$\frac{Q \cdot C_{X_B,in} + q_R \cdot C_{X_B,SSsludge} - q_{PS} \cdot C_{X_B,PSsludge}}{(Q + q_R - q_{PS})} \quad \left[\frac{kg\ X_B}{liter}\right] \qquad (22)$$

and

$$(Q + q_R - q_{PS}) \cdot C_{X_B,bio} =$$

$$(q_R + q_{SS}) \cdot C_{X_B,SSsludge} + (Q - q_{SS} - q_{PS}) \cdot C_{X_B,SSout} \Leftrightarrow$$

$$C_{X_B,SSsludge} =$$

$$\frac{(Q + q_R - q_{PS}) \cdot C_{X_B,bio} - (Q - q_{SS} - q_{PS}) \cdot C_{X_B,SSout}}{(q_R + q_{SS})} \quad \left[\frac{kg\ X_B}{liter}\right] \qquad (23)$$

The sludge in the WWTP basically consists of two different “species”. In the inlet and in the primary settler the active biomass concentration is low and the suspended organic matter is mainly consisting of degradable or slowly degradable organic matter in concentrations around $5 \cdot 10^{-4}$ kg $X_B \cdot litre^{-1}$. In the biological reactors and the secondary settler the sludge concentration is high and is predominantly consisting of active biomass formed during the aerobic, anoxic and anaerobic processes. The concentration in the biological reactors are approximately $5 \cdot 10^{-3}$ kg $X_B \cdot litre^{-1}$.

The sludge is recycled once a day with a flow of $0.6 \cdot Q$, and the sludge age is approximately 20 days, which implies that the sludge at the biological reactor inlet predominantly consists of one sludge “species”, i.e. recycled biomass generated from the growth processes.

# 5 Experimental data

An experimental series was performed during the 15 to the 23 of May 1999. The following samples were taken

- With an automatic sampler, see Figure **11**, 6 composite sewage inlet samples were collected each day in 1 litre glass bottles.

The sampler was placed after the grating and before the fat trap approximately 1.5 m above the sewage stream. Every half hour 80 ml was pumped into a glass bottle and every 4 hours the bottle was automatically renewed, resulting in a total sample volume of 640 ml per bottle. To avoid cross contamination in the tubes a rinsing cycle was executed prior to and after every sampling.

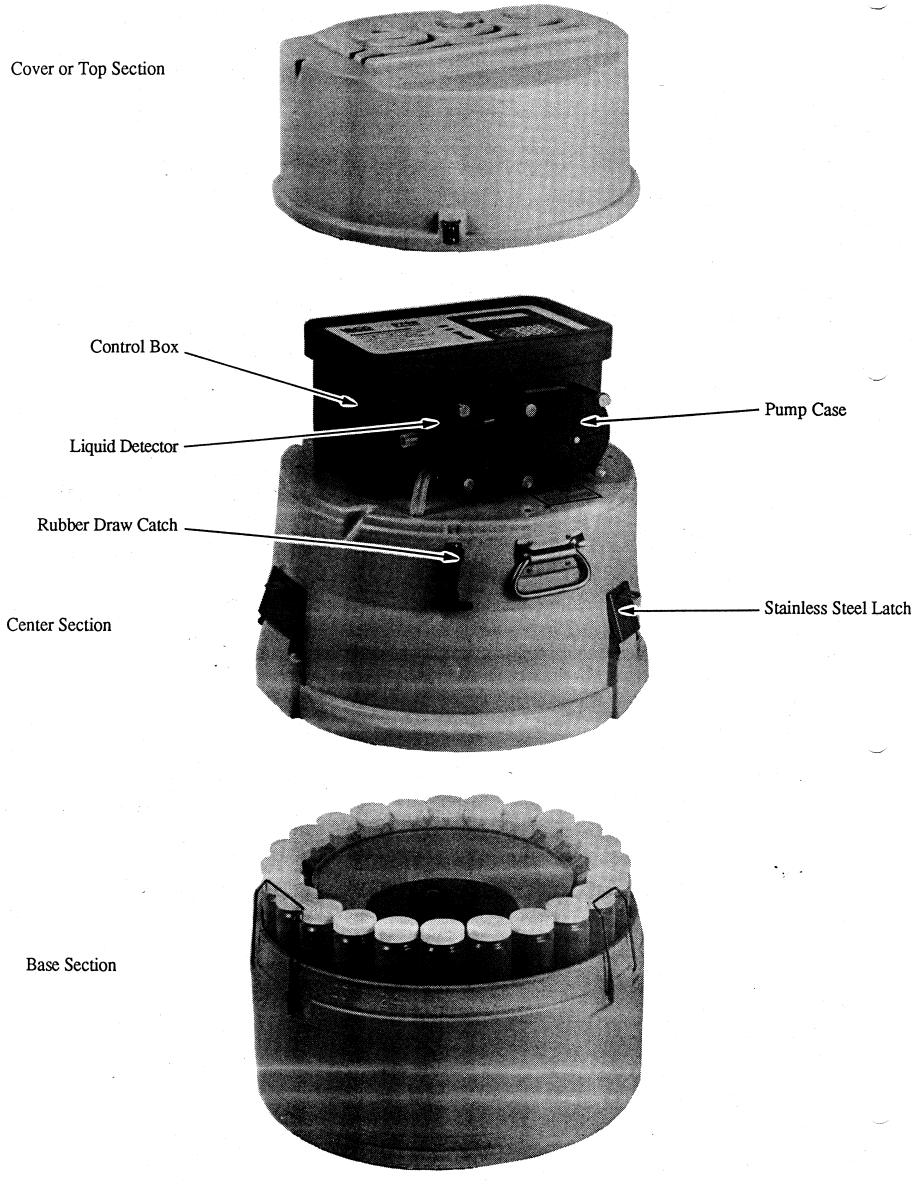



***Figure 11.*** *ISCO 3700 portable sampler.*

To obtain a picture of the daily mean sewage flow *one* composite inlet sample was produced per day by mixing the 6 samples proportional to flow variations, that was registered continuously in 1 hour intervals, cf. Figure **12**.

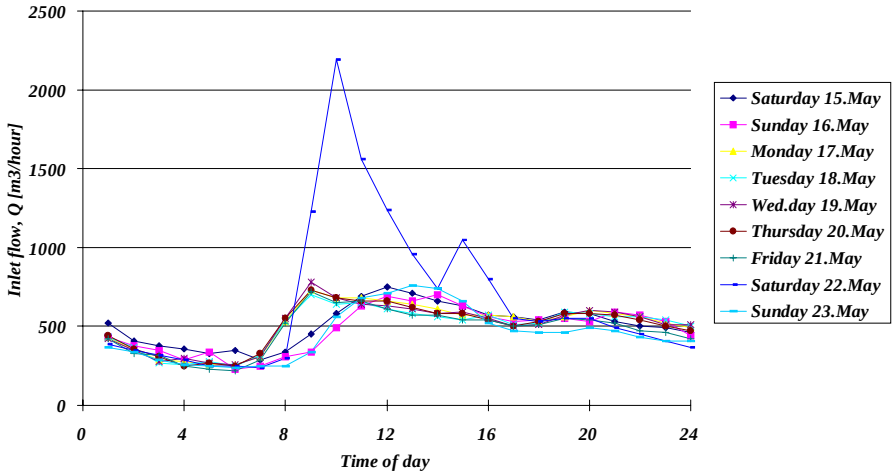



***Figure 12.*** *Inlet flow variations during sampling period in May 1999.*

***Table 9.*** Measured inlet flow data during 9 days in May 1999. The rain sampler was placed at the WWTP.

| ***Day*** | ***Mean hourly inlet flow, $Q_{h,mean}$ [$m^3 \cdot hour^{-1}$]*** | ***Maximum hourly inlet flow, $Q_{h,max}$ [$m^3 \cdot hour^{-1}$]*** | ***Minimum hourly inlet flow, $Q_{h,min}$ [$m^3 \cdot hour^{-1}$]*** |
|---|---|---|---|
| Saturday 15. May<br>1.4 mm rain | 511 ± 129 | 750 | 290 |
| Sunday 16. May<br>0.0 mm rain | 482 ± 142 | 700 | 230 |
| Monday 17. May<br>0.0 mm rain | 510 ± 145 | 730 | 260 |
| Tuesday 18. May<br>0.0 mm rain | 497 ± 134 | 700 | 250 |
| Wed.day 19. May<br>0.0 mm rain | 506 ± 143 | 780 | 260 |
| Thursday 20. May<br>0.0 mm rain | 503 ± 141 | 730 | 250 |
| Friday 21. May<br>0.0 mm rain | 475 ± 139 | 720 | 220 |
| Saturday 22. May<br>0.0 mm rain | 669 ± 485 | 2190 | 240 |
| Sunday 23. May<br>3.2 mm rain | 451 ± 165 | 760 | 240 |
| 8 day mean<br>0.5 ± 1.1 mm rain | 492 ± 356 | 734 ± 28 | 250 ± 21 |

The flow data from Saturday 22. May is omitted as outlier. The extreme values are caused by rainfall in the outskirts of the catchment area that were not registered on the rain sampler at the WWTP.

The 8 day mean hourly inlet flow is thus

$Q_{h,mean8days} = 492 \pm 356\ m^3 \cdot hour^{-1}$

The pooled standard deviation is calculated from (*Skoog et al., 1992*)

$$s_{pooled} = \sqrt{\frac{\sum_{i=1}^{N_1}\left(x_i - \overline{x_1}\right)^2 + \sum_{j=1}^{N_2}\left(x_j - \overline{x_2}\right)^2 + \sum_{k=1}^{N_3}\left(x_k - \overline{x_3}\right)^2 + .....}{N_1 + N_2 + N_3 + ..... - N_s}} \quad (\mathbf{24})$$

where $N_1$ is the number of data in series 1 (Saturday 15. May), $\overline{x_1}$ is the mean value for series 1 and $N_s$ is the number of subseries (days) being pooled ($N_s = 8$). $s_{pooled}$ is an estimate of the standard deviation that is superior to the value for any individual subseries (day) or the overall standard deviation.

$Q_{h,mean8days}$ will be used to calibrate the models when the sludge concentrations are concerned. When the outlet concentrations for a given day is simulated the daily mean inlet flow (column 2 in Table **9**) for the same day, $Q_{h,mean}$, is used as input parameter.

- One 1.2 litre bulk water sample was taken at 12 o'clock each day in a glass bottle at the WWTP outlet.

The concentration variations that can be found at the sewage inlet are under normal conditions not discernible at the outlet, due to the mixing and degradation in the reactors. The alternate flow cycle can, however, cause some fluctuations in the outlet concentrations depending on the removal rates and flow. This will be discussed further in the modelling section.

- One grab sample was taken from the primary sludge immediately before the concentration reactor and from the secondary sludge, respectively, during the sampling period.

The residence time of the primary sludge is approximately 1 day, and approximately 20 days (sludge age) for the secondary sludge. The final digested sludge that is ready for soil amendment is a mixture with varying ratios of the primary and secondary sludge, and it is therefore not feasible to relate any overall sludge concentration to a specific daily inlet concentration.

The inlet and sludge samples are centrifuged. LAS is measured in the supernatant and the settled matter according to the experimental procedure described in *Carlsen et al. (2000)* omitting the microwave extraction and initial solid phase extraction for the aqueous samples. Phthalates, NP and NPDE are measured according to the experimental procedure in *Vikelsøe et al. (2000)*.

Preliminary experiments showed low concentrations in the outlet bulk phase and measurement of total samples are therefore performed.

To avoid contamination and adsorption losses to glass surfaces the samples are stored in as few bottles as possible.

Tables **10** and **11** show the measured daily mean concentrations for the composite inlet samples and for the outlet, primary and secondary sludge grab samples respectively, with respect to total, dissolved and adsorbed LAS, phthalate, NP and NPDE concentrations, respectively. In Table **12** the 8 day mean concentrations derived from Table **10** are stated.

The experimental results will be used to calibrate the models with respect to $k_{1N}$, $k_{1D} \cdot k_{1N}^{-1}$ and $K_d$.

***Table 10.*** Measured inlet and outlet concentrations from WWTP allowing for blank values. Sampled during eight days in May 1999.
Phthalates, NP and NPDE in µg · litre$^{-1}$. LAS in mg · litre$^{-1}$. Phthalates, NP and NPDE inlet total measurements are duplicate determinations unless otherwise stated.
LAS inlet supernatant and outlet total are duplicate determinations.

| | ***Saturday 15. May*** | | | | ***Sunday 16. May*** | | | | ***Monday 17. May*** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ***Inlet total*** | ***Inlet supernat.*** | ***Inlet settled*** | ***Outlet total*** | ***Inlet total*** | ***Inlet supernat.*** | ***Inlet settled*** | ***Outlet total*** | ***Inlet total*** | ***Inlet supernat.*** | ***Inlet settled*** | ***Outlet total*** |
| **LAS** | - | 1.41 | 3.12 | | | | | 0.007 | - | 1.38 | 1.83 | 0.009 |
| **DEHP** | 13.1 ± 0.52 | 2.37 | 17.8 | | | | | 0.11 | 34.5 ± 1.52 | 7.83 | 31.6 | 0.20 |
| **DPP** | 0.02 ± 0.01 | n.d. | 0.07 | | | | | n.d. | 0.05 ± 0.0 | 0.04 | 0.04 | n.d. |
| **DBP** | n.d. | n.d. | n.d. | | | | | n.d. | n.d. | n.d. | n.d. | n.d. |
| **BBP** | 0.53 ± 0.03 | 0.46 | 0.34 | | | | | n.d. | 0.05 ± 0.03 | 0.12 | 0.14 | n.d. |
| **DnOP** | 0.22 ± 0.0 | 0.00 | 0.45 | | | | | 0.00 | 0.43 ± 0.23 | 0.10 | 0.62 | 0.00 |
| **DnNP** | 0.11 ± 0.01 | n.d. | 0.29 | | | | | 0.00 | 0.56 ± 0.21 | 0.02 | 0.53 | 0.00 |
| **NP** | 2.75 ± 0.15 | 3.42 | 2.45 | | | | | 0.14 | 7.38 ± 1.12 | 3.71 | 3.99 | 0.18 |
| **NPDE** | 37.1 ± 1.17 | 13.9 | 30.6 | | | | | 0.68 | 155.4 ± 16.65 | 62.2 | 84.1 | 1.20 |
| | ***Tuesday 18. May*** | | | | ***Wednesday 19. May*** | | | | ***Thursday 20. May*** | | | |
| | ***Inlet total*** | ***Inlet supernat.*** | ***Inlet settled*** | ***Outlet total*** | ***Inlet total*** | ***Inlet supernat.*** | ***Inlet settled*** | ***Outlet total*** | ***Inlet total*** | ***Inlet supernat.*** | ***Inlet settled*** | ***Outlet total*** |
| **LAS** | - | 1.48 | 1.54 | 0.017 | - | 1.20 | 2.12 | 0.009 | - | 1.27 | 1.51 | 0.007 |
| **DEHP** | 36.6 ± 0.00 | 5.89 | 35.8 | 0.27 | 39.5 ± 4.10 | 5.85 | 39.5 | 0.76 | 44.3 ± 0.62 | 3.87 | 47.4 | 1.72 |
| **DPP** | 0.14 | n.d. | 0.10 | n.d. | n.d. | 0.06 | 0.08 | 0.00 | n.d. | n.d. | 0.10 | 0.00 |
| **DBP** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | 0.23 | n.d. | n.d. | n.d. | 0.71 |
| **BBP** | 0.40 ± 0.06 | 0.14 | 0.17 | n.d. | 0.40 ± 0.39 | 0.21 | 0.17 | 0.06 | 0.20 ± 0.05 | 0.08 | 0.10 | 0.10 |
| **DnOP** | 0.57 ± 0.11 | 0.07 | 0.66 | 0.0 | 0.67 ± 0.00 | 0.18 | 0.54 | 0.01 | 0.73 ± 0.10 | 0.04 | 0.71 | 0.03 |
| **DnNP** | 0.44 ± 0.16 | 0.0 | 0.47 | 0.0 | 0.48 | 0.12 | 0.42 | 0.01 | 0.56 ± 0.15 | n.d. | 0.54 | 0.02 |
| **NP** | 6.18 ± 0.98 | 3.47 | 4.00 | 0.37 | 10.2 ± 2.29 | 4.75 | 6.46 | 0.32 | 6.62 ± 0.47 | 3.16 | 3.64 | 0.29 |
| **NPDE** | 60.0 ± 0.80 | 16.6 | 33.6 | 2.95 | 157.1 ± 53.64 | 63.5 | 113.2 | 2.59 | 113.2 ± 17.25 | 19.7 | 60.4 | 2.29 |

-: Not measured.
Blank space: No sample.
n.d.: Not detected (blank samples cf. Table **13**).

***Table 10***. Continued

| | ***Friday 21. May*** | | | | ***Saturday 22. May*** | | | | ***Sunday 23. May*** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ***Inlet total*** | ***Inlet supernat.*** | ***Inlet settled*** | ***Outlet total*** | ***Inlet total*** | ***Inlet supernat.*** | ***Inlet settled*** | ***Outlet total*** | ***Inlet total*** | ***Inlet supernat.*** | ***Inlet settled*** | ***Outlet total*** |
| **LAS** | - | 1.58 | 1.46 | 0.009 | - | 0.88 | 1.59 | | | | | 0.020 |
| **DEHP** | 43.9 ± 6.44 | 4.31 | 43.0 | 1.01 | 36.1 ± 10.74 | 6.61 | 24.7 | | | | | 2.65 |
| **DPP** | 0.10 | 0.01 | n.d. | 0.01 | 0.05 ± 0.00 | 0.04 | 0.05 | | | | | 0.02 |
| **DBP** | n.d. | n.d. | n.d. | 0.18 | 1.03 ± 0.14 | 0.28 | 0.33 | | | | | 2.50 |
| **BBP** | 0.21 ± 0.01 | 0.06 | 0.25 | 0.09 | 0.97 ± 0.08 | 0.53 | 0.37 | | | | | 0.27 |
| **DnOP** | 0.79 ± 0.08 | 0.04 | 0.87 | 0.02 | 0.56 ± 0.11 | 0.37 | 0.44 | | | | | 0.03 |
| **DnNP** | 0.56 ± 0.17 | n.d. | 0.76 | 0.02 | 0.34 ± 0.02 | 0.06 | 0.37 | | | | | 0.04 |
| **NP** | 9.65 ± 0.21 | 3.24 | 3.46 | 0.31 | 7.28 ± 1.29 | 3.32 | 2.50 | | | | | 0.69 |
| **NPDE** | 216.8 ± 15.41 | 42.3 | 93.7 | 1.85 | 82.6 ± 2.89 | 24.0 | 25.0 | | | | | 2.54 |

-: Not measured.
Blank space: No sample.
n.d.: Not detected (blank samples cf. Table **13**).

