Dynamic modelling of an activated sludge process at a pulp and paper mill

Jon Bolmstedt

Master thesis

Lund, November 2000

Abstract

This master thesis presents a dynamic model describing the performance of one of the activated sludge basins at Hylte, a pulp and paper mill in the southwest of Sweden. Flow through the reactor was described with three CSTR's and the settler was modelled with a one-dimensional layer model. Biological reactions were described by a modified Activated Sludge Model No 1 (ASM1). Modifications included the addition of a soluble slowly biodegradable substance and the introduction of nitrogen limitation to heterotrophic growth. The wastewater originates from mechanical pulp and recycled newspaper. No chemical pulp is manufactured, although a small amount is added in the process. The activated sludge basin operates at neutral pH conditions and at temperatures around 35°C.

Summary

The current master thesis presents a dynamic model describing the performance of one of the activated sludge basins at Hylte, a pulp and paper mill in the southwest of Sweden.

Hylte produces newspaper mainly from mechanical pulp and recycled newspaper, although a small amount of chemical pulp must sometimes be added to the process. The modelled activated sludge basin has surface aerators, operates at neutral pH conditions and at temperatures around 35°C. It has a volume of 4500 m^3 and receives a flow of 11000 m^3/d. The sludge age is about 3 days.

A slightly modified IAWQ activated sludge model no 1 (ASM1) was used to describe the biological reactions. Modifications included the addition of a soluble slowly biodegradable substance and the introduction of nitrogen limitation for heterotrophic growth. Altered parameter values were the growth rate, the decay rate and the ammonification rate, which were all increased due to high temperatures. The ratios of suspended solids to particulate COD fractions were found to differ from recommended values, but the ASM2 recommendations of the nitrogen content in these fractions were verified.

The hydraulic model describing flow paths was not validated by experimental work and hence design values were used. The reactor was modelled as three ideally mixed compartments and the settler with a robust one-dimensional layer model.

For two reasons in particular it is impossible to identify the necessary parameters from the current measurements. The first reason is the choice of measured variables. Most measurements are performed on samples let to settle and hence both soluble and some particulate components are detected. These measurements give no information regarding the total concentration in the sample, which is especially important for modelling reasons. The second reason is that measuring precision is mistaken for measuring accuracy. Precision is proven to be high for COD measurements and is evaluated using control samples prepared in the laboratory. Accuracy, however, depends on many factors starting with the circumstances surrounding sample collection and storing. The steps from sample collection to data storage are not well documented resulting in precise measurements of variables other than the planned. Oxygen concentrations are deliberately not measured along with several flows, which are guessed instead.

It was found that for model evaluation the characterization of the influent water was the most important step, followed by knowledge of the effluent concentrations. With only minor changes of the current measuring procedures, sufficient information was extracted for successful model calibration. New measurements involved measuring the concentration of the studied substance on a total sample (shaken, not stirred), as well as on a filtered sample. In this way both the particulate and the soluble components could be determined.

The proposed biological model gives good correlation with measurements of COD (both soluble and particulate) and with average nitrogen concentrations. Effluent suspended solids are not well predicted and a study of the hydraulics in the settler should be performed. Biological parameters do not need to be the same since the plant operates at conditions greatly different from the ones in municipal waters, which ASM1 was designed for. Batch tests with the actual water could describe the current fauna more accurately, or verify the default parameters.

Acknowledgements

My interest in wastewater treatment had not resulted in this thesis, had I not taken the course ‘Control of biological wastewater treatment’ for Professor Gustaf Olsson. I also thank Dr Ulf Jeppsson for valuable discussions and proof-reading, and for his interest in my future academic career.

At Hylte I thank plant personnel, especially Johan and Stig, for helping me understand the plant layout. Also Lillian’s laboratory work is greatly acknowledged.

Finally I thank Zoegas for their blend ‘Skånerost’. During the work on this thesis, I have consumed about 100 L coffee.

1 Introduction

We all use models to understand and describe our perception of the reality surrounding us. Models help us communicate and just like pictures they contain a lot of information. Observing, and enjoying, a cup of coffee could result in the construction of the following mental model of the temperature change:

A mug of hot coffee gets cooler

Put in mathematical terms, the equation of heat transfer for our coffee mug becomes:

$$\frac{dT_{coffee}}{dt} = -k \cdot (T_{coffee} - T_{room})$$

With the lumped *parameter* k describing physical properties and with the *variable* T_{coffee} it is now possible to describe a vast number of cooling coffee mugs of various sizes in rooms at various temperatures. One can also determine the increasing rate at which the coffee must be enjoyed before it assumes an unpleasantly cool temperature.

Modelling is an important concept in information technology and an effective tool in information transfer. Although the current master thesis is not about modelling coffee mugs, the steps in developing models are principally the same.

The current wastewater treatment plant (WWTP) at Hyltebruk was originally built in the 1970's, and has since then been extended on several occasions in order to cope with higher loads and stronger environmental regulations. Several processes are currently used, such as activated sludge, anaerobic treatment, trickling filters, chemical treatment and sedimentations, forming a system optimised neither economically nor with respect to the quality of the effluent water.

Optimisation may start with designing a dynamic model of the plant, which can be used to simulate the outcome of hypothetical modifications. Modelling and simulation serve other purposes as well, of which one is to incorporate the use of mathematical tools in research and development.

The thesis starts with introducing the forest industry, some of its pollutants and means of wastewater treatment. In Chapter 2 the modelling concept is introduced, and ways to describe the hydraulics and the biology are described. Chapter 3 presents the wastewater treatment plant at Hylte, flows and reactors, and the measurements performed to monitor the contents of the water. These measurements are discussed in Chapter 4; wastewater characterization. Evaluation of the proposed model, combining hydraulics and biology, is performed in Chapter 5 and a discussion on these results is finally found in Chapter 6.

1.1 The forest industry in Sweden

The manufacturing of paper started in Sweden in the late 16th century. From the mid 19th century mechanical pulp, sulphate pulp and sulphite pulp were manufactured, but it was not until the mid 20th century that the actual production of paper began at Nymölla and Husum. As early as in 1978 Hylte started using recycled newspaper in the production.

1.1.1 Pollutants

Industrial revolutions and economic growth is often linked with a decline in biological diversity. A few decades ago, dead rivers were common and more recently chlorine bleaching was found to be harmful. Efficient forestry leads to clear-cut forests and nutrient depletion on land. Fewer, but more efficient paper mills cause elevated concentrations of heavy metals in paper mill effluents.

Chlorinated organic compounds will end up in the effluent if the pulp is bleached with elementary chlorine or with products containing chlorine. These are all more or less toxic and accumulate in the biomass.

Oxygen consuming compounds are a group of pollutants partly biologically degradable. In the degradation process oxygen is consumed and an oxygen deficient environment may form in the recipient. Only a few organisms may live in such an environment and the aesthetical value is lowered. Oxygen consuming compounds may be measured as COD, *chemical oxygen demand* or as BOD, *biological oxygen demand*. BOD is often measured during 5 or 7 days, giving an estimate of some of the biodegradable substances. There are many compounds from the forest industry that are biologically degradable. Cellulose and starch are two dissolved substances that create an oxygen demand in the recipient, but these may also be degraded without oxygen. Lignin, on the other hand, can only be degraded in the presence of oxygen. Of the total emissions of COD in Sweden 1994 the forest industry accounted for 8.5% (Skogsindustrins Utbildning i Markaryd AB, 1997).

Nutrients are often emitted as nitrogen and phosphorous, but depending on the chemical conditions of the recipient, sulphur and many trace elements may also serve as nutrients. Nutrients permit accelerated growth of plants and organisms, a phenomenon called eutrophication when the nutrients are abiotic in origin. This may have devastating consequences for the aquatic biosphere, partly due to the oxygen depletion following the decay of the increased biomass. Algal blooms are problems arising from eutrophication that are directly harmful to humans. Wastewaters from mechanical pulps are usually nutrient deficient, and nitrogen and phosphorous must be added in some form.

If the pulp is bleached with oxygen EDTA, see Figure 1.1, must be added. EDTA, ethylenediaminetetraaceticacid is a chelating agent, which strongly binds metal ions that otherwise would catalyse peroxide degradation. EDTA contains nitrogen, which could be used in the treatment process. Trained EDTA-degrading bacteria reproduce slowly (van Ginkel, 1999), and other bacteria degrade EDTA into products where the nitrogen is inert (Virtapohja, 1998).

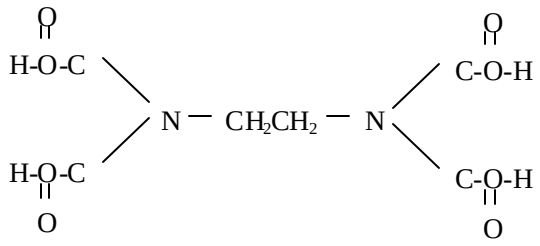

Figure 1.1. EDTA

Suspended solids (TSS) and mixed liquor suspended solids (MLSS), depending on the method of measurement, are visible particles of fibres, bark or bacterial flocks. They create visual problems and may disturb the aquatic environment on the macroscopic level. They are also made of oxygen-consuming compounds.

1.2 Wastewater treatment

The objective of wastewater treatment is to ensure that only a fraction of the unwanted substances reach the recipient. There are many ways to achieve this goal, but they all obey the law of conservation that clearly states that neither mass nor energy is destroyed in the process. The task is therefore to transform harmful substances into less harmful and preferably useful substances. Major products from the treatment of mechanical pulp wastewaters are sludge and carbon dioxide. Sludge may of course be viewed as a number of products, depending on its potential use. The carbon dioxide emitted does not add to the global warming, since growing trees absorb an equal amount. Perhaps nitrogen and phosphorous compounds should also be regarded as products, when they are added in the process.

The usefulness of a by-product, actual or theoretical, depends on one's imagination. An excellent example of by-product usefulness in waste treatment is the Swedish export of elk droppings to German tourists. A useful substance from the wastewater treatment plants of the forest industry is methane formed under anaerobic digestion. Methane may be used either for combustion or used as a carbon source in anoxic processes (Houbron *et al.*, 1999). Emissions of methane should be avoided, as methane is a potent greenhouse gas.