***Table 11.*** Measured primary and secondary sludge concentrations from WWTP allowing for blank values. Sampled 18. May 1999. Phthalates, NP and NPDE in μg · gD.W.$^{-1}$. LAS in mg · gD.W.$^{-1}$. LAS supernatant, phthalates, NP and NPDE are duplicate determinations.

| | ***Tuesday 18. May*** | | | | | |
|---|---|---|---|---|---|---|
| | ***Primary sludge total*** | ***Primary sludge supernat.*** | ***Primary sludge settled*** | ***Sec. sludge total*** | ***Sec. sludge supernat.*** | ***Sec. sludge settled*** |
| **LAS** | - | 0.67 | 4.37 | - | 0.010 | 0.084 |
| **DEHP** | 61.11 ± 3.20 | - | - | 3.51 ± 0.03 | - | - |
| **DPP** | 0.01 | - | - | n.d. | - | - |
| **DBP** | 0.65 ± 0.25 | - | - | 0.16 | - | - |
| **BBP** | 0.50 ± 0.32 | - | - | 0.01 ± 0.0 | - | - |
| **DnOP** | 1.00 ± 0.08 | - | - | 0.05 ± 0.0 | - | - |
| **DnNP** | 0.95 ± 0.11 | - | - | 0.05 ± 0.0 | - | - |
| **NP** | 11.95 ± 1.85 | - | - | 0.19 ± 0.01 | - | - |
| **NPDE** | 39.12 ± 3.81 | - | - | 1.28 ± 0.12 | - | - |

-: Not measured.
n.d.: Not detected (blank samples cf. Table **13**).

***Table 12.*** Measured 8 day mean inlet and outlet concentrations from WWTP allowing for blank values, derived from Table **10**. Phthalates, NP and NPDE in μg · litre$^{-1}$. LAS in mg · litre$^{-1}$.

| | ***8 day mean concentrations*** | | | |
|---|---|---|---|---|
| | ***Inlet total*** | ***Inlet supernat.*** | ***Inlet settled*** | ***Outlet total*** |
| **LAS** | - | 1.31 ± 0.23 | 1.88 ± 0.59 | 0.011 ± 0.005 |
| **DEHP** | 35.4 ± 10.6 | 5.25 ± 1.84 | 34.3 ± 10.4 | 0.96 ± 0.94 |
| **DPP** | 0.07 ± 0.05 | 0.04 ± 0.02 | 0.07 ± 0.03 | 0.008 ± 0.009 |
| **DBP** | 1.03 | 0.28 | 0.33 | 0.91 ± 1.09 |
| **BBP** | 0.39 ± 0.30 | 0.23 ± 0.19 | 0.22 ± 0.10 | 0.13 ± 0.09 |
| **DnOP** | 0.57 ± 0.19 | 0.11 ± 0.13 | 0.61 ± 0.15 | 0.013 ± 0.014 |
| **DnNP** | 0.44 ± 0.17 | 0.05 ± 0.05 | 0.48 ± 0.15 | 0.013 ± 0.015 |
| **NP** | 7.15 ± 2.46 | 3.58 ± 0.55 | 3.79 ± 1.34 | 0.33 ± 0.18 |
| **NPDE** | 118 ± 63.1 | 34.6 ± 21.4 | 62.8 ± 35.0 | 2.01 ± 0.82 |

-: Not measured.

In Table **13** the blank measurements are stated.

***Table 13.*** Blank values for inlet, outlet and sludge samples. Lower detection limit ≈ mean blank + 3 · standard deviation. All inlet and sludge analyses are duplicate determinations. Outlet are triplicate determinations.

| | ***Inlet total and supernatant [μg · litre$^{-1}$]*** | ***Inlet settled [μg · litre$^{-1}$]*** | ***Outlet total [μg · litre$^{-1}$]*** | ***Sludge total [μg · gD.W.$^{-1}$]*** |
|---|---|---|---|---|
| **DEHP** | 2.51 ± 0.02 | 2.29 ± 0.48 | 0.13 ± 0.01 | 0.26 ± 0.28 |
| **DPP** | 0.01 ± 0.01 | 0 | 0 | 0 |
| **DBP** | 5.14 ± 1.34 | 3.32 ± 1.00 | 0.47 ± 0.24 | 0.12 ± 0.04 |
| **BBP** | 0.15 ± 0.04 | 0.11 ± 0.01 | 0.01 ± 0.0 | 0 |
| **DnOP** | 0.11 ± 0.04 | 0 | 0 | 0 |
| **DnNP** | 0.11 ± 0.04 | 0 | 0 | 0.01 ± 0.01 |
| **NP** | 0.95 ± 0.04 | 0.69 ± 0.02 | 0.03 ± 0.03 | 0.03 ± 0.01 |
| **NPDE** | 1.92 ± 0.06 | 1.56 ± 0.20 | 0.07 ± 0.04 | 0.06 ± 0.01 |

The LAS blank value is an average of three determinations based on the analysis in *Carlsen et al. (2000)*. The value is used for all samples.

Blank (LAS) = 2.31 ± 0.13 mg LAS · (g or ml sample)$^{-1}$.

# 6 Modelling

## 6.1 Model parameters

For each number in the flow-sheet in Figures **8** and **9** (model 1) and Figure **16** (model 2) the following parameters are used or calculated in the model.

***Table 14.*** Input and output variables in WWTP model.

| ***N° in fig.*** *8 + 9* | ***Flow [litre · sec$^{-1}$]*** | | ***Suspended matter (sludge) [kg $X_B$ · litre$^{-1}$]*** | | ***Dissolved substance concentration [kg S · litre$^{-1}$]*** | |
|---|---|---|---|---|---|---|
| **0** | Q | [1] | $C_{XB,in}$ | [1+2] | $C_0$ | [3+5] |
| **1** | 0.7 · Q | [2] | $C_{XB,in}$ | [1+2] | $C_0$ | [3+5] |
| **2** | 0.3 · Q | [2] | $C_{XB,in}$ | [1+2] | $C_0$ | [3+5] |
| **3** | $q_{PS}$ = 0.3 · 0.15 · Q | [2] | $C_{XB,PSsludge}$ | [1+2] | $C_3$ | [4+5] |
| **4** | 0.3 · Q - $q_{PS}$ | [2] | $C_{XB,PSout}$ | [2] | $C_4$ | [4] |
| **5** | Q + $q_R$ - $q_{PS}$ | [2] | $C_{XB,bioin}$ | [2] | $C_5$ | [4] |
| **6** | Q + $q_R$ - $q_{PS}$ | [2] | $C_{XB,bio}$ | [2] | $C_6$ | [4] |
| **7** | Q + $q_R$ - $q_{PS}$ | [2] | $C_{XB,bio}$ | [2] | $C_7$ | [4] |
| **8** | 0 | [2] | $C_{XB,bio}$ | [2] | $C_8$ | [4] |
| **9** | Q + $q_R$ - $q_{PS}$ | [2] | $C_{XB,bio}$ | [2] | $C_9$ | [4] |
| **10** | Q + $q_R$ - $q_{PS}$ | [2] | $C_{XB,bio}$ | [2] | $C_{10}$ | [4] |
| **11** | Q + $q_R$ - $q_{PS}$ | [2] | $C_{XB,bio}$ | [2] | $C_{11}$ | [4] |
| **12** | Q + $q_R$ - $q_{PS}$ | [2] | $C_{XB,bio}$ | [2] | $C_{12}$ | [4] |
| **13** | Q - $q_{PS}$ -$q_{SS}$ | [2] | $C_{XB,SSout}$ | [1+2] | $C_{13}$ | [4+5] |
| **14** | $q_R$ = 0.6 · Q | [2] | $C_{XB,SSsludge}$ | [1+2] | $C_{14}$ | [4+5] |
| **15** | $q_{SS}$ = 0.6 · 0.05 · Q | [2] | $C_{XB,SSsludge}$ | [1+2] | $C_{15}$ | [4+5] |
| **(16)** | - | [2] | - | [2] | - | [4] |

[1]: Model input, measured.
[2]: Model input, estimated.
[3]: Model input, estimated from emission survey.
[4]: State variable, calculated in model.
[5]: State variable, measured.

**Measured model inputs**

$C_0$: Daily mean concentrations of dissolved substances in influent sewage [mg · litre$^{-1}$] (Table **10**)

Q: Hourly mean inlet flow = 492 ± 356 m$^3$ · hour$^{-1}$ (Table **9**)

$C_{XB,in}$: Concentration of influent SPM (7 day mean)
= 0.53 ± 0.40 gD.W. · litre$^{-1}$ (centrifuged).

$C_{XB,PSsludge}$: Concentration of SPM in primary sludge (Tuesday 18. May)

$$= \begin{cases} 2.46 \ \dfrac{\text{g D.W.}}{\text{liter}} \ \text{(centrifuged)} \\ 2.63 \ \dfrac{\text{g D.W.}}{\text{liter}} \ \text{(calculated from Equation 18)} \end{cases}$$

$C_{XB,SSout}$: Concentration of SPM in effluent from secondary settler = 0.03 gD.W. · litre$^{-1}$ (centrifuged).

$C_{XB,SSsludge}$: Concentration of SPM in secondary sludge (Tuesday 18. May)

$$= \begin{cases} 11.06 \ \frac{\text{g D.W.}}{\text{liter}} \text{ (centrifuged)} \\ 12.30 \ \frac{\text{g D.W.}}{\text{liter}} \text{ (calculated from Equation 21)} \end{cases}$$

$V_{PS}$: Volume of 2 primary settlers = 3000 m$^3$

$V_P$: Volume of 4 anaerobic P-reactors = 3000 m$^3$

$V_N$: Volume of 1 aerobic nitrifying reactor (4 bio-reactors in all) = 3650 m$^3$

$V_D$: Volume of 1 anoxic denitrifying reactor = see above for $V_N$

$V_{SS}$: Volume of 9 secondary settlers = 19.000 m$^3$

**Estimated model inputs**

$C_{XB,bio}$: Concentration of SPM in bio-reactors = 5 g D.W. · litre$^{-1}$

$q_{PS}$: Flow of primary sludge = 0.15 · 0.3 · Q = 22.1 ± 16.0 m$^3$ · hour$^{-1}$

$q_R$: Flow of recycled sludge = 0.6 · Q = 295 ± 214 m$^3$ · hour$^{-1}$

$q_{SS}$: Flow of secondary sludge = 0.05 · 0.6 · Q = 14.8 ± 12.7 m$^3$ · hour$^{-1}$

$f_{PS}$: Volume fraction of sludge in primary settler = 0.25 sludge volume · $V_{PS}^{-1}$

$f_{SS}$: Volume fraction of sludge in secondary settler = 0.25 sludge volume · $V_{SS}^{-1}$

**Measured state variables**

$C_3$: Concentration of dissolved substances in primary sludge (Tuesday 18. May) (Table **11**) [mg · (g D.W.)$^{-1}$]

$C_{13}$: Daily mean concentrations of dissolved substances in outlet from secondary settler (Table **10**) [mg · litre$^{-1}$]

$C_{14} = C_{15}$: Concentration of dissolved substances in secondary sludge (Tuesday 18. May) (Table **11**) [mg · (g D.W.)$^{-1}$]

**Calculated state variables**

$C_3$ - $C_{15}$: Daily mean concentrations of dissolved substances [mg · litre$^{-1}$]

**Calibration parameters**

$k_1$: Pseudo 1$^{st}$ order removal rate constant [sec$^{-1}$]

$K_d$: Sorption equilibrium coefficient [litre · (kg D.W.)$^{-1}$]

## 6.2 Model set-ups

The WWTP system has been described above. The predominant chemical and physical processes have been evaluated and the mathematical expressions have been fitted for the desired purposes according to the following assumptions

- Microbial and abiotic degradation expressed as a pseudo 1$^{st}$ order reaction rate, $k_1$, (section 4.2.1).
- Linear sorption with equilibrium partitioning coefficient, $K_d$ (section 4.2.2).

An experimental series has been performed with the purpose to calibrate the models with respect to $k_{1N}$ and $K_d$.

In the previous section all the necessary input parameters are stated as mean values and standard deviations.

2 model set-ups will be considered.

*Model 1*: Dynamic description of the alternate operation, i.e., differentiation of biological reactors (Figures **8** and **9**).

*Model 2*: Dynamic and steady-state description of the system, i.e., the biological reactors being aggregated to one reactor (Figure **16**).

In both models the following assumptions are made

- Constant flows (Q, $q_R$, $q_{PS}$, $q_{SS}$).
- Constant inlet concentrations of substances ($C_0$).
- Constant organic matter and sludge concentrations in biological reactors and settlers ($C_{XB}$).
- Equilibrium between concentrations of dissolved and adsorbed substances.
- Totally mixed reactors and settlers (liquid and settled sludge phases).
- No degradation in settlers.

### 6.2.1 Governing model equations

The concentration of state variable m to the time (t + Δt) is expressed by the first order numerical equation

$$C_m(t + \Delta t) = C_m(t) + \Delta t \cdot \frac{dC_m\left(C_1(t), C_2(t), ..., C_m(t), ..., C_M(t)\right)}{dt} \qquad (25)$$

where Δt is the time step and M is the total number of state variables. The concentrations calculated from Equation **25** will converge to the exact solutions for $\Delta t \rightarrow 0$.

The error from substituting differential expressions with numerical solutions can be found from the Taylor expansion about the time t

$$C(t + \Delta t) = C(t) + \frac{\Delta t}{1!} \cdot \frac{dC}{dt} + \frac{\Delta t^2}{2!} \cdot \frac{d^2C}{dt^2} + \frac{\Delta t^3}{3!} \cdot \frac{d^3C}{dt^3} + .... + \frac{\Delta t^p}{p!} \cdot \left.\frac{d^pC}{dt^p}\right|_t \qquad (26)$$

From the differential equations presented in the following section it is seen that the first order terms are constant in time. The second and higher order terms in Equation **26** can therefore be neglected since the error related to this approximation (truncation error) will be zero.

The time derived term, $dC_m \cdot dt^{-1}$, for a completely mixed reactor consists of advective contributions/losses and degradation losses

$$\frac{dC_m}{dt} = \frac{\left(Q + q_R - q_{PS}\right)}{V_{reactor}} \cdot \left(C_m^{in} - C_m^{out}\right) - \frac{k_1}{R_{reactor}} \cdot C_m^{out} \qquad (27)$$

where R is defined below.

It is important to notice that $C_m$ is the dissolved substance concentration. The total mass (dissolved + adsorbed) can be calculated in a completely mixed reactor to be

$$C_{m,total} \cdot V_{reactor} = \left(V_{reactor} \cdot \theta + C_{X_B} \cdot K_d \cdot V_{reactor}\right) \cdot C_m \quad [kg\ m] \qquad (28)$$

where $C_{XB}$ is the concentration of suspended organic particulate matter.

If the water volume/total reactor volume ratio, θ, is unity, which means that the total reactor volume consists of water, Equation **28** becomes

$$C_{m,total} \cdot V_{reactor} = \left(1 + C_{X_B} \cdot K_d\right) \cdot V_{reactor} \cdot C_m \quad [kg\ m] \qquad (29)$$

The term $(1 + C_{XB} \cdot K_d)$ will in the following be referred to as the retention factor, $R_{XB}$, where the indices $X_B$ refers to the suspended organic particulate matter concentration, $C_{XB}$.

Equations **27** and **29** defined for each of the M state variables (concentrations), will constitute a system of M coupled linear differential equa-

tions that are solved numerically by employing Equation **25** (Euler's approximation).

All algorithms are coded in Visual Basic Macro's in Excel 95.

The steady-state solutions in model 2 are calculated analytically.

## 6.3 Model 1: Dynamic description of the alternate operation, i.e., differentiation of biological reactors

In Figure **8** and **9** the schematic description of the modelled system is shown. In each of the 6 phases the changes in total concentrations, as defined by Equations **27** and **29**, are calculated for each time step, $\Delta t$, from the mass balances compiled in Appendix **1**.

To obtain an estimate of the accumulated error related to the numerical solutions as a function of the time step, $\Delta t$, and to confirm the correctness of the system equations, a mass balance is established, and for each time step the relative error is calculated as

$$\text{Error}_{\text{step i}} = \frac{\text{total inflow - total outflow - accumulated}_{\text{step i}}}{\text{total inflow}} \cdot 100\ \% \quad (\mathbf{30})$$

In Table **15** the error is calculated for different time steps.

***Table 15.*** Relative error of numerical solutions as a function of time step.

| | **$\Delta t$ = 300 sec.** | **$\Delta t$ = 30 sec.** | **$\Delta t$ = 3 sec.** |
|---|---|---|---|
| $\text{Error}_{\text{step i}}$ | 62% | 6.2% | 0.62% |

A time step of 30 seconds is chosen since no considerable reduction in the error is achieved from further time step reduction. The proportional decrease in error with decreasing time step is an indication that the mathematical formulations and computer codings are correct.

To illustrate the qualitative output from model 1, the calculated *dissolved* concentrations in the outlet, $C_{13}$, and secondary sludge, $C_{14} = C_{15}$, are shown in Figure **13**. Parameter values for LAS, cf. section 6.6.1, are used.

$k_{1N} \cdot R_{bio}^{-1} = 1.5 \cdot 10^{-4}\ \text{sec}^{-1}$
$k_{1D} = 0.1 \cdot k_{1N}$
$K_d = 2{,}500\ \text{litre} \cdot (\text{kg D.W.})^{-1}$
$C_0 = 4\ \text{mg} \cdot \text{litre}^{-1}$

The concentrations are calculated for a time span of one cycle (= 4 hours). The situation is steady-state since the profile repeats itself subsequently. The concentrations fluctuate around a mean "cycle steady-state" concentration with a peak value that is dependent on the hydraulic retention time, degradation rate and adsorption coefficient.

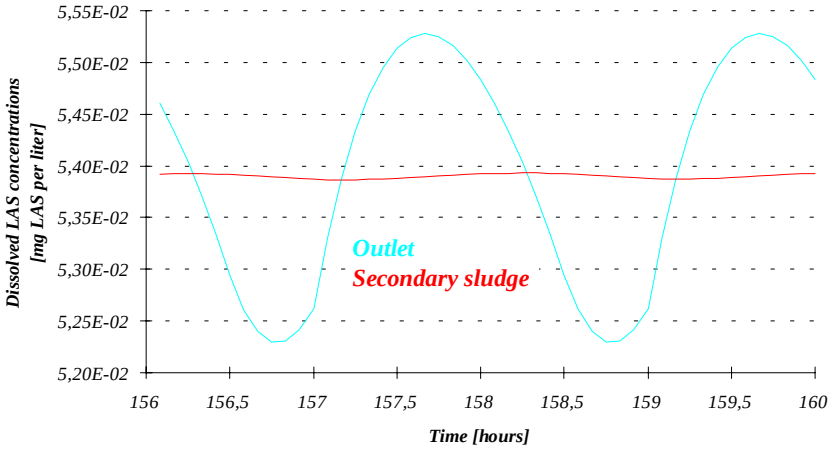



***Figure 13.*** *Concentrations of dissolved LAS in outlet (blue) and secondary sludge (red) during one cycle = 4 hours.* $k_{1D} = 0.1 \cdot k_{1N}$.

The delay in the sludge peaks compared to the outlet peaks arise from the retention in the suspended phase in the secondary settler. The smoother sludge curve is a consequence of lower inlet flow to the sedimented sludge volume compared to the liquid volume.

The cycle in Figure **13** consists of two identical peaks produced from the symmetric "half-cycles" A-C and D-F. The fluctuations within one bio-reactor, e.g. the upper reactor in Figure **9**, are as shown in Figure **14**.

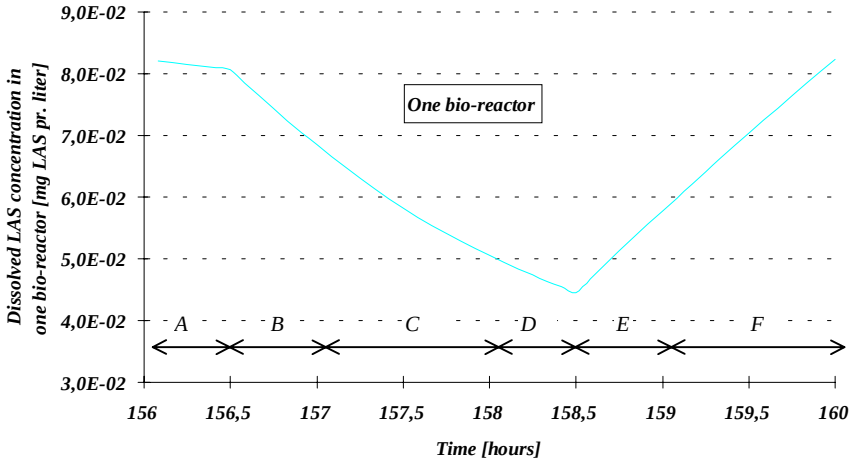



***Figure 14.*** *Concentration fluctuations in one bioreactor within one cycle.*

The description of the concentration development can start with the minimum occurring in the shift from phase D to E. In the following three phases (E, F and A) the bio-reactor receives its influent from the anaerobic P-reactors where no substance degradation takes place, and consequently the concentration increases constantly in phases E and F where the reactor is denitrifying under anoxic conditions. In phase A the reactor is aerated and the degradation takes place at a higher rate resulting in a small decrease in concentration.

In phase B the reactor operates in batch mode resulting in a decrease in concentration. This decrease continues, but at a lower rate, when the reactor influent comes from the denitrifying reactor in phase C and from

the nitrifying reactor in phase D. The minimum in the shift from phase D to E occurs when the influent to the reactor is from the P-reactors.

In the model assumptions the concentrations of the electron acceptors are always much larger than the corresponding half saturation constants. In practice the increase in substance concentration will be steeper in the latter part of phase E and in phase F due to the "total" consumption of nitrate during anoxic growth in the first part of phase E. If this process is to be included the model must be extended with oxygen, nitrate, ammonium and biomass growth/reduction kinetics.

The slope of the curve in Figure **14** is important since it determines the size of the fluctuations within an operation cycle and thus the maximum concentrations that can be found in the effluent. The mean outlet concentration within a 4 hour cycle will be referred to as the "cycle steady-state" concentration in the following.

In Figure **15** the maximum deviations, within one cycle, from the "cycle steady-state" outlet concentration of dissolved substance, are shown as functions of the hydraulic retention time in the total system, $T_{h,total}$, and the removal rate with respect to total substance (dissolved + adsorbed), $k_{1N} \cdot R_{bio}^{-1}$, which are the determining physical and chemical state variables.

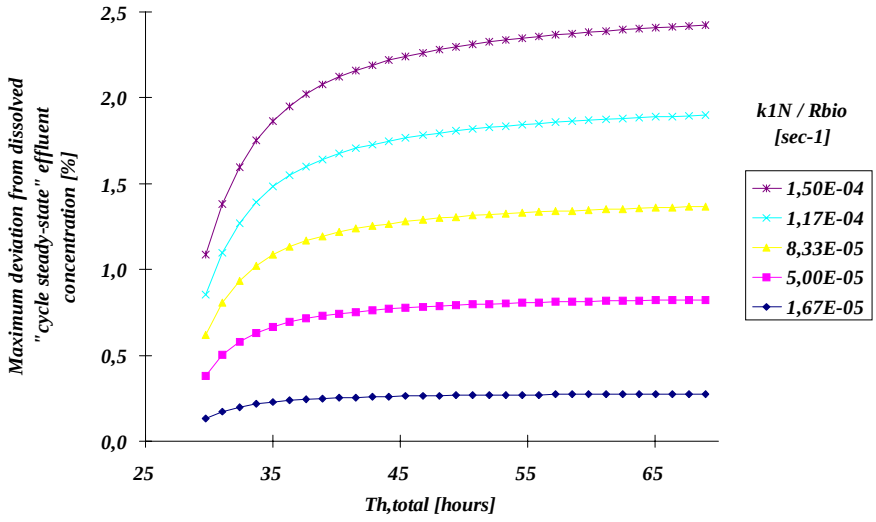



***Figure 15.*** *Maximum deviation from "cycle steady-state" effluent concentration as a function of hydraulic retention time, $T_{h,total}$ (cf. Equation **54**), and aerobic pseudo 1st order degradation rate, $k_{1N} \cdot R_{bio}^{-1}$. Assuming: $k_{1D} = k_{1N}$.*

When the degradation rate increases the faster the steady state concentration is reached in the individual reactors as well as in the total system. This implies that the concentration differences in the individual reactors increase and the fluctuations relative to the mean "cycle steady-state" concentrations in the outlet increase.

When the hydraulic retention time decreases the substances are washed through the system resulting in a more uniform concentration distribution and a lower deviation from the mean outlet concentration. The same effect is seen for low degradation rates, the substances are obviously being washed through the system without being degraded.

The concentration peaks occur in the shifts from phase B to C and from E to F, respectively, (see Figure **13**) when the flow through the nitrifying reactor shifts from zero (batch) to ($Q + q_r - q_{ps}$). The concentration in the reactor has been built up in the three preceding phases where the influent has come from the P-reactors.

When the hydraulic retention time in phase B is shorter in the batch reactor (N-reactor) (0.5 hours), than in the flow reactor (D-reactor), the shift from phase B to C will be succeeded by an increase in effluent concentration, under the assumption that $k_{1D} = k_{1N}$.

If the deviations from the mean effluent concentration are to reach a minimum the following two scenarios can be considered with respect to the shift from phase B to C.

A) When the retention times are identical (0.5 hours) the anoxic degradation rate in the flow reactor must be

$$\text{Retention time} = \frac{2 \cdot V_D}{(Q + q_R - q_{PS})} \cdot \frac{k_{1D}}{k_{1N}} = 0.5\,\text{hour} \quad \Rightarrow$$

$$k_{1D} = \frac{0.5\,\text{hour} \cdot 5 \cdot 10^{-4}\ \frac{1}{\text{sec.}} \cdot (492 + 295 - 29.5) \cdot \frac{\text{m}^3}{\text{hour.}}}{2 \cdot 3650\,\text{m}^3} =$$

$$2.6 \cdot 10^{-5}\ \frac{1}{\text{sec.}}$$

Or B) if $k_{1N} = k_{1D}$, the bio-reactor volumes must be

$$V_D = \frac{0.5\,\text{hour} \cdot (492 + 295 - 29.5) \cdot \frac{\text{m}^3}{\text{hour}} \cdot 1}{2} = 189\,\text{m}^3$$

Leading to

$$T_{h,bio} = \frac{4 \cdot 189\,\text{m}^3}{(492 + 295 - 29.5)\ \frac{\text{m}^3}{\text{hour}}} = 1\ \text{hour}$$

and is represented by a minimum in the curves in Figure **15**. When $V_D$ decreases below this value the retention time in the batch reactor becomes larger than in the flow reactor and accordingly the effluent concentration, in the transition from phase B to C, will increase and result in increasing fluctuations around the mean effluent concentration.

For decreasing $k_{1D}$ values the minimum shifts to a higher $V_D$ value, since the flow reactor requires larger retention times to degrade the same amount of substances as the batch reactor.

Anoxic conditions prevail in each reactor during 1.5 hours in a 4 hour cycle. Anoxic degradation data reported in the litreature is sparse.

The influence of the anoxic degradation rate in the denitrifying reactors, expressed through $k_{1D} \cdot R_{bio}^{-1}$, on the maximum deviation can be derived

through curve fittings in Figure 15 and estimates of the influence of the $k_{1D} \cdot k_{1N}^{-1}$ ratio

$$\frac{\text{Max. deviation}}{\text{Cycle st.-state}} = f\left(T_{h,total}, \frac{k_{1N}}{R_{bio}}, \frac{k_{1D}}{k_{1N}}\right) =$$

$$g\left(T_{h,total}, \frac{k_{1N}}{R_{bio}}\right)_{figure\ 15} \cdot$$

$$\left(\left(1.2 \cdot 10^{-4} \cdot T_{h,total}^2 - 1.6 \cdot 10^{-2} \cdot T_{h,total} + 0.52\right) \cdot \frac{k_{1D}}{k_{1N}} +\right.$$

$$\left.\left(-1.3 \cdot 10^{-4} \cdot T_{h,total}^2 + 1.7 \cdot 10^{-2} \cdot T_{h,total} + 0{,}44\right)\right) \qquad \textbf{(31)}$$

Increasing $k_{1D} \cdot k_{1N}^{-1}$ ratios result in increasing maximum deviations from the cycle steady-state concentrations. Low $k_{1D}$ values imply low degradation in the flow reactor during phase B and the shift to phase C yield a lower increase in the outlet concentration than is observed for higher $k_{1D}$ values.

From Equation **31** it can be deduced that shorter hydraulic retention times enhance the influence of the $k_{1D} \cdot k_{1N}^{-1}$ ratio on the maximum deviation. For biological reactor volumes larger than $3 \cdot 10^6$ litre ($T_{h,total} \approx$ 45 hours) the influence is negligible and the maximum deviation becomes independent of $T_{h,total}$ and $k_{1D} \cdot k_{1N}^{-1}$, thus transforming into a function linear dependent on the aerobic 1st order degradation rate, $k_{1N}$, according to

$$\frac{\text{Maximum deviation}}{\text{Mean cycle steady - state conc.}} = 1.6 \cdot 10^4 \cdot \frac{k_{1N}}{R_{bio}} + 2 \cdot 10^{-2} \quad [\%] \qquad \textbf{(32)}$$

When the aerobic degradation rate in a WWTP is lower than $2 \cdot 10^{-4}$ $sec^{-1}$, which is valid for the investigated substances, the deviation is no more than 50% of the mean concentration.

Model 1 reveals that the outlet concentrations from the alternately operated WWTP are associated with fluctuations around the mean values. If these fluctuations and the uncertainties related to them are insignificant compared to the uncertainties related to the input parameters the model complexity can be simplified in a way that these fluctuations are not incorporated in the model. This can be done by replacing the alternating operation cycle with one totally mixed bio-reactor comprising the P-, N- and D-reactors (model 2). In this way concordant deviations can be reached with respect to uncertainties and precision.

## 6.4 Model 2: Unsteady-state and steady-state, one bio-reactor

The uncertainties related to input variables may cause deviations in the model calculations that exceed the fluctuations caused by the alternating operation. The fluctuations in the substance concentrations are not taken into account when the alternating operation cycle is approximated with

one totally mixed bio-reactor comprising the P-, N- and D-reactors, as illustrated in Figure **16**.

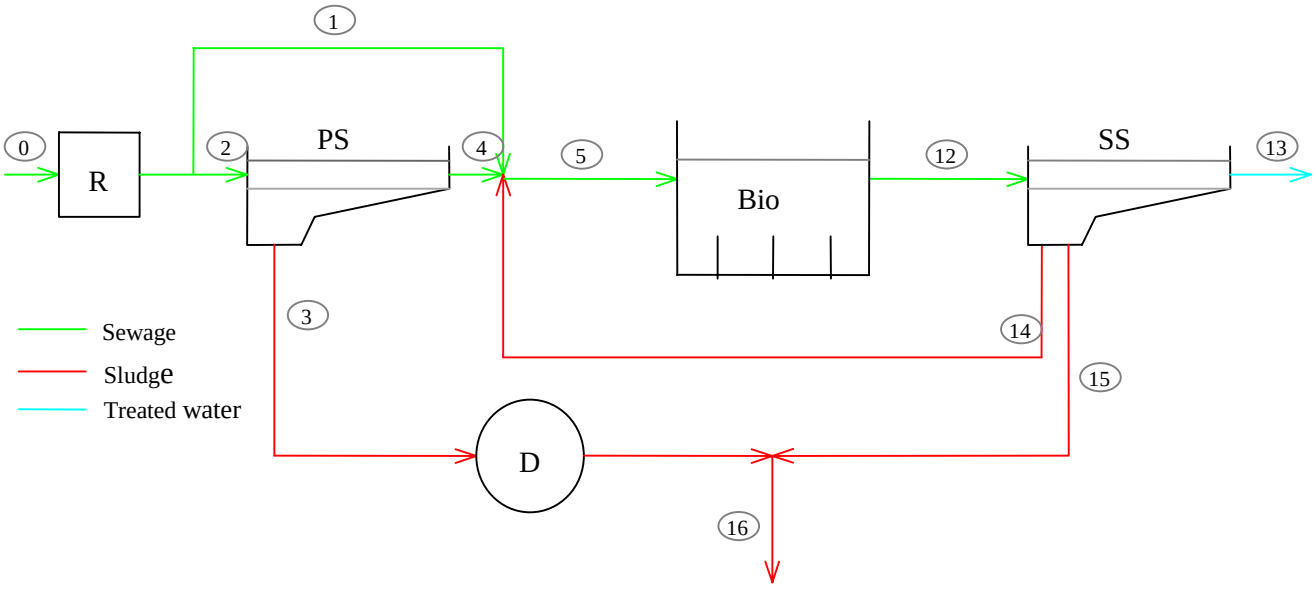



***Figure 16.*** *Flow-sheet of WWTP approximated with one bio-reactor. Each number denotes a concentration that is calculated in the model*

The mean hydraulic retention time in the biological reactors, with an effective volume $V_{bio} = V_N + V_D + V_P$, can be approximated from

$$T_{h,bio} = \frac{V_{bio}}{(Q + q_R - q_{PS})} = \frac{V_N \cdot 2}{(Q + q_R - q_{PS})} \quad \textbf{(33)}$$

The degradation rate for the total substance is dependant on the total hydraulic retention time, the aerobic degradation rate and the aerobic-anoxic degradation rate ratio.

$$\frac{k_1(\text{model 2})}{R_{bio}} = f\left(T_{h,total}, \frac{k_{1N}}{R_{bio}}, \frac{k_{1D}}{k_{1N}}\right) \quad \textbf{(34)}$$

$k_{1D}$ is initially set to $k_{1N}$.

Analogous to model 1 the following differential equations can be set up.

<u>Primary settler, liquid phase, $C_4$:</u>

$$\frac{dC_4}{dt} = \frac{1}{V_{PS} \cdot (1 - f_{PS})} \cdot$$

$$\left(0.3 \cdot Q \cdot C_0 \cdot \frac{R_{in}}{R_{PSout}} - \left(0.3 \cdot Q - q_{PS} - q_{PS} \cdot \frac{R_{PSsludge}}{R_{PSout}}\right) \cdot C_4\right) \quad \textbf{(35)}$$

Primary settler, settled phase, $C_3$:

$$\frac{dC_3}{dt} = \frac{q_{PS}}{f_{PS} \cdot V_{PS}} \cdot (C_4 - C_3) \quad (36)$$

Bio-reactor, $C_{12}$:

$$\frac{dC_{12}}{dt} = \frac{1}{V_{bio} \cdot R_{bio}} \cdot (0.7 \cdot Q \cdot C_0 \cdot R_{in} + q_R \cdot C_{14} \cdot R_{SSsludge}$$

$$+ (0.3 \cdot Q - q_{PS}) \cdot C_4 \cdot R_{PSout} - (Q + q_R - q_{PS}) \cdot C_{12} \cdot R_{bio}$$

$$- k_1 \cdot C_{12} \cdot V_{bio}) \quad (37)$$

Secondary settler, liquid phase, $C_{13}$:

$$\frac{dC_{13}}{dt} = \frac{1}{V_{SS} \cdot (1 - f_{SS})} \cdot ((Q + q_R - q_{PS}) \cdot C_{12} \cdot \frac{R_{bio}}{R_{SSout}}$$

$$- (Q - q_{SS} - q_{PS}) \cdot C_{13} - (q_{SS} + q_R) \cdot C_{13} \cdot \frac{R_{SSsludge}}{R_{SSout}}) \quad (38)$$

Secondary settler, settled phase, $C_{14} = C_{15}$:

$$\frac{dC_{14}}{dt} = \frac{(q_{SS} + q_R)}{f_{SS} \cdot V_{SS}} \cdot (C_{13} - C_{14}) \quad (39)$$

Figure **17** illustrates the development in dissolved outlet and secondary sludge concentrations during 40 cycles when the initial inlet concentration is set to zero and $k_{1N}$ and $K_d$ for LAS (Table **20**) are inserted.