The sludge from activated sludge processes can be used in a number of ways. After mechanical dewatering, and in some cases also after drying, the sludge may be combusted. Sludge may also serve as a weed suppressor if placed on the ground absorbing the sunlight. It may also be used as a soil amendment since it contains nitrogen or will host species that assimilate nitrogen from the air.

1.2.1 Unit operations

The process mostly used in wastewater treatment is the *activated sludge (AS)* process. In an activated sludge process a high concentration of bacteria is achieved by re-circulating thickened sludge. Sufficient mixing and aeration is today supplied by compressed air introduced at the bottom of the basin, but earlier fans and stirrers at the surface were used. Stirrers expose bacterial flocks to higher shear forces that may demote the formation of bacterial flocks. Supplying sufficient oxygen for biological growth is the major control issue in an activated sludge process and there is a trade off between clean water and low energy costs. High oxygen levels will have a negative influence on the biology in any subsequent anaerobic or anoxic step and low levels may impair flock formation, causing problems in the settler. In processes with dissolved oxygen (DO) control another issue is to cut any peaks in the power consumption, since these may constitute a large part of the energy cost (Olsson, 1999).

In combination with aerobic treatment an anoxic step is often used, especially when the objective is to remove nitrogen. To an anoxic step no oxygen is added and nitrate is reduced to nitrogen gas in a process called *denitrification*. Microbial growth in the absence of oxygen is less efficient, thus producing more gas and less biomass. This is desirable if the treatment of excess sludge is costly, or if the gas can be utilized. In anoxic process is methane produced, which may later be combusted for energy conversion.

In addition to these biological steps also purely physical separation processes are used. Of these *filtration* and *sedimentation* are the ones most widely used in wastewater treatment applications. All visible particles may be removed with filters. Membrane filtration have recently found many applications in separation processes and could also be used to produce thicker sludge.

Sedimentation can be seen as three sub-processes: clarification, thickening and compaction. Clarification takes place at the top of the basin where the solution is dilute. Thickening is the process that takes place below the sludge blanket level where the concentration of particles is much higher and where there no longer is unhindered sedimentation. At the very bottom of the settler where sludge concentrations are very high, compaction takes place. Factors with negative influences on sedimentation are hydraulic shocks and sludge swelling. Hydraulic shocks are the result of a rapid change in flow velocity, causing turbulence that increases the concentration of suspended solids in the effluent. Sludge swelling could be the result of too high a concentration of filamentous bacteria, forming sludge with poor settling properties. This problem may be avoided by creating an environment with the right relationship between filamentous bacteria and floc-forming bacteria. Factors that favour filamentous species are low concentrations of oxygen, substrate and nutrients. This is due to their larger specific surface area that allow them to operate more efficiently at lower concentrations of nutrients, as seen Figure 1.2. Poor settling conditions may also be the result of denitrification, where particles adhese to bubbles of nitrogen gas and are brought to the surface (rising sludge). This opposite process of sedimentation is also deliberately used in some cases and called *flotation*.

Since sedimentation is a crucial step in current wastewater treatment there are ways to improve the process. Settling velocity is increased if the settling particles have a higher density. This may be achieved by *flocculation*, where a flocculent, often a polymer, is added to create larger flocks of particles. A way to create particles that later may settle is by *precipitation*. An example is the removal of phosphate by precipitation with an iron- or aluminium salt, a process that of course leads to emissions of other ions.

In order to reduce the importance of the settler in sludge recovery, the bacteria may be cultivated in fixed *biofilms*. The carrier material, on which the bacteria grow, may be suspended and float around in the reactor or may be a fixed grid with a large surface area.

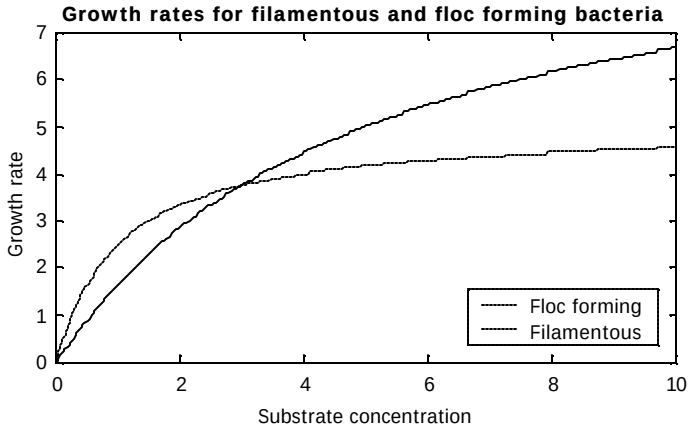

Figure 1.2. At lower substrate concentrations the filamentous bacteria are the fittest.

1.2.2 Biology

A wastewater treatment plant hosts species from several trophic levels, and it is not likely that one can control or model them all completely. Bacteria are the most common group of organisms (in a wastewater treatment plant) and deserve special attention. They are divided into several groups with regards to their source of energy and carbon, and what they look like. In the IAWQ activated sludge model no 1, which is used in this work to describe biological reactions, all organisms are separated with regard to their required source of carbon into *heterotrophic* and *autotrophic* bacteria.

Heterotrophs assimilate organic carbon that is also used for beneficial energy conversion. Autotrophs absorb carbon dioxide and oxidize ammonium for energy purposes. Heterotrophic strands grow both in the absence and presence of oxygen and without oxygen nitrate is used as an electron acceptor and reduced to nitrogen gas. This anaerobic respiration is less efficient than aerobic, thereby forming less biomass and more carbon dioxide from the substrate. Autotrophs are only active in the presence of oxygen and have significantly lower growth rates due to their choice of food. Thus they are sensitive to changes in flow rates and substrate concentrations.

A separation based on appearance gives flock forming bacteria and filamentous bacteria. Flocks have desirable settling properties, and are the preferred type. However, a small amount of filamentous bacteria will improve the settleability, as they form a backbone for flocks to adhese to. At low sludge ages flock-forming proteins are not formed and settling is poor. Much research has been done to understand the criteria that determine the ratio of flock-forming bacteria to filamentous bacteria. The objective is primarily to achieve good settling properties that originate from both physical and chemical properties of the flocks.

Higher up in the food chain the eucaryotes live, such as the protozoan. Protozoan are uni-cellular organisms that feed primarily on bacteria. As the bacteria consumed are mostly free swimming, protozoan may improve the effluent quality by reducing the amount of particles. Protozoan are not as numerous as bacteria since more evolved species need high sludge ages to reproduce sufficiently. However, when a fixed biofilm is used and the sludge age is high, the concentration of higher organisms may be so high that bacterial growth is impaired.

2 Developing models

Models vary from black-box models, where the underlying chemistry and biology is unknown, to white-box models, where this underlying chemistry and biology is modelled explicitly. They all have their advantages and disadvantages, but as a rule of thumb - the more information they give, the more information they need.

Black box models, *statistical models*, correlate observed variables to each other. Vast amounts of data are used to achieve a low standard deviation. The data have to be limited to specific conditions, (season, normal operating conditions) or the predictions would have large margins of errors. They have the disadvantage of only being able to predict results at observed operating conditions and the advantage of only using observed variables as a basis for the model.

White-box models, *mechanistic models*, describe the mechanisms behind the coupling of variables and may, consequently, be used for almost any operating condition. The predictions are limited by the intricacy of the model, which is limited by both the knowledge of the chemistry and biology involved, as well as by the limited number of actually measurable variables. Not only must all variables from the black box model be measured, but also a great number of variables specific to the mechanisms behind the biology involved, such as growth rates, half-saturation coefficients, kinetic coefficients and mass transfer coefficients. These should be estimated by experiments, but could also be determined from measured data. When necessary variables and constants are measurable, a white-box model is an excellent tool for optimisation and plant development. A mechanistic model describes the everyday situation as easily, or hard, as it describes unexpected events that will be poorly described by a black-box model.

How well, and in what way, the model describes reality is determined by its potential use. A discrepancy between the outputs of the model and reality can be treated in several ways:

1. The error is accepted
2. Data will be interpreted differently
3. The model is altered

The first alternative is the goal for any (other) action taken, as there will always be errors. If the error can be described by any known function or relationship data could be recalculated afterwards to fit reality. However, any such function is rarely known and could be the result of circumstances that also should be modelled. If it is not possible to reach an acceptable error by recalculation afterwards, or the theoretical ground for this is weak, there is reason to alter the model. Alterations may be relatively simple, as is the case for a change of a parameter value, to more complex if more variables should be included.

Biological reactions are in this work described by a mechanistic model: the activated sludge model no 1, ASM1. It was developed by the International Association on Water Pollution Research and Control, IAWPRC (now IWA) and first published in 1987.

2.1 Modelling the activated sludge process

Two aspects of almost equal importance are the physical and the biological properties of the plant. Physical properties describe the dimensions of reactors and the flows between them. The flow distribution inside each reactor, the *hydraulics*, determines the time for biological reactions, or the *hydraulic retention time*, for wastewater quanta.

2.1.1 Modelling biology

Biological reactions in an activated sludge process are often described by the IAWQ activated sludge model no 1, described in detail in Appendix I. This model has the advantage of being well known and is proven for numerous applications with municipal wastewaters.

ASM1 describes substrate, bacteria, nutrients and oxygen with 15 variables in eight equations. All variables describing organic material are expressed as COD, as this is a measurable variable that respects the conservation principle. Both soluble (S_n) and particulate (X_n) material is modelled, with different degradation and settling properties. Figure 2.1 shows the pathways of the biological reactions used in ASM1, where the inner loop describes nitrogen, and the outer carbon. In the centre are the heterotrophic bacteria (X_{BH}), which assimilate soluble organic substrate (S_S). A complete description of the biological model is found in Appendix I.