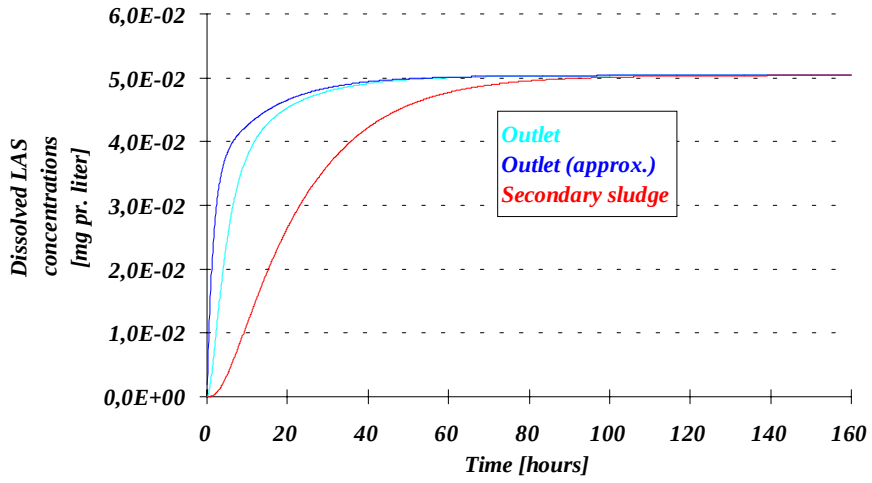



***Figure 17.*** *Concentrations of dissolved outlet and secondary sludge LAS concentrations, Model 2. $k_1$(model 2) = $k_{1N}$. Approximated curve cf. Equation* ***46****.*

After approximately 20 cycles (80 hours) the concentrations reach steady-state. In this situation the following relationships exist $C_0$(inlet) = $C_3$(primary sludge) = $C_4$(outlet primary settler) and $C_{12}$(inlet secondary settler) = $C_{13}$(outlet secondary settler) = $C_{14}$(secondary sludge), respectively, and the following approximation of the effluent concentration can be made

$$\frac{dC_{13}(approx.)}{dt} = \left( \frac{0.7 \cdot Q \cdot R_{in} + \left(0.3 \cdot Q - q_{PS}\right) \cdot R_{PSout}}{V_{bio} \cdot R_{bio}} \right) \cdot C_0 +$$

$$\left( \frac{q_R \cdot R_{SSsludge}}{V_{bio} \cdot R_{bio}} - \frac{k_1}{R_{bio}} - \frac{\left(Q + q_R - q_{PS}\right)}{V_{bio}} \right) \cdot C_{13}(approx.) \qquad (\mathbf{40})$$

According to Figure **17**, Equations **38** and **40** are concordant within acceptable limits. The 1st order differential Equation **40** can be solved analytically by employing e.g. Equation 18.2 in *Spiegel (1968)*

$$\frac{dC}{dt} + P(t) \cdot C = T(t) \cdot C_0$$

with the solution

$$C \cdot e^{\int P(t) \cdot dt} = \int T(t) \cdot C_0 \cdot e^{\int P(t) \cdot dt} \cdot dt + K \qquad (\mathbf{41})$$

When P and T are constant in time, i.e. inlet concentrations, flows, biomass concentrations, reactor volumes and degradation rates are constant, Equation **41** becomes

$$C \cdot e^{\int_0^t P \cdot dt} = \int_0^t T \cdot C_0 \cdot e^{\int_0^t P \cdot dt} \cdot dt + K \quad \Rightarrow$$

$$C \cdot e^{P \cdot t} = \int_0^t T \cdot C_0 \cdot e^{P \cdot t} \cdot dt + K \quad \Rightarrow$$

$$C \cdot e^{P \cdot t} = \frac{T}{P} \cdot C_0 \cdot \left(e^{P \cdot t} - 1\right) + K$$

The initial condition C(0) = 0, yields

$$C \cdot 1 = \frac{T}{P} \cdot C_0 \cdot (1 - 1) + K = 0 \quad \Leftrightarrow \quad K = 0 \quad \Rightarrow$$

$$C(t) = \frac{T}{P} \cdot C_0 \cdot \left(1 - e^{-P \cdot t}\right) \qquad (\mathbf{42})$$

From Figure **18** it can be seen that $C \rightarrow T \cdot P^{-1} \cdot C_0$ when $t \rightarrow \infty$.

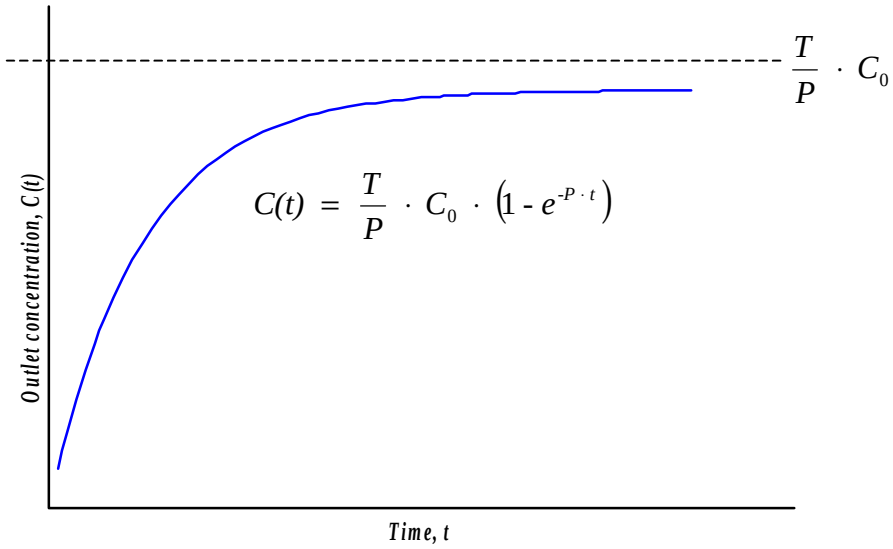



***Figure 18*** *Analytical solution to single box system (model 2).*

P and T can be found from Equation **40** and the general solution to the dissolved effluent steady-state concentration is thus

$$C_{13}(\text{approx.}) = \frac{\left(\frac{0.7 \cdot Q \cdot R_{in} + (0.3 \cdot Q - q_{PS}) \cdot R_{PSout}}{V_{bio} \cdot R_{bio}}\right)}{\left(\frac{-q_R \cdot R_{SSsludge}}{V_{bio} \cdot R_{bio}} + \frac{k_1}{R_{bio}} + \frac{(Q + q_R - q_{PS})}{V_{bio}}\right)} \cdot C_0 \quad \textbf{(43)}$$

According to Equation **21**

$$R_{PSout} = 1 + K_d \cdot C_{X_B,PSout} \quad \Rightarrow$$

$$R_{PSout} = \left(1 - \frac{0.075 \cdot Q}{(0.3 \cdot Q - q_{PS})}\right) + \frac{0.075 \cdot Q}{(0.3 \cdot Q - q_{PS})} \cdot R_{in} \quad \textbf{(44)}$$

and according to Equation **23**

$$R_{SSsludge} = 1 + K_d \cdot C_{X_B,SSsludge} \quad \Rightarrow$$

$$R_{SSsludge} = 1 +$$

$$K_d \cdot \left(\frac{(Q + q_R - q_{PS}) \cdot C_{X_B,bio}}{(q_R + q_{SS})} - \frac{(Q - q_{SS} - q_{PS}) \cdot C_{X_B,SSout}}{(q_R + q_{SS})}\right) \quad \Rightarrow$$

$$R_{SSsludge} = \frac{(Q + q_R - q_{PS})}{(q_R + q_{SS})} \cdot R_{bio} - \frac{(Q - q_{SS} - q_{PS})}{(q_R + q_{SS})} \cdot R_{SSout} \quad \textbf{(45)}$$

Insertion of Equations **44** and **45** and the conditions $q_R = 0.6 \cdot Q$, $q_{SS} = 0.05 \cdot 0.6 \cdot Q$ and $q_{PS} = 0.15 \cdot 0.3 \cdot Q$ in Equation **43**, gives

$$\frac{C_{13}(approx.)}{C_0} = \frac{0.497 \cdot \frac{R_{in}}{R_{bio}} + 0.115 \cdot \frac{1}{R_{bio}}}{\left(0.048 + 0.565 \cdot \frac{R_{SSout}}{R_{bio}} + \frac{k_1 \cdot V_{bio}}{R_{bio} \cdot 1.56 \cdot Q}\right)} \quad \textbf{(46)}$$

where $1.56 \cdot Q = (Q + q_R - q_{PS})$.

By varying $k_{1N} \cdot R_{bio}^{-1}$ and $V_{bio}$, Equation **46** can be used to determine the deviations between the "cycle steady-state" dissolved effluent concentrations calculated in model 1 and the steady-state dissolved effluent concentrations calculated in model 2, see Figure **19**.

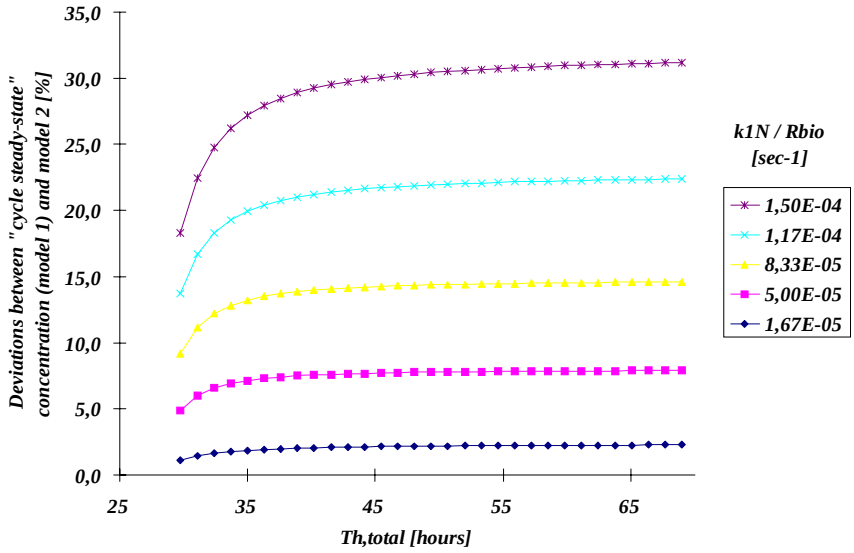



***Figure 19.*** *Deviations in dissolved steady-state effluent concentrations between model 1 and model 2. Assuming $k_1$(model 2) = $k_{1N}$ = $k_{1D}$.*

The deviations can be minimised by employing the so called *golden ratio search* (*e.g. Mathews, 1987*), thus finding the optimum $k_1$ (model 2) · $R_{bio}^{-1}$ value in model 2 that reduces the deviations to less than 0.5% compared to model 1, cf. Figure **20**.

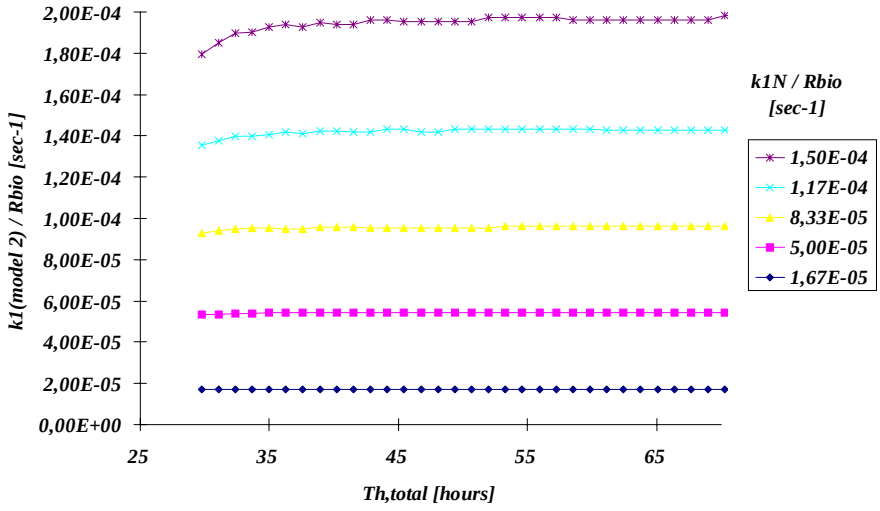



***Figure 20.*** *Optimum $k_1$(model 2) · $R_{bio}^{-1}$ values yielding deviations of max. 0.5% compared to model 1. Assuming: $k_{1D}$ = $k_{1N}$.*

For realistic reactor volumes the degradation rate is independent of $T_{h,total}$. A proportionality relationship between $k_1$(model 2) and $k_{1D} \cdot k_{1N}$ yields the following equation for calculating the half-life derived from the pseudo 1st order degradation rate valid for model 2.

$$\frac{k_1(\text{model 2})}{R_{bio}} = f\left(\frac{k_{1N}}{R_{bio}}, \frac{k_{1D}}{k_{1N}}\right) = \frac{2279 \cdot \left(\frac{k_{1N}}{R_{bio}}\right)^2 + 0.963 \cdot \left(\frac{k_{1N}}{R_{bio}}\right)}{\left(0.275 \cdot \left(\frac{k_{1D}}{k_{1N}}\right)^2 - 0.822 \cdot \frac{k_{1D}}{k_{1N}} + 1.55\right)} \quad \textbf{(47)}$$

Equation **47** combined with Equation **46** yield dissolved steady state outlet concentrations for the single box system (model 2), that lie within approximately 2% of the mean dissolved outlet concentration found from model 1. The increase in error is a consequence of the curve fittings.

*On the above basis it can be concluded that it is possible to set up a system containing one bio-reactor that simulates the complex operation cycle of an alternately operated WWTP. The errors in the calculated mean outlet concentrations are less than 2% compared to the more complex model 1 that includes the alternating cycle.*

## 6.5 Uncertainty analysis

Model 2 has been set up assuming that the fluctuations around the cycle steady-state concentrations and the uncertainties related to them are insignificant compared to the uncertainties related to the input variables.

One approach to obtain information of the uncertainties, or errors, is by combining sensitivity analysis and first-order analysis.
In first-order analysis the uncertainties, or variations, in the model dependent variables are estimated from the uncertainties, or variations, in the model independent variables and parameters. By approximating the mathematical relationship, f, between the dependent, y, and the independent variables, $x_i$, with a Taylor expansion, and linearising it by excluding the 2nd and higher order terms, the uncertainty of y can be expressed as the variance, $S_y^2$, of the function about any point from the mean values of the independent input variables. The procedure assumes that the variations of the variables, $\delta f \cdot \delta x_i^{-1}$, are constant or small in an interval around the mean value of the variable.

For a multivariate relationship, involving n independent variables, $S_y^2$ becomes (e.g. *Schnoor, 1996*)

$$S_y^2 = \sum_{i=1}^{n}\left(\frac{\delta f}{\delta x_i}\right)^2 \cdot S_{x_i}^2 + 2 \cdot \sum_{j=1}^{n-1}\sum_{i=j+1}^{n}\left(\frac{\delta f}{\delta x_i}\right) \cdot \left(\frac{\delta f}{\delta x_j}\right) \cdot S_{x_i} \cdot S_{x_j} \cdot \rho_{x_i, x_j} \quad \textbf{(48)}$$

where

$S_{xi}^2$ = Variance of input variables, assuming normal distribution of data

$\delta f \cdot \delta x_i^{-1}$ = Sensitivity of f compared to changes in the input variable $x_i$

$\rho_{xi,xj}$ = Correlation coefficient between the input variables $x_i$ and $x_j$

There are four input variables, i.e., $k_{1N}$, $K_d$, $T_h$ and $C_0$, that are mutually uncorrelated, thus $\rho_{xi,xj} = 0$ for all i and j. The variance of the dissolved outlet concentration, $C_{13}$, is now given by

$$S_{C_{13}}^2 = \left(\frac{\delta C_{13}}{\delta k_{1N}}\right)^2 \cdot S_{k_{1N}}^2 + \left(\frac{\delta C_{13}}{\delta K_d}\right)^2 \cdot S_{K_d}^2 + \left(\frac{\delta C_{13}}{\delta T_h}\right)^2 \cdot S_{T_h}^2 + \left(\frac{\delta C_{13}}{\delta C_0}\right)^2 \cdot S_{C_0}^2 \qquad (\mathbf{49})$$

Data for degradation rates and adsorption coefficients determined under relevant conditions is scarce in the literature, therefore the uncertainty analysis is reduced to LAS and DEHP that have been most extensively studied. The data is compiled in Table **16** as intervals and as mean values and standard deviations under the assumption that the values are equally distributed within the intervals.

$Q = 492 \pm 356\ m^3 \cdot hour^{-1}$ is found from hourly measurements of the inlet flow. The retention time in the bio-reactor becomes

$$T_{h,bio} = \frac{V_N \cdot 4}{(Q + q_R - q_{PS})} = \frac{3650\ m^3 \cdot 4}{1.56 \cdot (492 \pm 356)\ \frac{m^3}{hour}} = 19.0 \pm 13.7\ hours$$

$C_0$ is found from the emission survey. DEHP is estimated to account for 20% of the total phthalate load.

***Table 16.*** Mean values and standard deviations of input variables. LAS data from *Berna (1999) and Feijtel et al., (1995).* DEHP data from *Furtmann (1986).*

| | **$k_{1N}$, aerobic degradation rate [$sec^{-1}$]** | **$K_d$, adsorption coefficient [litre · $kg^{-1}$]** | **$C_0$, daily mean dissolved inlet concentration** |
|---|---|---|---|
| **LAS** | $4.19 \cdot 10^{-6}$ - $5.26 \cdot 10^{-7}$<br>$(4.71 \pm 4.19) \cdot 10^{-6}$ | 1000 - 4000<br>$(2500 \pm 1500)$ | $4 \pm 4$<br>mg · $litre^{-1}$ |
| **DEHP** | $3.50 \cdot 10^{-7}$ - $1.60 \cdot 10^{-6}$<br>$(12.5 \pm 3.45) \cdot 10^{-7}$ | 2000 - 20000<br>$(11000 \pm 9000)$ | $3.8 \pm 3.3$<br>µg · $litre^{-1}$ |

Equation **49** can be used for model 2 (Equation **46**) to calculate the uncertainties related to the dissolved outlet concentration, $C_{13}$

$$C_{13} = C_{13}(mean) \pm S_{C_{13}} \qquad (\mathbf{50})$$

$C_{13}(mean)$ is calculated from the mean values of the input variables. The standard deviation, $S_{C13}$, sums up the uncertainties from the input variables and gives an estimate of the relative contributions, cf. table **17**. $S_{C13}$

is not a true standard deviation to a normal distribution because the derived expressions in Equation **49** are not constant.

The standard deviations are stated in Table **16** and the derived terms are found from Equations **46** and **47**.

***Table 17.*** Uncertainty analysis for dissolved outlet concentration in model 2.

| **Model 2** | $\left(\frac{\delta C_{13}}{\delta k_{1N}}\right)^2 \cdot S^2_{k_{1N}}$ | $\left(\frac{\delta C_{13}}{\delta K_d}\right)^2 \cdot S^2_{K_d}$ | $\left(\frac{\delta C_{13}}{\delta T_h}\right)^2 \cdot S^2_{T_h}$ | $\left(\frac{\delta C_{13}}{\delta C_0}\right)^2 \cdot S^2_{C_0}$ | $C_{13}$ **[mg · l$^{-1}$]** |
|---|---|---|---|---|---|
| **LAS** | $7.38 \cdot 10^{-9}$ (~ 0%) | $1.10 \cdot 10^{-4}$ (5%) | $6.86 \cdot 10^{-4}$ (32%) | $1.34 \cdot 10^{-3}$ (63%) | $3.66 \cdot 10^{-2} \pm 4.63 \cdot 10^{-2}$ mg · litre$^{-1}$ |
| **DEHP** | $6.92 \cdot 10^{-8}$ (~ 0%) | 0.03 (19%) | 0.05 (29%) | 0.09 (51%) | $0.35 \pm 0.41$ µg · litre$^{-1}$ |

The uncertainties related to $C_0$ comprise 63% and 51% of the total uncertainties for LAS and DEHP respectively. This was anticipated from the emission survey, where the emission pathways for the chemicals are very complex. The flow variations, expressed through $T_{h,bio}$ are also significant for the precision of the results. These are, however, measured *in situ* and will therefore always involve variations from consumers and precipitation. Although the standard deviation of the $K_d$ and $k_{1N}$ values are large the uncertainties toward the calculated outlet concentrations are relatively low.

Analogously the uncertainties related to the maximum deviations compared to the cycle steady-state outlet concentrations in model 1 can be calculated from

$$\frac{C_{13}(\text{max.dev.})}{C_{13}(\text{st.-state})} = \frac{C_{13}(\text{max.dev.})}{C_{13}(\text{st.-state})}(\text{mean}) \pm S_{\frac{C_{13}(\text{max.dev.})}{C_{13}(\text{st.-state})}} \qquad (\mathbf{51})$$

where

$$S^2_{\frac{C_{13}(\text{max.dev.})}{C_{13}(\text{st-state})}} = \left(\frac{\delta\left(\frac{C_{13}(\text{max.dev.})}{C_{13}(\text{st.}-\text{state})}\right)}{\delta\, k_{1N}}\right)^2 \cdot S^2_{k_{1N}} + \left(\frac{\delta\left(\frac{C_{13}(\text{max.dev.})}{C_{13}(\text{st.}-\text{state})}\right)}{\delta\, K_d}\right)^2 \cdot S^2_{K_d} +$$

$$\left(\frac{\delta\left(\frac{C_{13}(\text{max.dev.})}{C_{13}(\text{st.}-\text{state})}\right)}{\delta\, T_h}\right)^2 \cdot S^2_{T_h} + \left(\frac{\delta\left(\frac{C_{13}(\text{max.dev.})}{C_{13}(\text{st.}-\text{state})}\right)}{\delta\, C_0}\right)^2 \cdot S^2_{C_0} \qquad (\mathbf{52})$$

The values for the standard deviations of the input variables in Table **16** are still valid since they are independent of the model structure. The derived terms with respect to $k_{1N}$, $R_{bio}$ and $T_h$ are determined empirically through sensitivity analysis, as shown in Figure **15**, where the independent input parameters are varied one at a time to determine the changes in maximum deviations.

***Table 18.*** Uncertainty analysis for maximum deviation compared to cycle staedy-state outlet concentrations in model 1. D = maximum deviation · cycle steady-state concentration$^{-1}$ [%] (cf. Equation **32**).

| **Model 1** | $\left(\frac{\delta D}{\delta k_1}\right)^2 \cdot S^2_{k_1}$ | $\left(\frac{\delta D}{\delta K_d}\right)^2 \cdot S^2_{K_d}$ | $\left(\frac{\delta D}{\delta T_h}\right)^2 \cdot S^2_{T_h}$ | $\left(\frac{\delta D}{\delta C_0}\right)^2 \cdot S^2_{C_0}$ | **D·C$_{13}$** |
|---|---|---|---|---|---|
| **LAS** | $2.05 \cdot 10^{-5}$ | 1.38 | 0 | 0 | $8.56 \cdot 10^{-4} \pm 3.45 \cdot 10^{-3}$ mg · litre$^{-1}$ |
| **DEHP** | $6.91 \cdot 10^{-9}$ | $9.40 \cdot 10^{-3}$ | 0 | 0 | $5.70 \cdot 10^{-4} \pm 7.55 \cdot 10^{-4}$ µg · litre$^{-1}$ |

The sensitivity analysis reveals, that the maximum deviations are independent of the hydraulic retention time, $T_h$, when the bio-reactor volumes are larger than $3 \cdot 10^6$ litre ( $T_{h,total} > 45$ hours). Furthermore the deviations are independent of the inlet concentrations, $C_0$. Practically all the uncertainty arises from the variations in the $K_d$ values.

The last column in Table **18**

$$\left( \frac{C_{13}(\text{max.dev..})}{C_{13}(\text{st.–state})}(\text{mean}) \pm S_{\frac{C_{13}(\text{max.dev.})}{C_{13}(\text{st.–state})}} \right) \cdot C_{13}(\text{st.–state})(\text{mean})$$

is an estimate of the maximum deviations ± uncertainties compared to the cycle steady-state concentration in model 1, calculated for the mean values of the input variables. It can be seen that these figures are a factor of 54 and 720 smaller for LAS and DEHP respectively, than the uncertainties, $S_{C13}$, of the outlet concentrations in model 2 (last figure in the last column in Table **17**).

*Thus, the bio-reactors can be substituted by a single reactor, without the model uncertainties exceed the input uncertainties.*

## 6.6 Using model 2

It has been shown that for substances with half lives longer than approximately 2 hours, the pseudo 1$^{st}$ order degradation rate for the aggregated bio-reactor is equal to the 1$^{st}$ order aerobic degradation rate and for shorter half-lives Equation **47** can be used for the aggregate degradation rate.

### 6.6.1 Model calibration

The measured daily mean flows in Table **9** can be transformed to a hydraulic retention time in the bio-reactor and the total system respectively

$$T_{h,bio} = \frac{V_N \cdot 4}{(Q + q_R - q_{PS})} \qquad (\mathbf{53})$$

$$T_{h,total} = \frac{(1 - f_{PS}) \cdot V_{PS}}{0.3 \cdot Q} \cdot \frac{0.3 \cdot Q}{Q} + \frac{V_P}{(Q + q_R - q_{PS})}$$

$$+ T_{h,bio} + \frac{(1 - f_{SS}) \cdot V_{SS}}{(Q + q_R - q_{PS})} \quad \textbf{(54)}$$

When the 8 day hourly mean flow, Q = 492 $m^3 \cdot hour^{-1}$, is inserted the retention times become

$$T_{h,bio} = \frac{14600\ m^3}{(492 + 295 - 22.1)\ \frac{m^3}{hour}} = 19.1 \text{ hours}$$

$$T_{h,total} = \frac{(1 - 0.25) \cdot 3000\ m^3}{492\ \frac{m^3}{hour}} + \frac{3000\ m^3}{(492 + 295 - 22.1)\ \frac{m^3}{hour}}$$
$$+ 19.27 \text{ hours} + \frac{(1 - 0.25) \cdot 19000\ m^3}{(492 + 295 - 22.1)\ m^3} = 46.4 \text{ hours}$$

Model 1 yields the following 8 day hourly mean values

$T_{h,bio}$ = 18.3 hours

$T_{h,total}$ = 44.3 hours

The differences between Equations **53** and **54** and the numerical values in model 1 are obviously resulting from the batch reactors in phases B and E, that operate totally ½ hour in a 4 hour cycle. This is not accounted for in the equations.

Calibration of the model can now be performed for each individual substance by using the experimental data in Tables **10** and **11**.

With a total hydraulic retention time of approximately two days, the daily mean inlet concentration is coupled with the outlet concentration two days after. This corresponds to plug flow throughout the plant. In the model set-up the reactors are assumed to be totally mixed which implies that a change in the inlet to a reactor is immediately registered in the outlet of the same reactor. The plant comprises primary settlers, anaerobic P-reactors, N- and D-reactors and secondary settlers and the true flow pattern of the total plant therefore lies somewhere in between plug flow and total mixing.

According to Tables **9** the daily mean inlet flows are, apart from one outlier the 22. May, approximately constant. In Table **10** the measured concentrations show that there is no correlation between variations in the inlet and outlet concentrations neither for a 2 day nor for a 1 day coupling. The coefficients of variation (COV = standard deviation · mean value$^{-1}$) are approximately the same for inlet and outlet concentrations of LAS, NP and NPDE respectively, whereas COV is larger for the outlet concentrations of the phthalates compared to the inlet concentrations of the phthalates. This can probably be accounted for by the very low concentration levels in the outlet, which are associated with larger experimental uncertainties.

In Table **19** the measured daily mean inlet supernatant concentrations are shown together with calibrated total inlet and total outlet concentrations for each substance.

The total inlet concentrations are simulated by calibrating the adsorption equilibrium constant $K_d$. The total outlet concentrations are simulated by calibrating the aerobic pseudo 1$^{st}$ order degradation rate $k_{1N} \cdot R_{bio}^{-1}$ and $k_{1D} \cdot k_{1N}^{-1}$, occurring in the empirical pseudo 1$^{st}$ order aerobic degradation rate

$$\frac{k_1(\text{model 2})}{R_{bio}} = \frac{2279 \cdot \left(\frac{k_{1N}}{R_{bio}}\right)^2 + 0.963 \cdot \left(\frac{k_{1N}}{R_{bio}}\right)}{\left(0.275 \cdot \left(\frac{k_{1D}}{k_{1N}}\right)^2 - 0.822 \cdot \frac{k_{1D}}{k_{1N}} + 1.55\right)}$$

The $k_{1D} \cdot k_{1N}^{-1}$ ratio is estimated from aerobic and anaerobic degradation rates. The ratio is approximately constant 0.06 for the phthalates (*Thomsen et al., 1998*) and 0.5 for NP and NPDE (*Ekelund et al., 1993*). For LAS it is estimated to be 0.1.

The calibration factors are stated for each substance for each series (day). In Table **20** they are aggregated in mean values.

***Table 19.*** Inlet and outlet concentrations from WWTP allowing for blank values. Sampled during eight days in May 1999.
Phthalates, NP and NPDE in µg · litre$^{-1}$. LAS in mg · litre$^{-1}$.
Phthalates, NP and NPDE inlet supernatant measurements are single determinations unless otherwise stated.
LAS inlet supernatant and outlet total are duplicate determinations. Blank samples cf. Table **13**

| | ***Series 1*** *In: 15.May (Q = 511 m$^3$ · hour$^{-1}$)* *Out: 17.May* | | | | ***Series 2*** *In: 17.May (Q = 510 m$^3$ · hour$^{-1}$)* *Out: 19.May* | | | | ***Series 3*** *In: 18.May (Q = 497 m$^3$ · hour$^{-1}$)* *Out: 20.May* | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ***Calibration parameters*** | ***Inlet supernat. (exp.)*** | ***Inlet total (calc.)*** | ***Outlet total (calc.)*** | ***Calibration parameters*** | ***Inlet supernat. (exp.)*** | ***Inlet total (calc.)*** | ***Outlet total (calc.)*** | ***Calibration parameters*** | ***Inlet supernat. (exp.)*** | ***Inlet total (calc.)*** | ***Outlet total (calc.)*** |
| **LAS** | $k_{1N} = 3.07 \cdot 10^{-3}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.1$<br>$K_d = 4{,}200$ | 1.41 | 4.52 | 0.009 | $k_{1N} = 2.43 \cdot 10^{-3}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.1$<br>$K_d = 2{,}518$ | 1.38 | 3.21 | 0.009 | $k_{1N} = 1.48 \cdot 10^{-3}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.1$<br>$K_d = 1{,}975$ | 1.48 | 3.02 | 0.017 |
| **DEHP** | $k_{1N} = 1.09 \cdot 10^{-3}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 14{,}300$ | 2.37 | 20.20 | 0.21 | $k_{1N} = 5.85 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 7{,}680$ | 7.83 | 39.46 | 0.76 | $k_{1N} = 2.73 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 11{,}540$ | 5.89 | 41.64 | 1.72 |
| **DPP** | - | - | - | - | - | - | - | - | - | - | - | - |
| **DBP** | - | - | - | - | - | - | - | - | - | - | - | - |
| **BBP** | - | - | - | - | $k_{1N} = 3.20 \cdot 10^{-5}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 2{,}250$ | 0.12 | 0.26 | 0.06 | $k_{1N} = 1.00 \cdot 10^{-5}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 2{,}310$ | 0.14 | 0.31 | 0.10 |
| **DnOP** | - | - | - | - | $k_{1N} = 6.00 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 11{,}800$ | 0.10 | 0.72 | 0.01 | $k_{1N} = 2.70 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 17{,}900$ | 0.07 | 0.73 | 0.03 |
| **DnNP** | - | - | - | - | $k_{1N} = 7.00 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 50{,}500$ | 0.02 | 0.55 | 0.01 | - | - | - | - |
| **NP** | $k_{1N} = 3.70 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.5$<br>$K_d = 1{,}360$ | 3.42 | 5,87 | 0.18 | $k_{1N} = 2.73 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.5$<br>$K_d = 2{,}045$ | 3.71 | 7.70 | 0.32 | $k_{1N} = 2.87 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.5$<br>$K_d = 2{,}191$ | 3.47 | 7.47 | 0.29 |
| **NPDE** | $k_{1N} = 4.18 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.5$<br>$K_d = 4{,}176$ | 13.93 | 44.53 | 1.20 | $k_{1N} = 6.10 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.5$<br>$K_d = 2{,}572$ | 62.19 | 146.33 | 2.59 | $k_{1N} = 2.41 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.5$<br>$K_d = 3{,}849$ | 16.58 | 50.15 | 2.29 |

-: No calculation either due to missing sample or exp. value = 0 or n.d.

***Table 19.*** Continued

| | ***Series 4*** *In: 19.May (Q = 506 $m^3 \cdot hour^{-1}$)* *Out: 21.May* | | | | ***Series 5*** *In: 21.May (Q = 475 $m^3 \cdot hour^{-1}$)* *Out: 23.May* | | | |
|---|---|---|---|---|---|---|---|---|
| | ***Calibration parameters*** | ***Inlet supernat. (exp.)*** | ***Inlet total (calc.)*** | ***Outlet total (calc.)*** | ***Calibration parameters*** | ***Inlet supernat. (exp.)*** | ***Inlet total (calc.)*** | ***Outlet total (calc.)*** |
| **LAS** | $k_{1N} = 2.47 \cdot 10^{-3}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.1$<br>$K_d = 3{,}368$ | 1.20 | 3.33 | 0.009 | $k_{1N} = 1.29 \cdot 10^{-3}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.1$<br>$K_d = 1{,}760$ | 1.58 | 3.04 | 0.020 |
| **DEHP** | $k_{1N} = 5.38 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 12{,}850$ | 5.85 | 45.39 | 1.01 | $k_{1N} = 1.80 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 18{,}960$ | 4.31 | 47.29 | 2.65 |
| **DPP** | $k_{1N} = 1.40 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 2{,}570$ | 0.06 | 0.14 | 0.01 | - | - | - | - |
| **DBP** | - | - | - | - | - | - | - | - |
| **BBP** | $k_{1N} = 3.40 \cdot 10^{-5}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 1{,}550$ | 0.21 | 0.38 | 0.09 | $k_{1N} = 1.00 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 8{,}000$ | 0.06 | 0.31 | 0.27 |
| **DnOP** | $k_{1N} = 3.40 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 5{,}700$ | 0.18 | 0.72 | 0.02 | $k_{1N} = 4.33 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 41{,}400$ | 0.04 | 0.91 | 0.03 |
| **DnNP** | $k_{1N} = 3.10 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.06$<br>$K_d = 6{,}700$ | 0.12 | 0.54 | 0.02 | - | - | - | - |
| **NP** | $k_{1N} = 4.02 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.5$<br>$K_d = 2{,}586$ | 4.75 | 11.21 | 0.31 | $k_{1N} = 1.01 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.5$<br>$K_d = 2{,}200$ | 3.24 | 6.70 | 0.69 |
| **NPDE** | $k_{1N} = 9.38 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.5$<br>$K_d = 3{,}391$ | 63.45 | 176.62 | 1.85 | $k_{1N} = 5.49 \cdot 10^{-4}$<br>$k_{1D} \cdot k_{1N}^{-1} = 0.5$<br>$K_d = 4{,}210$ | 42.28 | 136.00 | 2.54 |

-: No calculation either due to missing sample or exp. value = 0 or n.d.