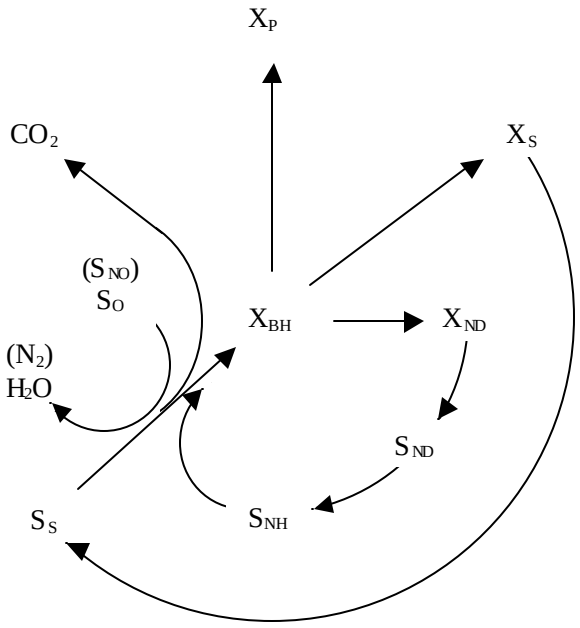

Figure 2.1. Variables in ASM1 as affected by aerobic and (anoxic) heterotrophic growth. (Also in Appendix I)

The literature study did not reveal any detailed cases where the ASM1 is used for applications with pulp and paper waters. To function with pulp and paper waters another fraction of soluble biodegradable COD was added and nitrogen was considered limiting for heterotrophic growth. Also Lopetegui (2000) uses an extra fraction when modelling pulp and paper waters and nitrogen limitation is included in the ASM1 sequel, ASM2 (Henze *et al.*, 1995).

In this work neither the biological parameters nor the parameters used in the model of the settler are determined by any field tests. Future work may address these issues as the need for a more accurate model evolves.

2.1.2 Modelling hydraulics

The hydraulics describes how flow propagates in and between reactors. The residence time for the different flow quanta is determined by the way the incoming flow is distributed in a reactor. Mixing in its simplest form is described by the continuously stirred tank reactor (CSTR) where all elements have residence times equal to the hydraulic residence time (HRT). The opposite of the CSTR, with regard to mixing, is the plug flow reactor (PFR). This describes the flow through a pipe where no mixing occurs in the dimension along the reactor, but complete radial mixing is achieved.

These two extremes may be altered and combined to describe any flow distribution. If multiple CSTR's are put in series they form a discrete description of a PFR. Back mixing or diffusion in a PFR may be described with a dispersion coefficient that should be determined experimentally.

To determine the hydraulic model that best describes reality tracer experiments are commonly used. The tracer produces a concentration pulse or an increase in incoming concentration and the measured concentration is compared with the predicted one from the proposed model, which may be approved or discarded.

2.1.3 Modelling sedimentation

Sedimentation is an integrated part of the activated sludge process and hence it requires some attention. Both the physical properties of the water and its contents as well as the hydraulics in the settler must be considered. Two principally different models are evaluated: an ideal settler and a one-dimensional layer-model.

Ideal sedimentation is instantaneous and neglects hydraulic effects. The settler itself is not modelled and its volume is neglected. Two concepts often used when describing sedimentation are the thickening factor, g, and the sludge retention time (SRT), or sludge age (SA). The sludge age is similar to the hydraulic retention time, except that it applies to the sludge. There are many ways to calculate SA depending on plant layout and on simplifications made. The sludge age is often used as a poor control parameter at wastewater treatment plants since it is assumed that flows and concentrations are at steady state. For modelling purposes the thickening factor is the only parameter to consider, thus it has great impact on the performance of the modelled settler. By default the effluent is free from suspended material, but may be assigned some arbitrarily chosen amount.

Figure 2.2 below shows a typical activated sludge process followed by a mathematical description of the ideal settler.

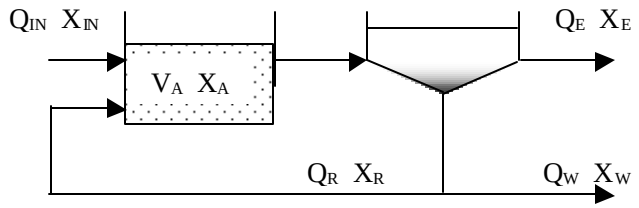

Figure 2.2. A typical activated sludge process with an aeration basin and a settler.

All particulate matter is lumped into the variable X. The sludge retention time, SRT, and the thickening factor, g, are defined as:

SRT = (Amount of sludge) / (Effluent sludge) [time]

$$g = X_W/X_A$$

The sludge retention time is usually calculated with equation 2.1, where it is implied that the sludge is inert in the settler. Any suspended solids in the influent are neglected, as they are not part of the activated sludge.

$$SRT = \frac{V_A \cdot X_A}{Q_E \cdot X_E + Q_W \cdot X_W} \left[\frac{m^3 \cdot \left[\frac{kg}{m^3}\right]}{\left[\frac{m^3}{d}\right] \cdot \left[\frac{kg}{m^3}\right]} \right] = [d] \qquad (2.1)$$

If the concentration in the effluent is considered negligible a simplified and overestimated SRT is described by Equation 2.2, which becomes Equation 2.3 if the waste sludge is withdrawn from the aerobic reactor directly:

$$SRT = \frac{V_A \cdot X_A}{Q_W \cdot X_W} \qquad (2.2)$$

$$SRT = \frac{V_A}{Q_W} \qquad (2.3)$$

The equations for the ideal settler must be used with care, especially those where the concentration in any flow is assumed negligible.

A more realistic model also describing dynamics is the layer model (Vitasovic, 1989). The settler is divided into several layers, each assumed completely mixed, and both gravity settling and hydraulics describe the sludge flux between each layer. Settling velocity is often modelled as a function of sludge concentration according to Takacs as seen in Figure 2.3. The correlation, Equation 2.4, is empirical where dilute and thick sludge settles poorly.

$$v = \max(0, \min(v_{max}, v_0 \cdot (e^{-rh \cdot (X - fns \cdot XF)} - e^{-rp \cdot (X - fns \cdot XF)}))) \qquad (2.4)$$

Where:

v_i – settling velocity
v_0 – maximum theoretical settling velocity
v_{max} – maximum practical settling velocity
XF – concentration of suspended solids in feed
rh – settling characteristic of the hindered settling zone
fns – non-settling fraction of sludge (used in settler calculations)
rp – settling characteristic at low concentrations of suspended solids

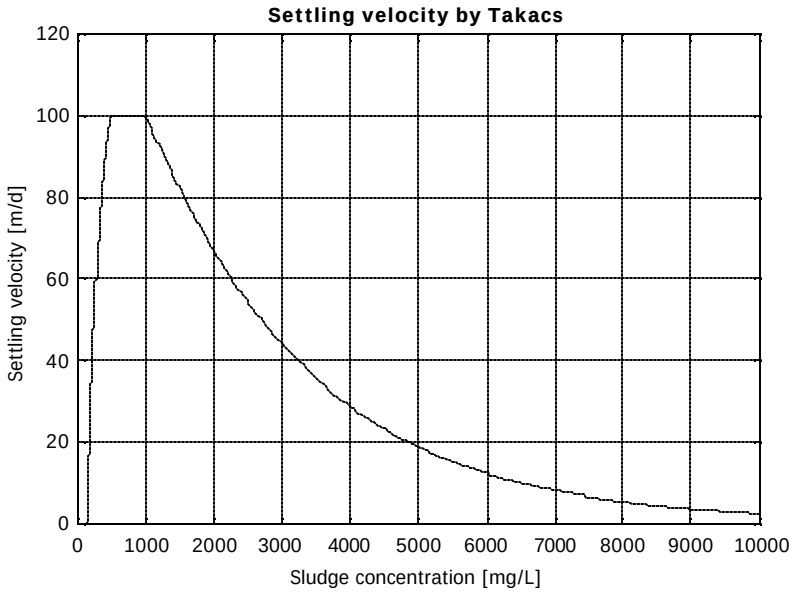

Figure 2.3. Settling velocity as described by the double exponential function by Takacs.

Flux is defined as concentration times velocity:

$$\text{Flux} = \left[\frac{\text{kg}}{\text{m}^3}\right] \cdot \left[\frac{\text{m}}{\text{s}}\right] = \left[\frac{\text{kg}}{\text{m}^2 \cdot \text{s}}\right]$$

In Figure 2.4 the flux to and from layer *i* (above the feed layer) is described by the layer model.

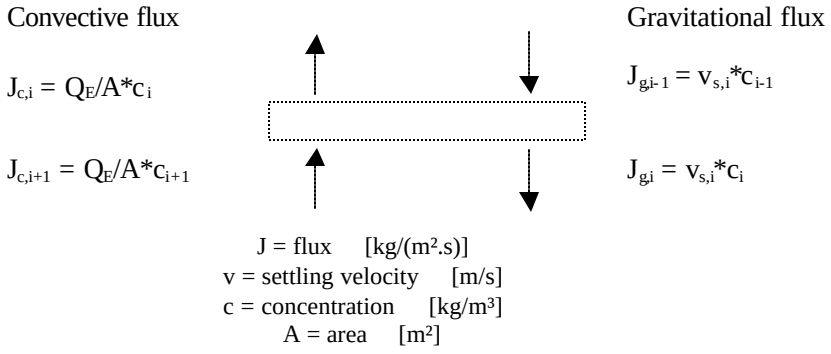

Figure 2.4. Mass balance over a layer in the settler model

The mass balance for layer *i* becomes:

$$V_i \frac{dc_i}{dt} = A \cdot \left(J_{c,i+1} - J_{c,i} + J_{g,i-1} - J_{g,i}\right)$$

One state variable for every layer describes the concentrations in the settler.

For particles with no interaction between each other Stoke's law (Equation 2.5) may be used to describe the settling velocity with good approximation. However, it is only valid for roughly spherical particles.

$$v = \frac{D_p^2 \cdot g \cdot (?_p - ?)}{18\mu} \quad \left[\frac{m}{s}\right] \tag{2.5}$$

D_p -	diameter of particle	[m]
ρ -	density of particle or water	[kg/m³]
μ -	viscosity of water	[kg/(m.s)]
g -	acceleration	[m/s²]

Increased computational speed leads to more space-distributed models that describe hydraulic propagation in the settler more accurately with two- or three-dimensional models. A true model describing sedimentation is yet to be developed.