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***Table 20.*** Mean calibration parameters for the investigated substances. n is the number of calibration runs. $t_{½}$ is the half-life for the total (dissolved + adsorbed) substance, cf. equation 19.

| | ***n*** | ***$k_{1N} \cdot R_{bio}^{-1}$ [$sec^{-1}$]*** | ***$t_{½}$(mean) [hours]*** | ***$K_d$ [litre $\cdot$ $kg^{-1}$]*** |
|---|---|---|---|---|
| **LAS** | 5 | $(1.45 \pm 0.19) \cdot 10^{-4}$ | 1.3 | 2,764 ± 1,015 |
| **DEHP** | 5 | $(8.93 \pm 5.93) \cdot 10^{-6}$ | 21.6 | 13,066 ± 4,112 |
| **DBP** | 0 | - | - | - |
| **DPP** | 1 | $1.01 \cdot 10^{-5}$ | 19.0 | 2,570 |
| **BBP** | 4 | $(2.43 \pm 1.27) \cdot 10^{-6}$ | 79.1 | 3,528 ± 3,002 |
| **DnOP** | 4 | $(6.65 \pm 4.81) \cdot 10^{-6}$ | 29.0 | 19,200 ± 15,616 |
| **DnNP** | 2 | $(5.87 \pm 4.40) \cdot 10^{-6}$ | 32.8 | 28,600 ± 30,971 |
| **NP** | 5 | $(2.66 \pm 1.40) \cdot 10^{-5}$ | 7.2 | 2,076 ± 448 |
| **NPDE** | 5 | $(3.04 \pm 1.70) \cdot 10^{-5}$ | 6.3 | 3,640 ± 682 |

The retention factors (cf. Equation **29**) for the investigated substances in the different reactors are

***Table 21.*** Retention factors, $R = 1 + C_{XB} \cdot K_d$. $C_{total} = C_{dissolved} \cdot R$.

| | ***Inlet ($R_{in}$)*** | ***Primary sludge ($R_{PSsludge}$)*** | ***Reactor ($R_{bio}$)*** | ***Sec. sludge ($R_{SSsludge}$)*** | ***Outlet ($R_{SSout}$)*** |
|---|---|---|---|---|---|
| **LAS** | 2.5 | 8.3 | 14.8 | 35.0 | 1.1 |
| **DEHP** | 7.9 | 35.4 | 66.3 | 162 | 1.4 |
| **DBP** | - | - | - | - | - |
| **DPP** | 2.4 | 7.8 | 13.9 | 32.6 | 1.1 |
| **BBP** | 2.9 | 10.3 | 18.6 | 44.4 | 1.1 |
| **DnOP** | 11.1 | 51.5 | 97.0 | 237 | 1.6 |
| **DnNP** | 16.0 | 76.2 | 144 | 353 | 1.9 |
| **NP** | 2.1 | 6.5 | 11.4 | 26.5 | 1.1 |
| **NPDE** | 2.9 | 10.6 | 19.2 | 45.8 | 1.1 |

With a sludge age of approximately 20 days the primary and secondary sludge concentrations are simulated by using the 8 day mean flow and mean inlet concentrations together with the mean calibration parameter values in Table **20**.

***Table 22.*** Primary and secondary sludge concentrations, experimental values and values simulated by model 2 (single box) using the mean calibration parameters in Table **20**. Units in $\mu g \cdot gD.W.^{-1}$.

| | ***Total conc. in primary sludge*** | | ***Total conc. in secondary sludge*** | |
|---|---|---|---|---|
| | ***Measured*** | ***Calculated*** | ***Measured*** | ***Calculated*** |
| **LAS** | 5040 | 4433 | 94 | 29.7 |
| **DEHP** | 61.11 ± 3.20 | 70.59 | 3.51 ± 0.03 | 8.58 |
| **DBP** | 0.65 ± 0.25 | - | 0.16 | - |
| **DPP** | 0.01 | 0.11 | n.d. | 0.02 |
| **BBP** | 0.50 ± 0.32 | 0.89 | 0.01 ± 0.0 | 0.36 |
| **DnOP** | 1.00 ± 0.08 | 2.23 | 0.05 ± 0.0 | 0.47 |
| **DnNP** | 0.95 ± 0.11 | 1.45 | 0.05 ± 0.0 | 0.34 |
| **NP** | 11.95 ± 1.85 | 8.79 | 0.19 ± 0.01 | 0.59 |
| **NPDE** | 39.12 ± 3.81 | 139.02 | 1.28 ± 0.12 | 6.46 |

The model calibration half-life for the total (dissolved and free) DEHP is 22 hours. In *EU RA DEHP (2000)* results for the degradation of DEHP in different media derived from various studies, are summarised. The results are obtained from different test methods and show large variations. Aerobic degradation tests according to the OECD Guidelines 301 B, F and C that uses non-adapted sludge gives 80%, 63% and 62% degradation, respectively, after 28 days. Semi Continuous Activated Sludge (SCAS) tests with adapted sludge gives from 70 to 89% degradation in 24 hours, which is more in accordance with the results from this work. No primary degradation of DEHP under anaerobic conditions is found.

The most aromatic phthalate, BBP, is found to have the longest half-life of the investigated substances, namely 79 hours. Results compiled in *EU RA BBP (2000)* will be mentioned in comparison. Inherent biodegradation tests using adapted inoculum or only measuring primary degradation gives half-lives ranging from 0.5 days to 15 days. Anaerobic degradation occurs for tests with domestic sludge, however, the rate is considerably lower than under aerobic conditions.

It must be emphasised that the values found in the literature are produced under conditions that are seldom coherent with the conditions in the actual WWTP. In laboratory experiments even faster degradation of the total substance could be anticipated due to the lower concentration of particles that remove the substance from the dissolved phase. On the other hand there exists a high concentration of micro-organisms in the WWTP, that are adapted to the prevailing conditions in terms of temperature, flow, substance concentrations etc. so that an immediate and efficient degradation is possible. It is thus very critical to compare and extrapolate results obtained from different test conditions and methods.

Volatilization of the unimers from the aqueous phase to the surrounding air is a process that could influence the removal efficiency of the phthalates. If volatilization is described as $1^{st}$ order removal, which is acceptable if the air concentration is negligible, the pseudo $1^{st}$ order degradation (or removal) rate, $k_1$, comprises a bio-degradation rate and a volatilization rate

$$k_1 = k_{1bio} + k_{1vol} \quad \textbf{(55)}$$

Volatilisation occurs in all reactors but most efficiently in the biological reactors during aeration, where the stirring of the water gives a high surface area of the water volume. Volatilisation in the secondary settlers is not included in the model. As a rough estimate the concentration in the secondary settler is 1% of the concentration in the biological reactor and the hydraulic retention times and surface areas are approximately the same. This rules out a reduction of $k_1$ due to volatilisation in the secondary settlers.

Experiments by *Cini et al. (1994)* where the removal of different phthalates in aqueous NaCl solutions through bubbling with $N_2$, showed that approximately 40% of the initial phthalate mass was found in the aerosol fraction.

Volatilisation is thus a process that must be considered for the phthalates and expressing it through a 1st order removal, cf. Equation **55**, a probable contribution will be about 50%.

In *EU RA DEHP (2000)* a $K_d$ value for DEHP of 5600 litre · kg is stated for a municipal sludge-water system and a mean value of 3700 litre · kg for adsorption to sediments. For BBP a $K_d$ value for sludge adsorption of 244 is stated *(EU RA BBP, 2000)*. These figures are a factor of 2 and 10 lower than the calibrated $K_d$ values for DEHP and BBP, respectively. In this work the measured dissolved fraction comprises unimers and aggregates. Even higher calibrated $K_d$ values would be found if the phthalate aggregates were defined as not dissolved. The retention factor, $R_{bio}$, would increase and the total degradation rate, $k_1 \cdot R_{bio}^{-1}$, would decrease and thus approach the degradation rates stated in the literature. If 50% of the dissolved fraction are aggregates $k_1 \cdot R_{bio}^{-1}$ is approximately a factor of 2 smaller.

From *Figge et al. (1991)*, *Marcomini et al. (1989)* and *Berna et al. (1989)* (cited by *Berna et al. (1999)*) the following half-lives for LAS were reported

| | |
|---|---|
| Biological treatment: | 1 - 2 hours |
| In stream: | 3 - 12 hours |
| Sewers: | 10 - 12 hours |
| Composting: | 6 - 14 days |
| Soils: | 10 - 33 days |
| Sludge: | 3 - 24 months |
| Land fill: | > 5 years |

$K_d$ values in the interval 1.000 – 2.000 litre · $kg^{-1}$ is stated in the literature (e.g. *Feijtel et al., 1995*), which is in accordance with the calibrated figures.

### 6.6.2 Mass balances

Mass balances are calculated using the 8 day mean experimental supernatant inlet concentrations in Table **12** and the mean calibration parameters in Table **20**.

In Table **23** the mass flows are presented as mean daily values [g · $day^{-1}$] for the dissolved and adsorbed inlet, outlet, primary and secondary sludge as well as the microbial degraded dissolved substances.

In the case of the phthalates 60 to 70% are removed by microbial degradation. Approximately 20 to 35% are removed adsorbed to primary and secondary sludge. The phthalates are sparingly soluble and the question is whether they participate in reversible equilibria with the suspended matter or if they are irreversibly adsorbed, e.g. through 1st order adsorption.

In the inlet the predominant part of the phthalates are adsorbed to organic matter that undergoes structural changes, i.e. degradation and hydrolysis, in the biological reactors. It is possible that the phthalates are either released or degraded by these processes but eventually they are quickly adsorbed on particulate matter (biomass) that is not degraded further. The strong adsorption combined with half-lives around 30 hours results in high removal through microbial activity and adsorption to sludge.

Approximately 85% of the total LAS is removed through biological degradation and approximately 15% is removed with the primary and secondary sludge, thus yielding a total removal of nearly 100%. These figures are in accordance with other investigations, e.g. *Berna et al. (1999)*.

NP and NPDE are only used in limited amounts in commercial products and the presence in the WWTP is due to the degradation of nonylphenol polyethoxylates with 3 to 20 ethoxylate groups, that are the most abundant oligomers in e.g. laundry detergents and other synthetic surface active substances. A mass balance for the nonylphenols therefore becomes difficult since the produced mass of NP and NPDE in the WWTP can exceed the influent mass. *Ahel et al. (1994)* found that 60 to 65% of the total influent nonylphenols to an activated sludge plant were recovered mainly in the sludge as NP, NPE and NPDE. In this work about 80% of the total NP and NPDE is degraded and approximately 15% is recovered in the sludge.

***Table 23.*** Calculated daily mean mass flows [g · day$^{-1}$] during the 8 day sampling period. Measured mean sewage flow and mean inlet concentrations are used together with mean calibration parameter values (cf. table **20**).

| | ***Inlet (100%)*** | | ***Outlet*** | | ***Degraded*** | ***Primary sludge*** | | ***Secondary sludge*** | |
|---|---|---|---|---|---|---|---|---|---|
| | ***Dissolved*** | ***Adsorbed*** | ***Dissolved*** | ***Adsorbed*** | ***Dissolved*** | ***Dissolved*** | ***Adsorbed*** | ***Dissolved*** | ***Adsorbed*** |
| **LAS** | 8284 | 12043 | 56.8 (0.2%) | 4.71 (0.02%) | 17119 (84.2%) | 373 (1.8%) | 2710 (13.3%) | 1.84 (0.01%) | 62.6 (0.3%) |
| **DEHP** | 30.8 | 212.0 | 3.5 (1.4%) | 1.4 (0.6%) | 170.2 (70.1%) | 1.4 (0.6%) | 47.7 (19.6%) | 0.1 (0.04%) | 18.5 (7.6%) |
| **DBP** | - | - | - | - | - | - | - | - | - |
| **DPP** | 0.220 | 0.298 | 0.034 (6.6%) | 0.003 (0.6%) | 0.369 (71.2%) | 0.010 (1.9%) | 0.067 (12.9%) | 0.001 (0.2%) | 0.034 (6.6%) |
| **BBP** | 1.35 | 2.50 | 0.55 (14.3%) | 0.06 (1.6%) | 1.83 (47.5%) | 0.06 (1.6%) | 0.56 (14.5%) | 0.02 (0.5%) | 0.77 (20.0%) |
| **DnOP** | 0.67 | 6.76 | 0.13 (1.7%) | 0.08 (1.1%) | 4.67 (62.9%) | 0.03 (0.4%) | 1.52 (20.5%) | 0.004 (0.01%) | 1.01 (13.6%) |
| **DnNP** | 0.29 | 4.42 | 0..06 (1.3%) | 0.05 (1.1%) | 2.86 (60.7%) | 0.01 (0.2%) | 0.99 (21.0%) | 0.002 (0.04%) | 0.72 (15.3%) |
| **NP** | 21.0 | 23.0 | 1.5 (3.4%) | 0.1 (0.2%) | 35.1 (79.8%) | 0.9 (2.1%) | 5.2 (11.8%) | 0.05 (0.1%) | 1.2 (2.7%) |
| **NPDE** | 203.2 | 389.0 | 9.4 (1.6%) | 1.0 (0.2%) | 471.0 (79.5%) | 9.1 (1.5%) | 87.5 (14.8%) | 0.3 (0.05%) | 13.7 (2.3%) |

### 6.6.3 Dynamic characteristics

In Figure **21** the dissolved steady state outlet concentrations are calculated from Equation **46**, by varying $T_{h,bio} = V_{bio} \cdot (Q + q_R - q_{PS})^{-1}$ and $k_1(\text{model 2}) \cdot R_{bio}^{-1}$.

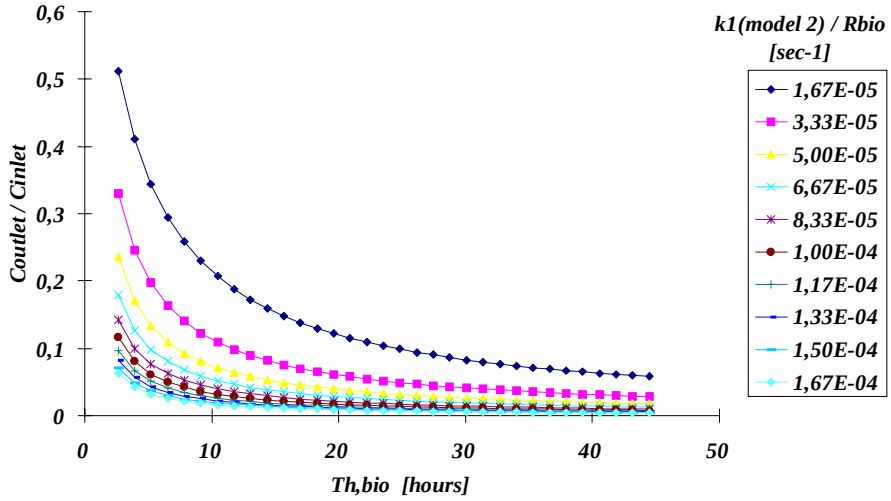


***Figure 21.*** *Dissolved outlet concentration as a function of $T_{h,bio} = V_{bio} \cdot (Q + q_R - q_{PS})^{-1}$ and $k_1(\text{model 2}) \cdot R_{bio}^{-1}$.*

Not surprising, increasing degradation rates and reactor volumes give rise to lower outlet concentrations. Increasing adsorption, i.e. retention factors, yield higher outlet concentrations.

In a WWTP it is of great interest to determine the time that passes from a change in inlet concentrations or flow to the steady state is reached. The steady state can be defined as when 90% of the steady state concentration is reached.

This period of time, denoted t(90%), can be found from the analytical solution, Equation **42**

$$C(t) = \frac{T}{P} \cdot C_0 \cdot \left(1 - e^{-P \cdot t}\right) \quad \Rightarrow$$

$$\left(1 - e^{-P \cdot t(90\,\%)}\right) = 0.90 \quad \Leftrightarrow \quad t(90\,\%) = \frac{-\ln(0.1)}{P} \qquad (\mathbf{56})$$

where P is the denominator in Equation **43**. The sludge balance around the secondary settler, Equation **23**, combined with the conditions $q_R = 0.6 \cdot Q$, $q_{SS} = 0.05 \cdot 0.6 \cdot Q$ and $q_{PS} = 0.15 \cdot 0.3 \cdot Q$, yield

$$t(90\,\%) = \frac{2.303}{\left(0.048 + 0.565 \cdot \frac{R_{SSout}}{R_{bio}}\right) \cdot \frac{1.56 \cdot Q}{V_{bio}} + \frac{k_1}{R_{bio}}} \qquad (\mathbf{57})$$

Where $1.56 \cdot Q = Q + q_R - q_{PS}$.

Figure **22** shows the relationships between t(90%), $T_h$ and $k_1$(model 2) · $R_{bio}^{-1}$.