2.1.4 Modelling oxygenation

The process of mass transfer is described by the expression:

(rate of mass transfer) =
(mass transfer coefficient) * (contact area) * (concentration difference)

All three factors on the right hand side are more or less controllable variables in the process. The mass transfer coefficient, k_L, is the least controllable, since it is determined by physical parameters in the water. The contact area, a, is more easily controlled as it is determined by how the air is added. The concentration difference depends on the amount of oxygen in the added air and the saturation concentration of oxygen in the water. Saturation concentrations are mostly temperature dependent, but factors specific for the water also has some effect. Pure oxygen may be added to increase the other factor in the concentration difference.

In experiments it is difficult to separate the mass transfer coefficient from the contact area and hence the product k_La is usually determined. This product can be determined by small-scale experiments, or some familiar empirical correlation may be used. Correlations are often based on the fact that if more air is added, turbulence and mass transfer increases. Since aeration at Hylte is constant the oxygen concentration will vary with the load. The predicted oxygen concentration could be used for validation of other parameters, such as biological parameters or characterisation of the water. This demands that the mass transfer coefficient and the solubility of oxygen in the water are experimentally determined.

2.2 Initial values

Initial values matter in an dynamic simulation, whereas in a static one they do not. Since the model uses more than the measured variables, these must be known also for the first day. A general approach to achieve predicted values for day one is to use the measured values from day one and let the simulation reach a steady state. However, this approach may lead to erroneous estimations of variables with slow dynamics, since these are determined by conditions much earlier than day one. The concentration of sludge in the reactor is for example not determined by the substrate concentrations at the same day. To reach good predictions for the first days the initial conditions for slow and fast variables are guessed in this work.

3 The wastewater treatment plant at Hylte

3.1 Site description

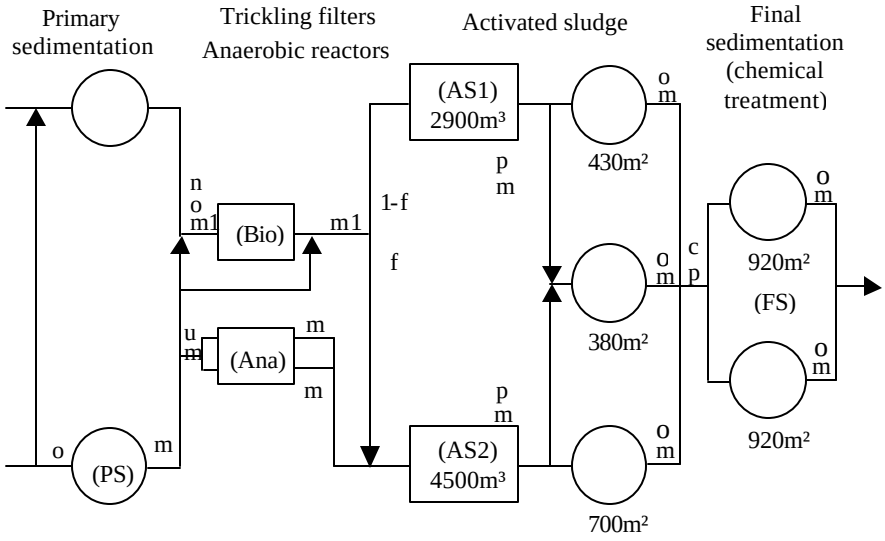

Figure 3.1. The wastewater treatment plant at Hylte.

'm' - samples for laboratory measurements are withdrawn, 'm1' – nitrogen not measured
'o' - flow is measured, 'u' - urea addition, 'n' - nitrogen salt addition, 'p' - polymer addition,
'c' – salt for chemical precipitation, 'f' – splitting ratio

Water from the manufacturing of pulp from wood and recycled newspaper is treated in the plant. In Figure 3.1 it is seen that the wastewater passes through primary sedimentation, aerobic or anaerobic treatment and activated sludge units prior to the final sedimentation. Figure 3.1 is simplified, as documentation does not exist for every extension since 1972. All data presented are averages for the period 1999-06-26 – 2000-06-26 unless stated otherwise.

3.1.1 Additives

Since the water is deficient in nitrogen, nitrogen must be added. Where additions are made is shown in Figure 3.1. Nitrogen and phosphorous are added as pure urea and as a salt containing 26% nitrogen and 6% phosphorous by mass. Several types of polymers are added. In the final sedimentation polymers are used for flocculation, and in the activated sludge basins polymers are used to reduce foaming. Polymers also aid dewatering of sludge before it is combusted. In the final sedimentation a salt containing iron and aluminium is added to precipitate phosphate. This salt will aid sedimentation of other particles as well, as gelatinous flocks are formed.

3.1.2 Measurements

Flows are measured on-line whereas most of the other measurements are done in the lab. Daily and weekly averages are achieved by collecting small quantities at constant intervals. The samples are stored at the measuring point, in some cases in a refrigerator. The various measurements are sometimes performed on the raw sample, and sometimes on a sample let to settle. The latter measurements describe the soluble material poorly, as revealed by detailed measurements. Although measuring precision is high, measuring

accuracy is unknown. This emphasizes the importance in acknowledging the fact that measuring starts with the collection of the sample and ends with the storing of the data. The following species are currently measured: COD, BOD_7, total nitrogen, total phosphorous, suspended solids, pH and flow.

3.2 Plant performance

When comparing reductions in COD between different plants and processes it must be recognized that both biology and hydraulics reduce the concentration of COD. A part of the particulate COD is removed via the excess sludge and should be added to the effluent COD if only biological oxidation is studied. Table 3.1 shows an overview of the measured concentrations of COD and BOD in various flows. These are measured values, which means that BOD is BOD_7 and COD is only the non-settling fraction (with exception for the water from Ana, where COD reflects the total concentration). The non-settling fractions in the flows are determined in the Chapter 4, wastewater characterization.

The activated sludge units contribute the most to the removal of both BOD and COD. Of the total COD and BOD removed in the biological steps, 72% of the COD removal and 66% of the BOD removal originates from the activated sludge units. The figures are based on samples that measure COD and BOD in only part of the water, and do not accurately describe the total removal of COD. It is also seen that the settlers remove a substantial amount of material. The final sedimentation removes half as much COD as is removed by the activated sludge units, which is more than what is removed from the other two biological steps combined (i.e. anaerobic treatment and trickling filters). The high removal by the activated sludge processes is partly due to the settlers. Simulations show that the settler in AS2 is responsible for 50% of the COD removal in AS2. Of the COD removed 50% is bacteria, which mainly consist of BOD.

Table 3.1. Loads and reductions. Measured COD is from settled samples for Bio, FS and AS. (Yearly averages of daily averages).

	COD mg/L	COD kg/d	Red kg/d	Red %	BOD mg/L	BOD kg/d	Red kg/d	Red %
To Bio	1500	19500			640	8320		
From Bio	1300	16900	2600	13	470	6110	2210	27
To Ana	2900	8410			1500	4350		
From Ana	1500	4350	4060	48	570	1653	2700	62
To AS	1540	29310			600	11483		
To AS1		11906				4689		
To AS2		17404				6794		
From AS1*	670	5152	6754	57	94	706	3983	85
From AS2*	750	7400	10004	57	110	1060	5734	84
From AS*	713	12552	16758	57	100	1766	9717	85
From FS	440	4270	8282	66	60	1068	698	40

* Waste sludge included and half the flow from AS3 added to AS1 and AS2 respectively.

The calculated reductions of BOD differ from the ones in an internal report, as seen in Table 3.2. Some reductions are found to be lower; some are found to be higher. A difference is expected, since average values are calculated for different time periods.

Table 3.2. Reductions in BOD (%) for the measuring period (990628 - 000628) compared to the ones in an internal report.

	Presented	Calculated
Trickling filters (Bio)	50	27
Anaerobic treatment (Ana)	70	62
Activated sludge (AS)	85	85
Final sedimentation (FS)	20	40

3.3 Flows

As seen in Figure 3.1 the flow paths are complicated. The collection of data was further complicated due to the fact that only a few flow rates were actual measurements; the rest was calculated using assumptions not necessary valid today. The flows that were the hardest to determine were those regarding the activated sludge basins. Figure 3.2 shows a flow balance over the whole unit, which consists of two basins and three settlers. The effluent from the basins and the influent from Ana are measured and the remaining flows calculated by plant personnel. There should be no difference, as the combined waste sludge flow must have been assumed in the calculations.

Flows from Ana vary a lot which is not good, since the slow anaerobic growth is especially sensitive to changes in the hydraulic retention time, HRT. The variations could on the other hand be deliberate attempts to improve an already poor performance. Another issue is the many shunts and bypasses. One of these is a shunt from the primary sedimentation to the final sedimentation (not shown in Figure 3.1) used mainly as a by-pass on those holidays when the mill is not running. Although the flow is small it has some high peaks that could cause disturbances in form of small hydraulic shocks.

In Table 3.3 the yearly averages of the daily averages of measured flow rates regarding the simulated part of the plant are presented.