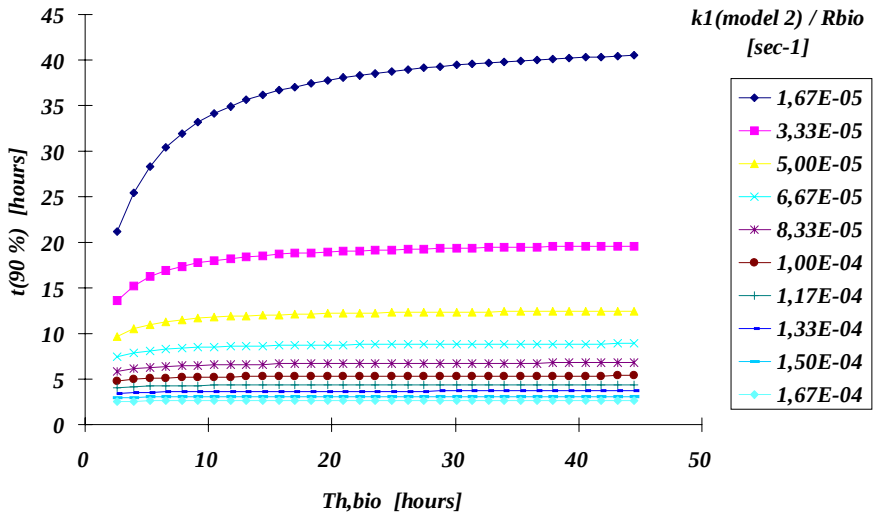


***Figure 22.*** *Time for reaching 90% of the steady state concentration as a function of* $T_{h,bio} = V_{bio} \cdot (Q + q_R - q_{PS})^{-1}$ *and* $k_1$*(model 2)* $\cdot R_{bio}^{-1}$.

High degradation rates and small retention times result in faster achievement of steady state conditions. Substances with low degradation rates are to a greater extent hydraulically dominated on account of the increased rush through of non degraded substance, which lead to small fluctuations in the alternate operation cycle, see Figure **13**.

The last term in the denominator in Equation **46** is determining with respect to changes in $R_{bio}$. Thus for increasing $C_{XBbio}$ (decreasing $k_1 \cdot R_{bio}^{-1}$) the time for reaching steady state increases as a result of the enhanced degradation and absorption capacity of the biomass.

Different scenarios can result in increased inlet water flows or substance concentrations. E.g. during rainfall, two scenarios are possible. A: Reduced substance concentration resulting from dilution from the increased water flow and B: Increased substance concentrations resulting from washout from roads, gutters etc.

The response in steady-state outlet concentrations can be found from table 25.

$$\frac{\delta C_{13}}{\delta T_{h,bio}} \cdot dT_{h,bio} = \begin{cases} \text{LAS}: -5.3 \cdot 10^{-7} \dfrac{\text{mg LAS}}{(\text{liter} \cdot \text{sec})} \cdot dT_{h,bio} \\ \text{DEHP}: -4.6 \cdot 10^{-6} \dfrac{\mu\text{g DEHP}}{(\text{liter} \cdot \text{sec})} \cdot dT_{h,bio} \end{cases} \quad (\mathbf{58})$$

and

$$\frac{\delta C_{13}}{\delta C_0} \cdot dC_0 = \begin{cases} \text{LAS}: 9.2 \cdot 10^{-3} \cdot dC_0 \\ \text{DEHP}: 9.1 \cdot 10^{-2} \cdot dC_0 \end{cases} \quad (\mathbf{59})$$

where the derived terms are previously used in the 1st order uncertainty analysis. In Table **24** the derived terms are aggregated. $\delta C_{13} \cdot \delta C_0^{-1}$ can also be found from Figure **21**.

***Table 24.*** Sensitivity of calculated outlet concentrations in model 2 in relation to changes in various model input parameters. The sign states an increase (+) or a decrease (-) in the outlet concentration.

| | $\frac{\delta C_{13}}{\delta k_{1N}}$ | $\frac{\delta C_{13}}{\delta K_d}$ | $\frac{\delta C_{13}}{\delta T_{h,bio}}$ | $\frac{\delta C_{13}}{\delta C_0}$ |
|---|---|---|---|---|
| **LAS** | - 20.5 | $+ 7.0 \cdot 10^{-6}$ | $- 5.3 \cdot 10^{-7}$ | $+ 9.2 \cdot 10^{-3}$ |
| **DEHP** | - 762 | $+ 2.0 \cdot 10^{-5}$ | $- 4.6 \cdot 10^{-6}$ | $+ 9.1 \cdot 10^{-2}$ |

Assuming an increased inlet flow, Q, by a factor of four compared to the measured 8. day hourly mean and a decrease in the inlet concentration by a factor of four

$$dT_{h,bio} = \frac{4 \cdot 3650\ m^3}{4 \cdot 1.56 \cdot 492\ \frac{m^3}{hour}} - \frac{4 \cdot 3650\ m^3}{1.56 \cdot 492\ \frac{m^3}{hour}} = - 14.3 \text{ hours}$$

and (from Table **12**)

$$dC_0 = \begin{cases} \text{LAS: } (0.25-1) \cdot 1.31\ \frac{mg\ LAS}{liter} = - 0.98 \frac{mg\ LAS}{liter} \\ \text{DEHP: } (0.25-1) \cdot 5.25\ \frac{\mu g\ DEHP}{liter} = - 3.94 \frac{\mu g\ DEHP}{liter} \end{cases}$$

the total increase (+) or decrease (-) in outlet concentrations are

$$dC_{13} = \begin{cases} \text{LAS: } 2.7 \cdot 10^{-2} - 8.98 \cdot 10^{-3} = + 1.8 \cdot 10^{-2}\ \frac{mg\ LAS}{liter} \\ \text{DEHP: } 0.24 - 0.36 = - 0.12\ \frac{\mu g\ DEHP}{liter} \end{cases}$$

This example shows that although the total substance mass through the system is unaltered, the dissolved outlet concentration increases for the more degradable and less hydrophobic substance (LAS) and decreases for the less degradable and more hydrophobic substance (DEHP).

The less hydrophobic substance is obviously being rushed through the reactors to a greater extent, although the more hydrophobic substance is less degradable and therefore should be more susceptible to washout with the effluent (cf. comments on Figure **21**). The coefficients in Equations **58** and **59** are deciding the predominant parameter.

The time for reaching steady-state is approximately a factor of five longer for DEHP (~ 20 hours) than for LAS (~ 4 hours), cf. Figure **22**, due to the larger adsorption capacity of DEHP. These times must be evaluated along with the half-lives which are 21.6 hours and 1.3 hours for DEHP and LAS respectively.

Therefore, during a rain incidents where the hydraulic load to the WWTP is increased, a worst case scenario can be defined for the less degradable and more hydrophilic substance. In this situation the half-life will be considerably longer than the time for reaching steady-state which means that the substance is washed through the reactors without being degraded.

Other scenarios can be simulated analogously, that reflect the system response to changes in hydraulic conditions (inlet flow) and/or substance properties (aerobic degradation rate, partition coefficient, inlet concentration) by employing the factors stated in Table 25.

# 7 Conclusion

The steady-state model description of the biological reactors and settlers in wastewater treatment plants that is used in SimpleTreat has been evaluated with respect to a model and experimental measurements of an alternately operated WWTP situated in Roskilde, Denmark. The effect of substituting a complex discontinuous operation in the model, involving alternating degradation and flow conditions between two reactors, with one single biological reactor with continuos flow (SimpleTreat) has been investigated by setting-up two models representing the respective operation schemes.

Through model simulations an empirical relationship between an aggregate pseudo 1$^{st}$ order degradation rate for the simple model and the aerobic and anoxic 1$^{st}$ order degradation rates, respectively, for the alternate operation has been established. When employing this aggregate degradation rate in the simple model an outlet concentration can be calculated that deviates no more than 2% from the alternate operation model. However, for substances with aerobic half-lives longer than approximately 2 hours, the aggregate 1$^{st}$ order degradation rate can be set equal to the aerobic 1$^{st}$ order degradation rate.

To calibrate the simple model an experimental series was performed where inlet, outlet, primary sludge and secondary sludge samples were taken and analysed for phthalates, nonylphenols and LAS. The aerobic 1$^{st}$ order degradation rate and the partition coefficient between solid phase and water were used as calibration factors for each individual substance. Generally the modelled half-lives for the phthalates were low and the removal efficiencies of the nonylphenols and phthalates were high compared to literature values. LAS half-life and adsorption properties corresponded well with previous investigations. The alternately operated WWTP is thus found to be very efficient with respect to biodegradation and overall removal of the investigated substances.

The results from the modelling work concludes that it is possible to substitute a model describing the complex alternating waste water treatment operation with a model containing one single biological reactor, corresponding to SimpleTreat, when a suggested empirical aggregate 1$^{st}$ order degradation rate is employed.

# 8 Symbols

To increase the clearness the constants, variables, abbreviations etc. are arranged in groups and roughly presented according to the chronology in the report.

### General definitions

| | |
|---|---|
| WWTP | Waste water treatment plant |
| $BOD_5$ | Biological oxygen demand in 5 days |
| PE | Person Equivalents |
| PEC | Predicted Environmental Concentration |

### Plant components

| | |
|---|---|
| R | Grating |
| PS | Primary settler |
| P | Anaerobic reactor for phosphorous removal |
| N | Aerobic (oxygen reducing) nitrifying reactor |
| D | Anoxic (nitrate reducing) denitrifying reactor |
| SS | Secondary settler |
| DR | Anaerobic (methane producing) sludge digestion reactor |

### Flows

| | | |
|---|---|---|
| Q | Inlet Flow | $m^3 \cdot hour^{-1}$ |
| $Q_{h,mean}$ | Hourly mean inlet flow | $m^3 \cdot hour^{-1}$ |
| $Q_{h,max}$ | Hourly maximum inlet flow | $m^3 \cdot hour^{-1}$ |
| $Q_{h,min}$ | Hourly minimum inlet flow | $m^3 \cdot hour^{-1}$ |
| $Q_{h,mean8day}$ | Hourly 8 day mean inlet flow | $m^3 \cdot hour^{-1}$ |
| $q_{PS}$ | Sludge flow from primary settler | $m^3 \cdot hour^{-1}$ |
| $q_R$ | Recycled sludge flow from secondary settler | $m^3 \cdot hour^{-1}$ |
| $q_{SS}$ | Sludge flow to treatment from secondary settler | $m^3 \cdot hour^{-1}$ |

### Reactor hydraulics

| | | |
|---|---|---|
| $V_{PS}$ | Volume of primary settler | $m^3$ |
| $V_P$ | Volume of anaerobic reactor | $m^3$ |
| $V_N$ | Volume of nitrifying reactor | $m^3$ |
| $V_D$ | Volume of denitrifying reactor | $m^3$ |
| $V_{SS}$ | Volume of secondary settler | $m^3$ |
| $V_{bio}$ | Total bio-reactor volume in model 2 (= $V_P+V_N+V_D$) | $m^3$ |
| $f_{PS}$ | Volume fraction of sludge in primary settler | |
| $f_{SS}$ | Volume of sludge in secondary settler | |
| $T_{h,bio}$ | Hydraulic retention time in P, N and D reactors | hours |
| $T_{h,total}$ | Hydraulic retention time in total WWTP | hours |

**Concentration denotations**

| | | |
|---|---|---|
| $C_0$ - $C_{16}$ | Dissolved substance concentration at position 0 to 16 (cf. Figures **8**, **9** and **16**) | mg · litre$^{-1}$ |
| $C_{13}$(approx) | Dissolved outlet concentration in model 2 | mg · litre$^{-1}$ |

**Suspended matter**

| | | |
|---|---|---|
| SPM | Supended particulate matter | |
| D.W. | Dry weight | |
| $C_{XB,in}$ | Concentration of SPM in inlet | g D.W. · litre$^{-1}$ |
| $C_{XB,PSsludge}$ | Concentration of SPM in primary sludge | g D.W. · litre$^{-1}$ |
| $C_{XB,PSout}$ | Concentration of SPM in outlet from PS | g D.W. · litre$^{-1}$ |
| $C_{XB,bioin}$ | Concentration of SPM in inlet to P-reactor | g D.W. · litre$^{-1}$ |
| $C_{XB,bio}$ | Concentration of SPM in P, N and D reactors | g D.W. · litre$^{-1}$ |
| $C_{XB,SSout}$ | Concentration of SPM in outlet from SS | g D.W. · litre$^{-1}$ |
| $C_{XB,SSsludge}$ | Concentration of SPM in secondary sludge | g D.W. · litre$^{-1}$ |

**Retention factors**

| | |
|---|---|
| $R_{in}$ | Retention factor in inlet |
| $R_{PSsludge}$ | Retention factor in primary sludge |
| $R_{PSout}$ | Retention factor in outlet from PS |
| $R_{bioin}$ | Retention factor in inlet to P-reactor |
| $R_{bio}$ | Retention factor in P, N and D reactors |
| $R_{SSout}$ | Retention factor in outlet from SS |
| $R_{SSsludge}$ | Retention factor in secondary sludge |

**Bio-degradation constants**

| | | |
|---|---|---|
| S | Bio-degradable substance | |
| O | Hydrolysable substance | |
| P | Product from bio-degradation | |
| μ | Maximum specific growth rate of biomass | sec$^{-1}$ |
| Y | Yield constant | mg $X_{B,bio}$ · (mg S)$^{-1}$ |
| ox. | Electron acceptor (aerobic: oxygen, anoxic: nitrate) | |
| $C_S$ | Conc. of dissolved bio-degradable substance | mg S · litre$^{-1}$ |
| $C_{ox.}$ | Concentration of electron acceptor | mg · litre$^{-1}$ |
| $K_S$ | Half saturation constant | mg S · litre$^{-1}$ |
| $K_{ox.}$ | Half saturation constant | mg ox. · litre$^{-1}$ |

### Adsorption parameters

| | | |
|---|---|---|
| $K_d$ | Adsorption equilibrium coefficient | litre · (kg D.W.)$^{-1}$ |
| $K_{d,inlet}$ | -"- in the inlet | litre · (kg D.W.)$^{-1}$ |
| $K_{d,outlet}$ | -"- in the outlet | litre · (kg D.W.)$^{-1}$ |
| $K_L$ | Langmuir adsorption equilibrium coefficient | litre · mol$^{-1}$ |
| $K_{ow}$ | Octanol/water partition coefficient | litre water · (litre octanol)$^{-1}$ |
| $K_{oc}$ | Organic carbon/water partition coefficient | litre water · (kg organic C)$^{-1}$ |
| $f_{oc}$ | Fraction of organic carbon in SPM | kg organic C · (kg D.W.)$^{-1}$ |
| $C_X$ | Concentration of available sites on adsorbate X | mol · litre$^{-1}$ |
| $C_{X,total}$ | Total conc. of available sites on adsorbate X | mol · litre$^{-1}$ |
| $C_{S-X}$ | Concentration of adsorption complex | mol · litre$^{-1}$ |

### Kinetic parameters

| | | |
|---|---|---|
| $k_{1bio}$ | Pseudo 1$^{st}$ order rate constant for bio-degradation | sec$^{-1}$ |
| $k_{1abio}$ | Pseudo 1$^{st}$ order rate constant for abiotic degradation | sec$^{-1}$ |
| $k_{1ox}$ | Pseudo 1$^{st}$ order rate constant for oxidation | sec$^{-1}$ |
| $k_{1ph}$ | Pseudo 1$^{st}$ order rate constant for photolysis | sec$^{-1}$ |
| $k_{1vol}$ | Pseudo 1$^{st}$ order rate constant for volatilisation | sec$^{-1}$ |
| $k_{1pr}$ | Pseudo 1$^{st}$ order rate constant for precipitation | sec$^{-1}$ |
| $k_h$, $k_{hy}$, $k_{1hy,O2}$, $k_{1hy,NO3}$ | Hydrolysis rate constants | sec$^{-1}$ |
| $K_X$, $K_{O2}$, $K_{NO3}$ | Hydrolysis half saturation rates | mg · litre$^{-1}$ |
| $k_{1N}$ | Pseudo 1$^{st}$ order rate constant for nitrification | sec$^{-1}$ |
| $k_{1D}$ | Pseudo 1$^{st}$ order rate constant for denitrification | sec$^{-1}$ |
| $k_1$(model 2) | Pseudo 1$^{st}$ order rate constant for total degradation in model 2 | sec$^{-1}$ |
| $t_{½}$ | Half-life | hours |

### Alternate operation parameters

| | |
|---|---|
| "cycle steady-state" | Mean concentration within one 4 hour cycle during steady-state |
| D | Maximum deviation from "cycle steady-state" concentration |
| Phase A - F | Phases in one 4 hour cycle |

### Mathematical constants

| | |
|---|---|
| P | Function in analytical solution |
| T | Function in analytical solution |
| K | Constant in analytical solution |

### Constants in numerical solution

| | | |
|---|---|---|
| t | Time | sec |
| $\Delta t$ | Time step in numerical method | sec |
| $C_m^{in}$ | Dissolved conc. of state variable m in inlet | mg · litre$^{-1}$ |
| $C_m^{out}$ | Dissolved conc. of state variable m in outlet | mg · litre$^{-1}$ |
| $C_{m,total}$ | Total conc. of state variable m | mg · litre$^{-1}$ |
| $C_m(t)$ | Dissolved conc. of state variable m to time t | mg · litre$^{-1}$ |
| M | Number of state variables | |

### Experimental abbreviation

| | |
|---|---|
| n.d. | Not detected |

### Statistical constants

| | |
|---|---|
| $s_{pooled}$ | Pooled standard deviation |
| $N_1$ - $N_s$ | Number of data in subseries 1 to s |
| $s_y$ | Standard deviation of model dependent variable y |
| $s_{xi}$ | Standard deviation of model independent variable $x_i$ |
| $\rho_{xi,xj}$ | Correlation coefficient between input variables $x_i$ and $x_j$ |
| $\frac{\partial C_y}{\partial x_i}$ | Sensitivity of concentration of dependent variable y to independent variable $x_i$ |

### Chemical abbreviations

| | |
|---|---|
| LAS | Linear alkylbenzene sulfonate |
| DEHP | Di-(2ethylhexyl)-phthalate |
| DBP | Dibutylphthalate |
| DPP | Dipentylphthalate |
| BBP | Benzylbutylphthalate |
| DnOP | Di-(n-octyl)-phthalate |
| DnNP | Di-(n-nonyl)-phthalate |
| NP | Nonylphenol |
| NPDE | Nonylphenol-diethoxylate |
| AE | Alcohol ethoxylate |
| AES | Alcohol ethoxy sulfate |

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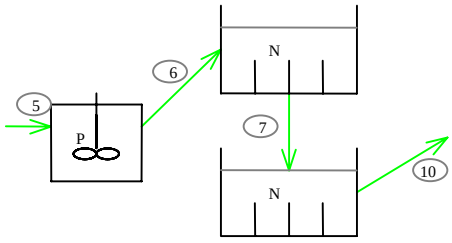
# Appendix 1

Alternate operation cycles, A to F cf. figure 9, with mass balances for each reactor.