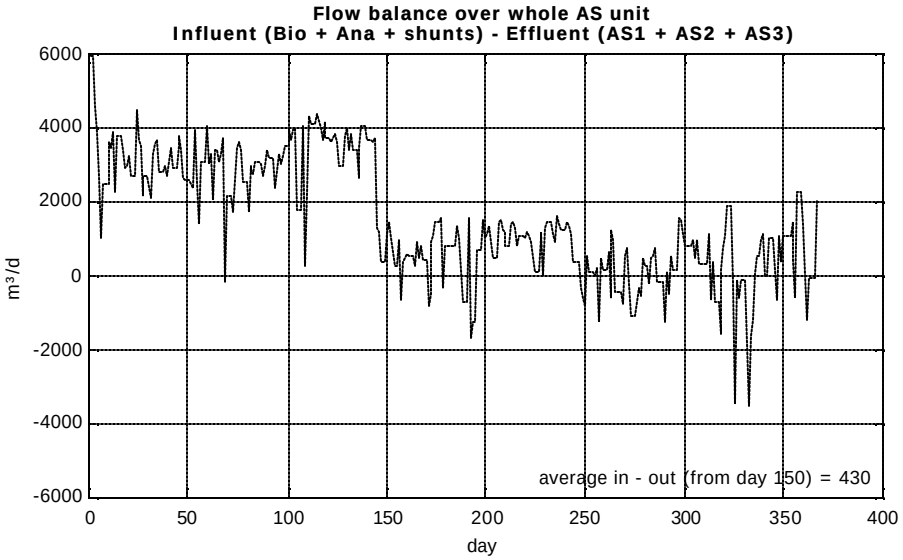

Figure 3.2. Flow balance over whole AS should reveal unmeasured waste sludge flow.

Table 3.3. Some of the flows at Hylte. Bold flows are actual measurements; others are calculated at Hylte. (Rounded figures).

	m³/d
Through Bio	13000
Through Ana	**2900**
Shunt to AS2 from PS	3100
To AS1 and AS2	19000
From AS1	**5600**
From AS2	**8100**
From AS3	4000
From AS1 and AS2 and AS3	17700
From final sedimentation	**17900**
Return sludge AS2	17000

3.3.1 Estimation of flows not measured

It is assumed at Hylte that 60% of the total flow is fed to AS2, which has 60% of the total activated sludge volume. An attempt to verify this and other flow rates calculated at Hylte is done. Two major questions are how much sludge that is withdrawn and in what proportions the flow from Bio is divided between AS1 and AS2 (the f-factor in Figure 3.1).

A detailed study of the AS units will be used to determine the flows with mass balances. From both AS2 and AS1 5000 m³/d is withdrawn to AS3, according to plant personnel. The effluent flow rate from AS3 is by plant personnel assumed to be constantly 4000 m³/d, leaving 6000 m³/d, minus the waste sludge, Q_{W3}, as return sludge to both AS1 and AS2, Q_{R32}.

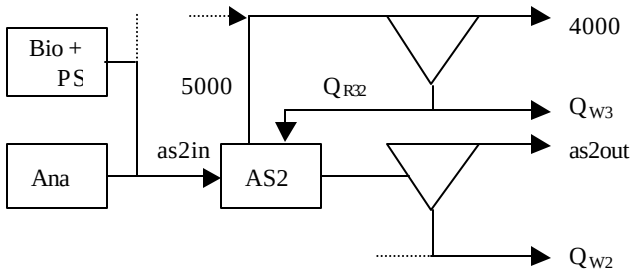

Figure 3.3. Detail of AS2 unit.

For the entire activated sludge unit (AS1 + AS2 + AS3):

$$\text{Influent} = \text{measured effluent} + \text{waste sludge}$$

For AS2 (assuming that this unit receives 60% of the total flow):

$$\text{as2in} = \text{as2out} + Q_{W2} + (5000 - Q_{R32})$$
$$\text{as2in} = 0.6*(\text{as1out} + \text{as2out} + 4000 + Q_{W1} + Q_{W2} + Q_{W3})$$

$$\Rightarrow \frac{\text{as2out} + Q_{W2} + (5000 - Q_{W32})}{(\text{as1out} + \text{as2out} + 4000 + Q_{W1} + Q_{W2} + Q_{W3})} = 0.6 \qquad (3.1)$$

The return sludge from AS3 to AS2, Q_{R32} (if divided between AS1 and AS2 in relation to their volumes):

$$Q_{R32} = 0.6(6000 - Q_{W3})$$

Expressing the unknown waste sludge flows Q_{Wi} (i = 1,2,3) as the total waste sludge flow (unknown) may be done in several ways. They may be equal, related to the area of the settler or related to the flow through the settler, which has changed significantly over the years Let f_i relate Q_{Wi} to the sum of all Q_W:

$$Q_{Wi} = f_i * (Q_{W1} + Q_{W2} + Q_{W3})$$

where

$f_i = 1/3$ for equal Q_{Wi}
$f_i = A_i/(A_1 + A_2 + A_3)$ for Q_{Wi} related to the settler area, A_i

With all unknowns expressed in the sum $(Q_{W1} + Q_{W2} + Q_{W3})$, Equation 3.1 is solved for the assumed flow and the assumed values of f_i. However, no positive solution exists for either of the assumed cases. Several flow divisions from Bio and several values of f were used (not shown). This means that some of the assumptions and/or the flow chart, must be wrong.

Rejecting mass balances as a suitable method for determination of the flows, the values assumed at Hylte will be evaluated instead. The activated sludge basins have volumes of 2900 and 4500 m^3 and the total calculated (based on assumptions also presented in Table 3.3) influent flow rate is:

Ana + Bio + Shunt from PS = influent
2910 + 12950 + 3032 = 18892 m^3/d

The AS basins use one settler each and share a third settler. Outgoing flow from the three settlers and the resulting waste sludge flow are calculated:

measured from AS1 + measured from AS2 + fixed from AS3 = effluent
5623 + 8054 + 4000 = 17677 m^3/d

influent – effluent = waste sludge
18892 – 17677 = 1215 m^3/d

The flows through AS1 and AS2 separately are not known, and for calculations at Hylte the assumption is that 60% goes through AS2:

Flow through AS1 = 0.4*18892 = 7557 m^3/d
Flow through AS2 = 0.6*18892 = 11335 m^3/d

HRT AS1 = 2900m^3 / 7557m^3/d * 24h/d = 9.2 h
HRT AS2 = 4500m^3 / 11335m^3/d *24h/d = 9.5 h

In which proportions the combined flows from Bio and PS are divided can be estimated if the original design gave equal HRT's for AS1 and AS2. In that case the splitting will be the inverse of the quotient between the volumes and the fraction of the flow that goes to AS2 calculated as:

AS1 volume / AS2 volume = Fraction to AS2 from flow splitter

2900/4500 = 0.644

Since the division of the flow from Bio was implemented earlier than anaerobic treatment began, the HRT's will not be equal today if they were equal in the past. Current flows and HRT's are with 64.4% splitting:

Flow through AS1 = (12950 + 3032)*(1-0.644) = 5690 m^3/d
Flow through AS2 = (12950 + 3032)*0.644 + 2910 = 13202 m^3/d

HRT AS1 = 2900m^3 / 5690m^3/d * 24h/d = 12.2 h
HRT AS2 = 4500m^3 / 13202m^3/d * 24h/d = 8.2 h

These HRT's predict that the performance of AS1 is better than the one for AS2, which is supported by observations at Hylte. If instead the assumption of 60% flow through AS2 is correct, the flow from Bio must be divided differently. Let f be the fraction going to AS2:

Through AS2: 11335 = 2910 + f*(12950+3032)
=> f = 0.527

Another way of estimating the flow through AS2 is to base the calculations on the measured flow from AS2 sedimentation. General assumptions are:

- Constant return and waste sludge flow rates
- Division of flow between AS1 and AS2 is proportional to the incoming flow to the splitter, which is the effluent from Bio and the shunt from PS

If the above assumptions are true, there will be a constant difference between the incoming flow from Bio, PS and Ana and the effluent measured flow from AS2. This constant difference will consist of:

- Activated sludge drawn to AS3 minus return activated sludge from AS3
- Waste sludge from AS2 settler

Validating the hypothesis of a constant withdrawn flow, the difference between the calculated influent and the measured effluent is investigated in Figure 3.4. Three different periods are clearly seen and hence the withdrawn flow is not always constant or directly proportional to the incoming flow.

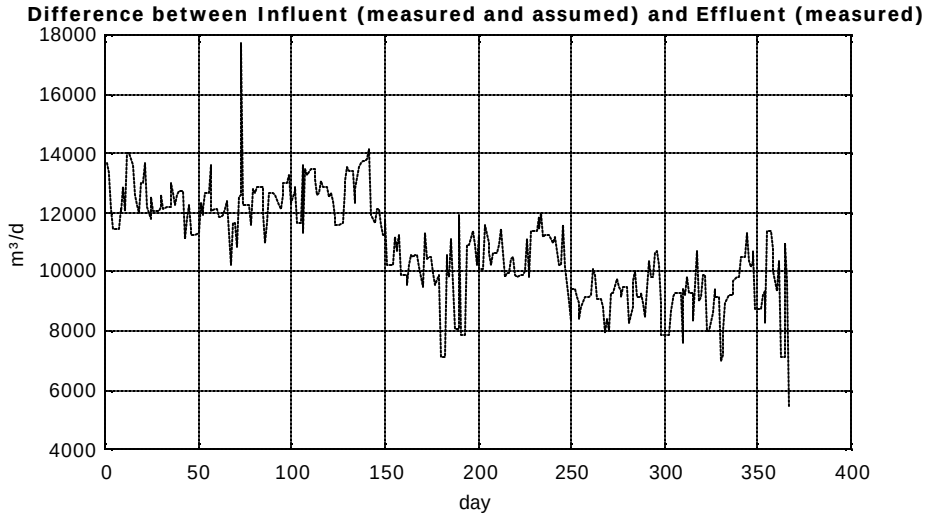

Figure 3.4. Rejecting constant withdrawn flows.

An alternative method for calculation of the incoming flow is now possible. Instead of a fixed division of the flow from Bio and PS, this division will be considered dynamic. Since the flows in reality cannot always be divided 60:40, this is a valid assumption. Assuming a constant withdrawn flow from AS2 and adding this to the measured effluent, the influent flow rate to AS2 is obtained. This influent consists of a measured flow from Ana and the flow from Bio and PS with the dynamic division. An evaluation of the dynamic division was performed (not shown), which resulted in better predictions for some periods and in worse for other.