**Phase A ($t_F \leq t < t_A$):**




*Phase A: ½ hour*

Primary settler, liquid phase, $C_4$:

Start concentration: $C_4(t_F)$.

$$\frac{dC_4 \cdot \left(1 + K_d \cdot C_{X_B,PSout}\right) \cdot \left(1 - f_{PS}\right) \cdot V_{PS}}{dt} =$$

$$0.3 \cdot Q \cdot C_0 \cdot \left(1 + K_d \cdot C_{X_B,in}\right)$$

$$- \left(0.3 \cdot Q - q_{PS}\right) \cdot C_4 \cdot \left(1 + K_d \cdot C_{X_B,PSout}\right)$$

$$- q_{PS} \cdot C_4 \cdot \left(1 + K_d \cdot C_{X_B,PSsludge}\right) \quad \Leftrightarrow$$

$$\frac{dC_4}{dt} = \frac{1}{V_{PS} \cdot \left(1 - f_{PS}\right)} \cdot$$

$$\left(0.3 \cdot Q \cdot C_0 \cdot \frac{R_{in}}{R_{PSout}} - \left(0.3 \cdot Q - q_{PS} - q_{PS} \cdot \frac{R_{PSsludge}}{R_{PSout}}\right) \cdot C_4\right) \quad \textbf{(60)}$$

Primary settler, settled phase, $C_3$:

Start concentration: $C_3(t_F)$.

$$\frac{dC_3 \cdot \left(1 + K_d \cdot C_{X_B,PSsludge}\right) \cdot f_{PS} \cdot V_{PS}}{dt} =$$

$$q_{PS} \cdot C_4 \cdot \left(1 + K_d \cdot C_{X_B,PSsludge}\right) - q_{PS} \cdot C_3 \cdot \left(1 + K_d \cdot C_{X_B,PSsludge}\right) \quad \Leftrightarrow$$

$$\frac{dC_3}{dt} = \frac{q_{PS}}{f_{PS} \cdot V_{PS}} \cdot \left(C_4 - C_3\right) \quad \textbf{(61)}$$

Anaerobic P-reactor, $C_6$:

Start concentration: $C_6(t_F)$.

$$\frac{dC_6 \cdot \left(1 + K_d \cdot C_{X_B,bio}\right) \cdot V_P}{dt} = 0.7 \cdot Q \cdot C_0 \cdot \left(1 + K_d \cdot C_{X_B,in}\right)$$

$$+ q_R \cdot C_{14} \cdot \left(1 + K_d \cdot C_{X_B,SSsludge}\right) + \left(0.3 \cdot Q - q_{PS}\right) \cdot C_4 \cdot \left(1 + K_d \cdot C_{X_B,PSout}\right)$$

$$- \left(Q + q_R - q_{PS}\right) \cdot C_6 \cdot \left(1 + K_d \cdot C_{X_B,bio}\right) \quad \Leftrightarrow$$

$$\frac{dC_6}{dt} = \frac{1}{V_P \cdot R_{bio}} \cdot (0.7 \cdot Q \cdot C_0 \cdot R_{in} + q_R \cdot C_{14} \cdot R_{SSsludge}$$

$$+ \left(0.3 \cdot Q - q_{PS}\right) \cdot C_4 \cdot R_{PSout} - \left(Q + q_R - q_{PS}\right) \cdot C_6 \cdot R_{bio}) \qquad (\mathbf{62})$$

1.st aerobic N-reactor, $C_7$:

Start concentration: $C_9(t_F)$.

$$\frac{dC_7 \cdot \left(1 + K_d \cdot C_{X_B,bio}\right) \cdot V_N}{dt} = \left(Q + q_R - q_{PS}\right) \cdot C_6 \cdot \left(1 + K_d \cdot C_{X_B,bio}\right)$$

$$- \left(Q + q_R - q_{PS}\right) \cdot C_7 \cdot \left(1 + K_d \cdot C_{X_B,bio}\right) - k_{1N} \cdot C_7 \cdot V_N \quad \Leftrightarrow$$

$$\frac{dC_7}{dt} = \frac{\left(Q + q_R - q_{PS}\right)}{V_N} \cdot C_6 - \left(\frac{\left(Q + q_R - q_{PS}\right)}{V_N} + \frac{k_{1N}}{R_{bio}}\right) \cdot C_7 \quad (\mathbf{63})$$

2.nd aerobic N-reactor, $C_{10}$:

Start concentration: $C_{12}(t_F)$.

$$\frac{dC_{10} \cdot \left(1 + K_d \cdot C_{X_B,bio}\right) \cdot V_N}{dt} = \left(Q + q_R - q_{PS}\right) \cdot C_7 \cdot \left(1 + K_d \cdot C_{X_B,bio}\right)$$

$$- \left(Q + q_R - q_{PS}\right) \cdot C_{10} \cdot \left(1 + K_d \cdot C_{X_B,bio}\right) - k_{1N} \cdot C_{10} \cdot V_N \quad \Leftrightarrow$$

$$\frac{dC_{10}}{dt} = \frac{\left(Q + q_R - q_{PS}\right)}{V_N} \cdot C_7 - \left(\frac{\left(Q + q_R - q_{PS}\right)}{V_N} + \frac{k_{1N}}{R_{bio}}\right) \cdot C_{10} \qquad (\mathbf{64})$$

Secondary settler, liquid phase, $C_{13}$:

Start concentration: $C_{13}(t_F)$.

$$\frac{dC_{13} \cdot \left(1 + K_d \cdot C_{X_B,SSout}\right) \cdot \left(1 - f_{SS}\right) \cdot V_{SS}}{dt} = \left(Q + q_R - q_{PS}\right) \cdot C_{10} \cdot \left(1 + K_d \cdot C_{X_B,bio}\right)$$

$$- (Q - q_{SS} - q_{PS}) \cdot C_{13} \cdot \left(1 + K_d \cdot C_{X_B,SSout}\right) - (q_R + q_{SS}) \cdot C_{13} \cdot \left(1 + K_d \cdot C_{X_B,SSsludge}\right) \Leftrightarrow$$

$$\frac{dC_{13}}{dt} = \frac{1}{V_{SS} \cdot (1 - f_{SS})} \cdot ((Q + q_R - q_{PS}) \cdot C_{10} \cdot \frac{R_{bio}}{R_{SSout}}$$

$$- (Q - q_{SS} - q_{PS}) \cdot C_{13} - (q_{SS} + q_R) \cdot C_{13} \cdot \frac{R_{SSsludge}}{R_{SSout}}) \quad \textbf{(65)}$$

Secondary settler, settled phase, $C_{14} = C_{15}$:

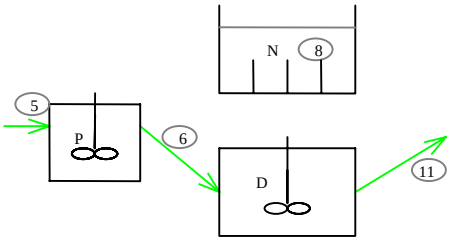
Start concentration: $C_{14}(t_F) = C_{15}(t_F)$.

$$\frac{dC_{14} \cdot \left(1 + K_d \cdot C_{X_B,SSsludge}\right) \cdot f_{SS} \cdot V_{SS}}{dt} =$$

$$(q_{SS} + q_R) \cdot C_{13} \cdot \left(1 + K_d \cdot C_{X_B,SSsludge}\right) - (q_{SS} + q_R) \cdot C_{14} \cdot \left(1 + K_d \cdot C_{X_B,SSsludge}\right) \Leftrightarrow$$

$$\frac{dC_{14}}{dt} = \frac{(q_{SS} + q_R)}{f_{SS} \cdot V_{SS}} \cdot (C_{13} - C_{14}) \quad \textbf{(66)}$$

**Phase B ($t_A \leq t < t_B$):**




*Phase B: ½*

Primary settler, liquid phase, $C_4$:

Identical to phase A (Equation **60**). Start concentration: $C_4(t_A)$.

Primary settler, settled phase, $C_3$:

Identical to phase A (Equation **61**). Start concentration: $C_3(t_A)$.

Anaerobic P-reactor, $C_6$:

Identical to phase A (Equation **62**). Start concentration: $C_6(t_A)$.

N-reactor, $C_8$:

Start concentration: $C_7(t_A)$.

$$\frac{dC_8 \cdot R_{bio} \cdot V_N}{dt} = - k_{1N} \cdot C_8 \cdot V_N \Leftrightarrow$$

$$\frac{dC_8}{dt} = \frac{-k_{1N}}{R_{bio}} \cdot C_8 \qquad (67)$$

Anoxic D-reactor, $C_{11}$:

Start concentration: $C_{10}(t_A)$.

$$\frac{dC_{11}}{dt} = \frac{(Q + q_R - q_{PS})}{V_D} \cdot C_6 - \left( \frac{(Q + q_R - q_{PS})}{V_D} + \frac{k_{1D}}{R_{bio}} \right) \cdot C_{11} \qquad (68)$$

Secondary settler, liquid phase, $C_{13}$:

Start concentration: $C_{13}(t_A)$.

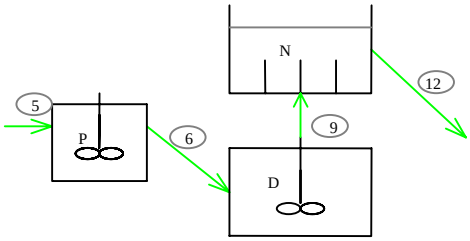
$$\frac{dC_{13}}{dt} = \frac{1}{V_{SS} \cdot (1 - f_{SS})} \cdot ((Q + q_R - q_{PS}) \cdot C_{11} \cdot \frac{R_{bio}}{R_{SSout}}$$

$$- (Q - q_{SS} - q_{PS}) \cdot C_{13} - (q_{SS} + q_R) \cdot C_{13} \cdot \frac{R_{SSsludge}}{R_{SSout}}) \qquad (69)$$

Secondary settler, settled phase, $C_{14} = C_{15}$:

Identical to phase A (Equation **70**). Start concentration: $C_{14}(t_A) = C_{15}(t_A)$.

**Phase C ($t_B \leq t < t_C$):**




*Phase C: 1 hour*

Primary settler, liquid phase, $C_4$:

Identical to phase A (Equation **60**). Start concentration: $C_4(t_B)$.

Primary settler, settled phase, $C_3$:

Identical to phase A (Equation **61**). Start concentration: $C_3(t_B)$.

Anaerobic P-reactor, $C_6$:

Identical to phase A (Equation **62**). Start concentration: $C_6(t_B)$.

Anoxic D-reactor, $C_9$:

Start concentration: $C_{11}(t_B)$.

$$\frac{dC_9}{dt} = \frac{(Q + q_R - q_{PS})}{V_D} \cdot C_6 - \left( \frac{(Q + q_R - q_{PS})}{V_D} + \frac{k_{1D}}{R_{bio}} \right) \cdot C_9 \qquad (71)$$

Aerobic N-reactor, $C_{12}$:

Start concentration: $C_8(t_B)$.

$$\frac{dC_{12}}{dt} = \frac{(Q + q_R - q_{PS})}{V_N} \cdot C_9 - \left( \frac{(Q + q_R - q_{PS})}{V_N} + \frac{k_{1N}}{R_{bio}} \right) \cdot C_{12} \qquad (72)$$

Secondary settler, liquid phase, $C_{13}$:

Start concentration: $C_{13}(t_B)$.

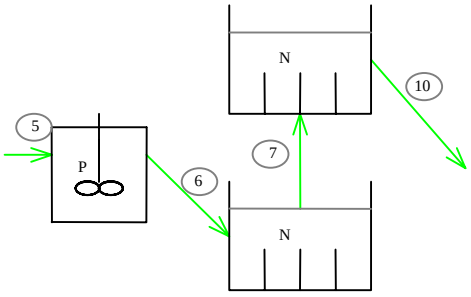
$$\frac{dC_{13}}{dt} = \frac{1}{V_{SS} \cdot (1 - f_{SS})} \cdot ((Q + q_R - q_{PS}) \cdot C_{12} \cdot \frac{R_{bio}}{R_{SSout}}$$

$$- (Q - q_{SS} - q_{PS}) \cdot C_{13} - (q_{SS} + q_R) \cdot C_{13} \cdot \frac{R_{SSsludge}}{R_{SSout}}) \qquad (73)$$

Secondary settler, settled phase, $C_{14} = C_{15}$:

Identical to phase A (Equation **74**). Start concentration: $C_{14}(t_B) = C_{15}(t_B)$.

**Phase D ($t_C \leq t < t_D$):**




*Phase D: ½ hour*

Primary settler, liquid phase, $C_4$:

Identical to phase A (Equation **60**). Start concentration: $C_4(t_C)$.

Primary settler, settled phase, $C_3$:

Identical to phase A (Equation **61**). Start concentration: $C_3(t_C)$.

Anaerobic P-reactor, $C_6$:

Identical to phase A (Equation **62**). Start concentration: $C_6(t_C)$.

1.st aerobic N-reactor, $C_7$:

Identical to phase A (Equation **63**). Start concentration: $C_9(t_C)$.

2.nd aerobic N-reactor, $C_{10}$:

Identical to phase A (Equation **64**). Start concentration: $C_{12}(t_C)$.

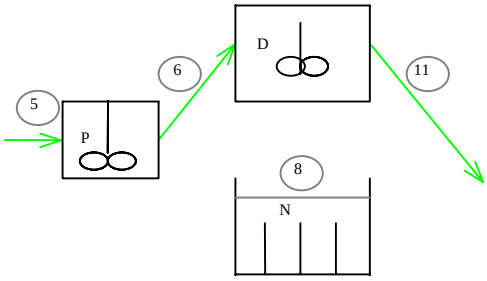
Secondary settler, liquid phase, $C_{13}$:

Identical to phase A (Equation **65**). Start concentration: $C_{13}(t_C)$.

Secondary settler, settled phase, $C_{14} = C_{15}$:

Identical to phase A (Equation **75**). Start concentration: $C_{14}(t_C) = C_{15}(t_C)$.

**Phase E ($t_D \leq t < t_E$):**




*Phase E: ½ hour*

Primary settler, liquid phase, $C_4$:

Identical to phase A (Equation **60**). Start concentration: $C_4(t_D)$.

Primary settler, settled phase, $C_3$:

Identical to phase A (Equation **61**). Start concentration: $C_3(t_D)$.

Anaerobic P-reactor, $C_6$:

Identical to phase A (Equation **62**). Start concentration: $C_6(t_D)$.

Aerobic N-reactor, $C_8$:

Identical to phase B (Equation **67**). Start concentration: $C_7(t_D)$.

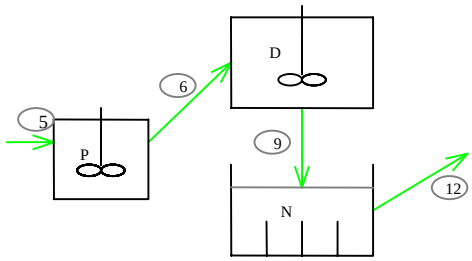
Anoxic D-reactor, $C_{11}$:

Identical to phase B (Equation **68**). Start concentration: $C_{10}(t_D)$.

Secondary settler, liquid phase, $C_{13}$:
Identical to phase B (Equation **69**). Start concentration: $C_{13}(t_D)$.

Secondary settler, settled phase, $C_{14} = C_{15}$:
Identical to phase A (Equation **76**). Start concentration: $C_{14}(t_D) = C_{15}(t_D)$.

**Phase F ($t_E \leq t < t_F$):**




*Phase F: 1 hour*

Primary settler, liquid phase, $C_4$:
Identical to phase A (Equation **60**). Start concentration: $C_4(t_E)$.

Primary settler, settled phase, $C_3$:
Identical to phase A (Equation **61**). Start concentration: $C_3(t_E)$.

Anaerobic P-reactor, $C_6$:
Identical to phase A (Equation **62**). Start concentration: $C_6(t_E)$.

Anoxic D-reactor, $C_9$:
Identical to phase C (Equation **71**). Start concentration: $C_{11}(t_E)$.

Aerobic N-reactor, $C_{12}$:
Identical to phase C (Equation **72**). Start concentration: $C_8(t_E)$.

Secondary settler, liquid phase, $C_{13}$:
Identical to phase C (Equation **73**). Start concentration: $C_{13}(t_E)$.

Secondary settler, settled phase, $C_{14} = C_{15}$:
Identical to phase A (Equation **77**). Start concentration: $C_{14}(t_E) = C_{15}(t_E)$.

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**2000**

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Nr. 318: Order Theoretical Tools in Environmental Sciences. Proceedings of the Second Workshop October 21st, 1999 in Roskilde, Denmark. By Sørensen, P.B. et al. ( in press)

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**2001**

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Nr. 351: PSSD – Planning System for Sustainable Development. A Methodical Report. By Hansen, H.S (ed.) (in press)

The steady-state compartment description of the biological reactors and settlers in wastewater treatment plants that is used in SimpleTreat has been evaluated with respect to an alternately operated WWTP situated in Roskilde, Denmark. The effect of substituting a complex discontinuous operation, involving alternating degradation and flow conditions between two reactors, with one single biological reactor with continuos flow (SimpleTreat) has been investigated by setting-up two models representing the respective operation schemes.

An experimental series was performed where inlet, outlet, primary sludge and secondary sludge samples were taken and analysed for phthalates, nonylphenols and LAS. Generally the modelled half-lives for the phthalates were low and the removal efficiencies of the nonylphenols and phthalates were high compared to literature values.

The results from the modelling work concludes that it is possible to substitute a complex alternating operation with a system containing one single biological reactor, corresponding to SimpleTreat, when a suggested empirical aggregate 1st order degradation rate is employed.

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