Neither mass balances nor reasonable assumptions result in full knowledge of the flows as there are too many uncertainties. In the simulations it will be assumed that 60% of the total flow passes through AS2 (assumed at Hylte) and that the flow division is constant at 0.527 (a consequence of the assumption). These assumptions give the following average flow rates through AS2:

Table 3.4. Flows to AS2 used in the simulations

Water from	Flow rate	To AS2	To AS2
	m³/d	%	m³/d
Trickling filters	12950	52.7	6825
Primary sedimentation shunt	3032	52.7	1598
Anaerobic treatment	2910	100	2910
Total	18892		11333

3.3.2 Estimation of the return sludge flow rate

The return sludge flow rate was estimated to 17000 m³/d using three different approaches. The first was a mass balance for suspended solids over the settler, shown below. The second was a simulation of the activated sludge unit with various return sludge flow rates, and the third was by looking up the pumps designed performance. The results from the two first approaches are based on the estimated influent flow rate, which includes a certain degree of uncertainty. The pumps should according to their design data provide a combined flow of 18000 m³/d to AS2 from the settler after AS2 and the settler AS3.

A mass balance over the settler gives with notations according to Figure 2.2 (X_P, p for process, has replaced X_A):

$$Q_R*X_P + Q_{IN}*X_P = Q_E*X_E + Q_R*X_W + Q_W*X_W$$
$$Q_{IN} * X_P - Q_E*X_E - Q_W*X_W = Q_R *(X_W - X_P)$$

This is solved for Q_R using yearly averages of measured values and the assumption that 60% of the total flow is directed to AS2. The following calculations are based on rough estimations of the flows and measured concentrations (yearly averages).

$$Q_{IN}*X_P - Q_E*X_E - Q_W*X_W = Q_R*(X_W - X_P)$$
$$11400*5063 - 10700*287 - 700*7930 = Q_R *(7930 - 5063)$$
$$Q_R = 17125 \text{ m}^3/\text{d}$$

A brief sensitivity analysis was performed (not shown), where Q_R ranged from 16000 to 22000 m³/d. The most important factor was the sludge concentration in the reactor, X_P. Using the design value, 18000 m³/d, as a maximum estimation of Q_R, Q_W is calculated to 350 m³/d.

Simulations with return sludge flow rates to match the observed thickening factor of 1.6 gave a flow rate of 17000 m³/d, as seen in Table 3.5. The waste sludge flow rate and the parameters describing settling velocity were found to have a limited effect on the result. The simulations show that 18000 m³/d, the design value, probably is too high an estimate of the return sludge flow. The simulations were using the fractionation of the influent achieved from the detailed measurements.

Table 3.5. Estimation of Q_R by running simulations.

Q_R	Gamma	Qw
16000	1.64	550
17000	1.60	550
18000	1.56	650
18000	1.57	550
19000	1.54	550

3.4 Sedimentation

The return sludge to AS2 is thickened between 1.5 and 2.0 times, with an average of 1.6. Even though deviations from the average usually are to higher concentration, this does not mean that the settler is correctly dimensioned for the current load. The concentration of thickened sludge changes slowly, whereas concentration variations in the effluent water are faster and of greater importance. The concentration of suspended solids in the flows to and from the settler is shown in Figure 3.5.

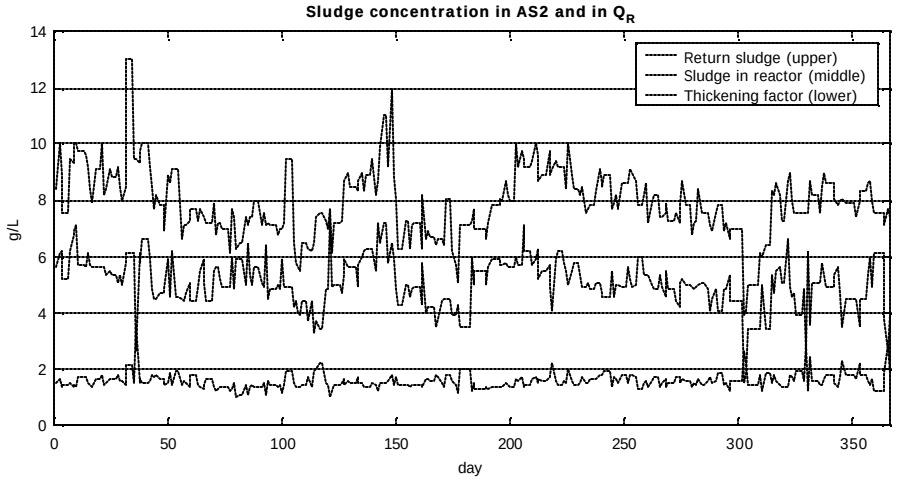

Figure 3.5. Suspended solids concentrations in AS2 reactor and in the return sludge. Lower curve is the thickening factor.

The load, sludge specific properties and the dynamics of the incoming flow affect the settler performance. The load is determined by the area of the settler and by the incoming flow. Of these factors the load is more or less controllable. More suspended solids will leave the settler with the effluent water if the load is too high or if sudden changes are made in the flow rate, as seen in Figure 3.6. Suspended solids in the effluent water from the AS2 settler often peaks, sometimes very high, when the flow rate increases. Figure 3.6 shows daily averages of measured values and may not be able to capture short-time dynamics.

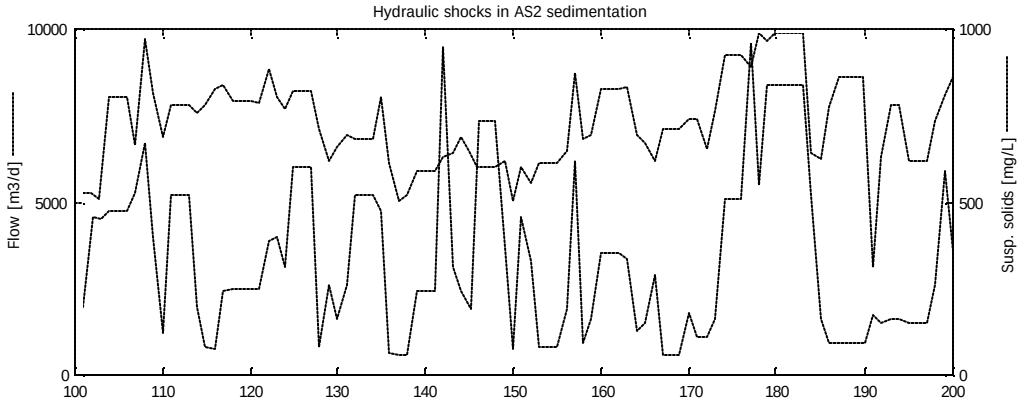

Figure 3.6. Measured suspended solids and measured flow from AS2 sedimentation.

4 Wastewater characterization

Parameters often used to describe a wastewater are COD, *chemical oxygen demand*, BOD, *biological oxygen demand*, the nitrogen content and the dry weight. The concentration of COD is obtained by oxidizing all organic material in the sample. Depending on the oxidizing agent different results may be obtained. BOD is the cumulative oxygen consumption, due to biological activity, after a certain time, usually five or seven days. Thus BOD depends on many factors of which all are not known and BOD does not respect the conservation principle. This makes BOD measurements unsuitable as a model variable. COD, on the other hand, respects the conservation principle and keeps track of the organic material on its way through the plant. This makes COD a suitable model variable and all organic components should be expressed in terms of COD.

There are many ways to relate a model variable to the measured (total) COD. Linear relationships may be used, as seen in Equation 4.1, and are used by Makinia *et al.*, (2000).

$$\text{COD variable i} = a_i * \text{COD}_{meas} + b_i \qquad (4.1)$$

To determine the parameters a_i and b_i, multiple measurements are needed, preferably over a long period of time. At Hylte the ratio of COD to BOD is fairly constant in all waters during the measuring period and the characteristic of the influent water, with respect to this ratio, will be regarded to be constant in this work. For all correlations to the total COD, it will be assumed that b_i, in Equation 4.1, is zero. The operating conditions, and how they change, are well known at Hylte, and the correlation should be determined for some of the most common cases.

The measurements currently performed at Hylte are not sufficient for wastewater characterization or model calibration, as BOD_7 is measured mostly on soluble components. COD is also measured on mostly soluble components and this value must be related to the total COD. For the calibration of the final model, the characterization of the influent is the most important factor, but knowledge of the fractions in the wastewater is useful also for other purposes. The wastewater is characterized to match the variables in ASM1 described in Appendix I. In addition to these, also the amount of suspended solids is modelled.

Total suspended solids, TSS, is calculated as a weighted sum of the particulate species, and not modelled explicitly. It is used for calculations in the settler that are on mass-basis rather than on COD-basis. The correlation, Equation 4.2, is empirical and the weights, or ratios of suspended solids to particulate COD, rsx, should be determined for each component. If the weight of the chosen species and the settler performance are calculated correctly independent of each other, TSS could be used to verify some part of the model of the total system.

$$TSS = rsx_S * X_S + rsx_I * X_I + rsx_{BH} * X_{BH} + rsx_{BA} * X_{BA} + rsx_P * X_P \qquad (4.2)$$

Detailed measurements were performed on two occasions: 2000-08-15 and 2000-08-23. On each day duplicate samples were withdrawn. Focus was on the incoming water to AS2 in order to achieve realistic input data to the model. It was not possible to use samples from the combined influent, as such an influent does not exist in reality. Measurements were performed on the water from Ana and Bio respectively, and then combined mathematically in relation to the flows. Although yearly averages differ from the ones achieved during the campaign the relationships between the various fractions

were assumed to be constant. This assumption is supported by the fairly constant ratios of COD to BOD in the influents. The campaign values differ 0.8% and 44% from the yearly averages for Bio + PS and Ana, respectively. This could mean that the average values used to describe the anaerobic water are not valid for the whole year.

4.1 Measurements of COD and BOD

As measurements mostly are performed on a sample let to settle it is necessary to know how much particulate material that is included in these measurements. Figure 4.1 shows what is measured in settled COD_{sed}, total COD_{tot} and in filtered COD_{filt}.

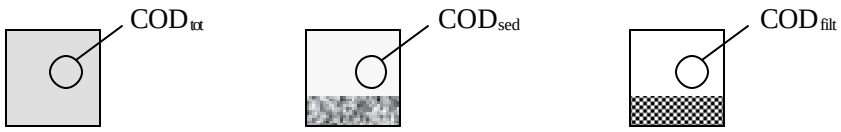

Figure 4.1. The difference between total, settled and filtered COD.

The non-settling fraction of the suspended solids remaining in the sample after sedimentation, i_{NS}, was determined by Equation 4.2 and used when recalculating the measured COD (COD_{sed}) to the total (COD_{part} + COD_{filt}).

$$COD_{sed} = COD_{filt} + i_{NS} * COD_{part} \quad (4.2)$$

In the used scheme for COD fractionation, see Figure 4.2, the traditional ASM1 has been extended with an additional variable, S_R. It is a soluble slowly biodegradable substance likely to be found in pulp and paper waters. Material that passes through the filter is assumed to be soluble, thus different estimations of the soluble matter may be done with different filters. In this case the filter used was Whatman, GF/A, 1µ. In Figure 4.2 bacteria are omitted. This leads to an error as they also are detected apart from substrate and inert material. The consequence is that X_I and X_S are slightly over estimated.

Another discrepancy was that the soluble inert fraction was found to be higher in the influent than in the effluent from the final sedimentation. This is not possible, as no soluble components should disappear, and hence the influent concentrations were recalculated as they are based on measurements on two occasions only. It was believed that the higher value was the result of a very slowly biodegradable fraction in the water.

There is also a difference between the measured BOD_{inf} and the total amount of biodegradable COD, COD_{bd}. This difference that arises from biomass decay (Makinia *et al.*, 2000) in the sample is neglected in this work. A serious inconsistency is that only a fraction of the total COD is detected when measuring on the cake after filtration. The following relationships should be equal, but the second gives a lower estimate of the particulate COD. It was first believed that this lower estimate was a result of only missing material, and that the COD:BOD ratios were equal. These ratios were not equal, and the latter way to estimate the particulate COD was discarded, as it involves more laboratory work.

$COD_{part} = COD_{tot} - COD_{filt}$
COD_{part} = measured COD on particulate after filtration

In the results from the detail measurements, see Table 4.1, and in the calculations for the different waters, both estimations of COD_{part} are included for comparison.

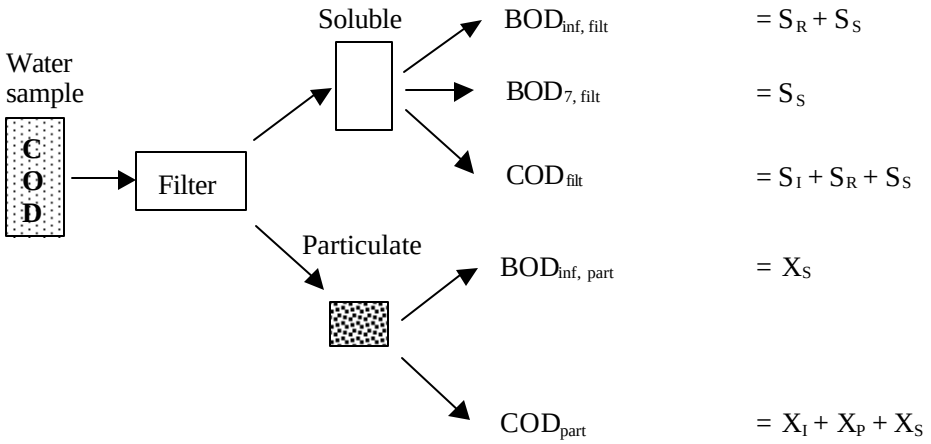

Figure 4.2. Scheme for determination of COD fractions in the influent wastewater.

BOD_{inf} was estimated as a function of time using a Monod relationship, as seen in Equation 4.3. It is assumed that the BOD curve is a function of two parameters, *k1* and *k2*. As time approaches infinity, BOD approaches the value of *k1*.

$$BOD(t) = k1*t/(k2+t) \qquad (4.3)$$

Different sets of parameters were used and the value from Equation 4.3 was compared to the measured by calculating the value of the error function. The error functions tried were the quadratic sum of errors, the square root of the quadratic sum of errors, and the standard deviation of the errors. Using Matlab, a mesh was formed with *k1* and *k2* as axis. For every point in this mesh, the value of the error function was then calculated and visualized as a plot of contour lines. Finding the best set of parameter values is then as easy as locating the top of a hill on a topographic map. This procedure is performed on the water from the anaerobic treatment in Figure 4.3 using various error functions.

The constant k1 does not necessarily mean BOD_{inf}, since BOD approaches k1 very slowly, and for estimations of BOD_{inf}, the value at day 60 is used. In Figure 4.2 the result for the anaerobic water is shown. For estimations 1, 2 and 3 the error function (to be minimized) is the standard deviation of the square root of the square of the three errors. With this error function, three minima are obtained, as seen in Figure 4.3 (left). The values of *k1* and *k2* at these minima are used in Equation 4.3 to estimate three possible BOD curves, as seen in Figure 4.3 (right) where minima 1 is the lower left. An additional estimation, 4, used the sum of the three errors as error function.

A general problem with the Monod function is parameter identification problems. Figure 4.3 shows that many sets of parameters with the same ratio *k1/k2* give the same result. Especially during the first days is the relationship a function of only one parameter, and hence it is impossible and unnecessary to determine the values of the two parameters independently.

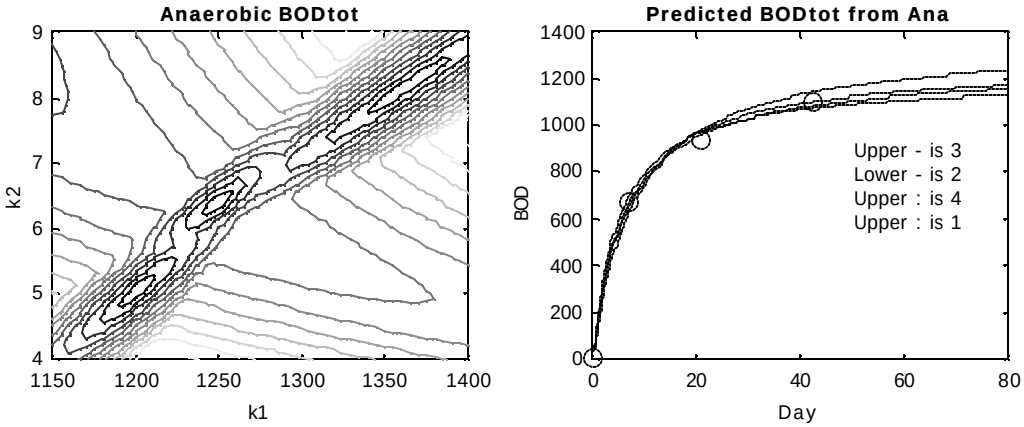

Figure 4.3. Determination of parameters for estimation of BOD in water from Ana.

In Table 4.1, below, the results from the detailed measurements are presented. They originate from samples collected on 2000-08-15 and 2000-08-23. Two estimations of the particulate COD are performed (lines 4 and 5), as discussed earlier. In the calculations, the value obtained from measured values of COD_{tot} and COD_{filt} will be used. Nitrogen measurements are uncertain, especially those noted with (**).

The subscripts, "tot", "sed" and "filt" applies to measurements on a well mixed (total) sample, a sample let to settle and on a filtered sample. They all originate from Figure 4.2.

4.1.1 Results from measurements

Table 4.1. Results and some derived values used in the calculations.

		Bio + PS	Ana	AS2 basin	Calculated as
1	COD_{tot}	2050	2150	8512	Measured (avg)
2	COD_{sed}	1515	1915		Measured (avg)
3	COD_{filt}	1200	1675	613	Measured (avg)
4	COD_{part}	850	475	7900	(1) – (3)
5	COD_{part}*	544	339		Measured (avg)
6	$BOD_{inf,filt}$	700	800		Day 60 of measured (avg)
7	$BOD_{inf,tot}$	950	1050		Day 60 of measured (avg)
8	$BOD_{inf,part}$	250	250		(7) – (6)
9	$BOD_{inf,part}$*	225	130		Day 60 of measured (avg)
10	$BOD_{7,filt}$	420	560		Measured (avg)
11	$BOD_{7,tot}$	610	650		Measured (avg)
12	$BOD_{7,part}$	190	90		(11)-(10)
13	N_{tot}	35**	29	325	Measured (avg)
14	N_{sed}	9	17**		Measured (avg)
15	N_{filt}			3.0	Measured (avg)
16	Suspended solids	480	240		Measured (avg)

* From measurements on particulate only where a large portion is missing

** Individual samples differ a lot

In Table 4.2, the measured values from Table 4.1 are used to fractionate the COD according to Figure 4.2.

Table 4.2. Results and some derived values used in the calculations.

	Bio + PS	Ana	AS2 basin	Calculated as
S_I	500	875		(3) - (6)
S_S	420	560		(10)
S_R	280	240		(6) – (10)
X_I*	319	209		(5) - (9)
X_S*	225	130		(9)
X_I	600	225		(4) - (8)
X_S	250	250		(8)
COD_{filt}/COD_{tot}	0.585	0.779		(3)/(1)
COD_{sed}/COD_{tot}	0.739	0.891		(2)/(1)
BOD_{inf}/COD_{tot}	0.463	0.488		(7)/(1)
$BOD_{7,filt}/BOD_{inf,filt}$	0.600	0.700		(10)/(6)
$BOD_{7,part}/BOD_{inf,part}$	0.760	0.360		(12)/(8)

* From measurements on particulate only where a large portion is missing

For estimations of the total amount of biodegradable material the expected value of BOD at day 60 is used. To the measurements from the two occasions, Equation 4.3 is fitted. Estimations are done with the particulate and the soluble fractions, as well as on the total sample. For reasons already discussed, BOD_{tot} does not equal BOD_{filt} + BOD_{part}, as some particulate material is missing. For calculations, $BOD_{inf,tot}$ from Figure 4.5 and $BOD_{inf,filt}$ from Figure 4.4 will be used.

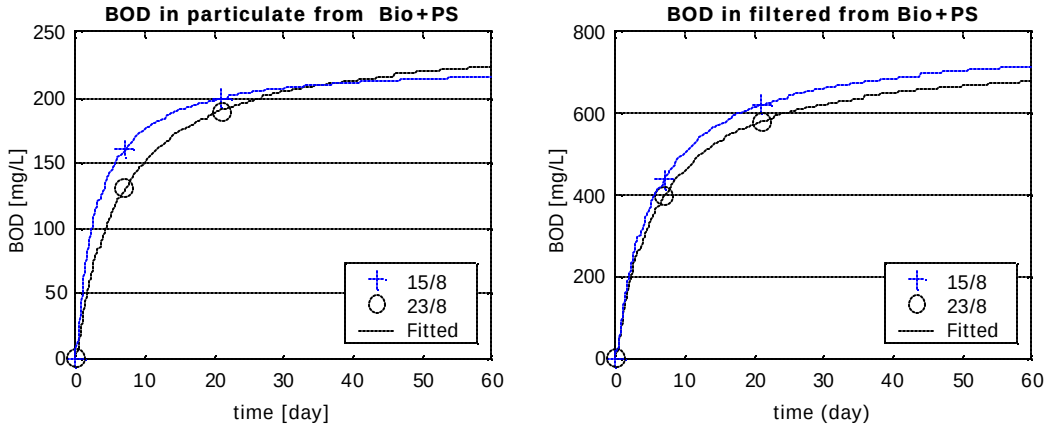

Figure 4.4. BOD in effluent from Bio+PS.

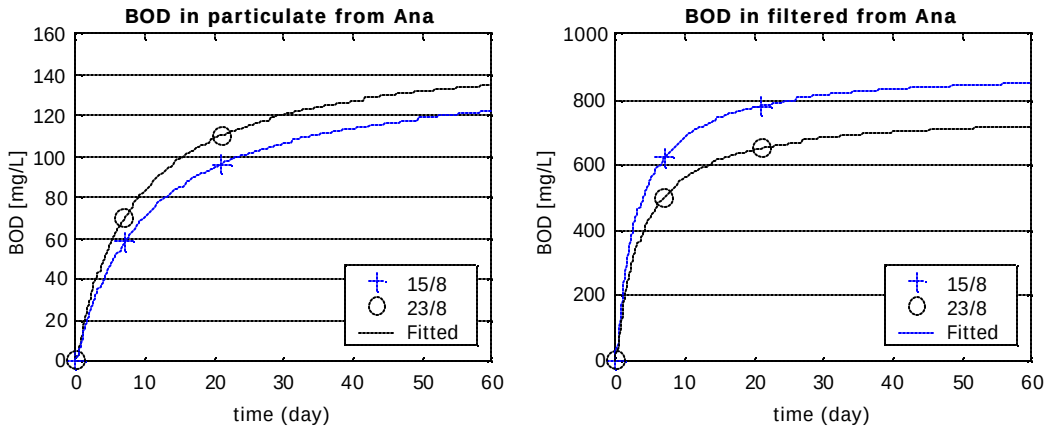

Figure 4.5. BOD in effluent from Ana.

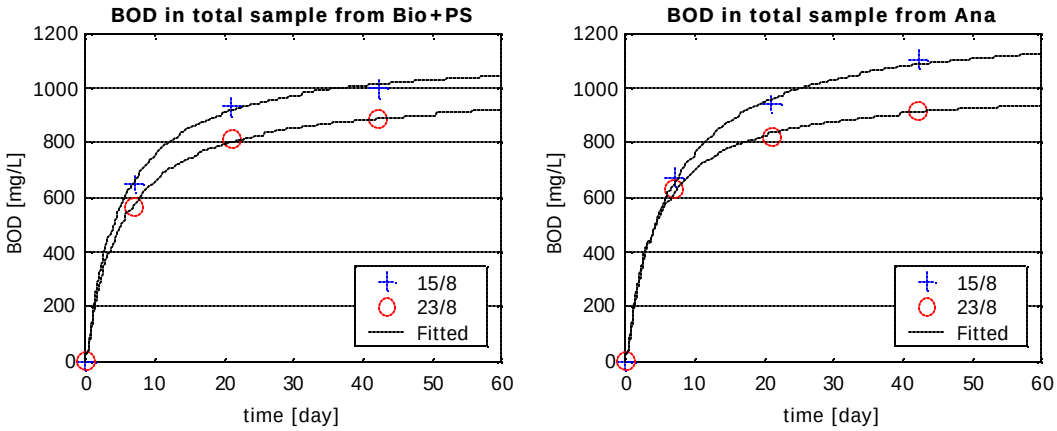

Figure 4.6. Total BOD in effluent from Bio+PS and Ana.

4.1.2 Water from trickling filters and primary sedimentation

These measurements are on the combined water from the trickling filters and the shunt from the primary sedimentation and hence it is not possible to distinguish them. In Figure 4.7, the difference between the total, measured and filtered COD is shown. Values originate from the detailed measurements presented in Table 4.1.

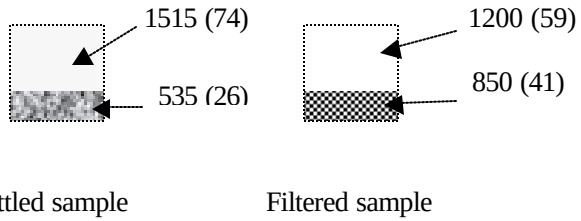

Figure 4.7. Fractionation of COD in water from Bio. Numbers in ( ) are in percent of total COD.

Equation 4.2 is used to calculate i_{NS}, which is used to relate the total COD to the measured.

$$COD_{sed} = COD_{filt} + i_{NS}*COD_{part}$$
$$1515 = 1200 + i_{NS}*(2050-1200)$$
$$i_{NS} = 0.37$$

The calculations aim to relate the model variables S_I, S_S, S_R, X_I, X_S to the measured COD_{meas} in the water. In the water from the aerobic pre-treatment, the measured value originates from a settled sample. All values in the calculations are from the detailed measurements on two occasions presented in Table 4.1.

For soluble matter:

$$S_I / COD_{sed,meas} = (COD_{filt} - BOD_{inf,filt}) / COD_{sed,meas} = 500/1515 = 0.33$$
$$S_S / COD_{sed,meas} = BOD_{7,filt} / COD_{sed,meas} = 420/1515 = 0.277$$
$$S_R / COD_{sed,meas} = (BOD_{inf,filt} - BOD_{7,filt}) / COD_{sed,meas} = 280/1515 = 0.185$$

Two sets of X_I and X_S are calculated with equal total COD. Different fractionation is reached if COD_{part} is calculated as $COD_{tot} - COD_{filt}$ or if COD_{part} is measured as COD_{tot} in the filtrated cake.

COD in particulate part calculated as: $COD_{part} = COD_{tot} - COD_{filt} = 2050 - 1200 = 850$

$$X_I / COD_{part} = 600/850 = 0.706$$
$$X_S / COD_{part} = 1 - 0.706 = 0.294$$

$$COD_{part} / COD_{sed,meas} = 850/1515 = 0.561$$

$$X_I / COD_{sed,meas} = 0.706*0.561 = 0.396$$
$$X_S / COD_{sed,meas} = 0.294*0.561 = 0.164$$

COD in particulate part measured

$$X_I / COD_{part} = 319/544 = 0.586$$
$$X_S / COD_{part} = 1 - 0.586 = 0.414$$

For relation to COD_{tot} all COD_{part} is used
$$COD_{part} / COD_{sed,meas} = 850/1515 = 0.561$$

$$X_I / COD_{sed,meas} = 0.586*0.561 = 0.329$$
$$X_S / COD_{sed,meas} = 0.414*0.561 = 0.232$$

Table 4.3 presents the fractionation that will be used with ASM1. Values are in percent of measured COD_{sed} (where about 25% of the flow is from the primary sedimentation). The sum of the percentages is higher than 100, since measurements are performed on a settled sample where not all COD is detected. Two estimations of the particulate fractionation are presented for comparison; however, due to uncertainties, only the first will be used.

Table 4.3. Fractionation of measured COD_{sed} in water from trickling filters.

X_I	X_S	S_I	S_S	S_R	
56.1			79.2		Sum
		33	27.7	18.5	
39.6	16.5				Calculated particulate
32.9	23.2				Measured particulate

4.1.3 Water from primary sedimentation

The ratio of measured COD to total COD in the combined water from Bio+PS is assumed to apply to the water from PS alone, since no specific detailed measurements exist on this water. The ratio between the particulate fractions in water from Bio+PS and water from PS is assumed to match the ratio between the suspended solids in these waters. In the calculations below, measured values presented in Appendix III and data from Table 4.1 are used. The particulate and soluble fractions in water from PS are calculated as:

$$COD_{part}/COD_{meas} = TSS_{PS}/TSS_{Bio}*COD_{part,Bio+PS}/COD_{meas,Bio+PS} =$$
$$177/297*850/1515 = 0.334$$
$$COD_{filt}/COD_{meas} = (COD_{tot,Bio+PS}/COD_{meas,Bio+PS} - COD_{part}/COD_{meas}) =$$
$$2050/1515 - 0.334 = 1.019$$

The fractionation of the soluble and the particulate part is assumed to be almost the same as for the water from Bio+PS. The water from PS alone is assumed to be less degraded, thus the less degraded components S_R and X_S are given larger weights. The final fractionation of this water is presented in Table 4.7.

4.1.4 Water from anaerobic treatment

Measurements at Hylte regarding this water are on the clear water phase of a filtered sample. (This was not completely understood, and COD is in this work assumed to be measured on a well mixed, total, sample. As a result, the COD content in this water, which equals 25% of the total flow to AS2, will be under estimated). The fractionation aims to relate the model variables to the total COD, instead of to the settled COD, as with the water from the trickling filters. All calculations are similar to the ones for the water from the trickling filters. Figure 4.8 shows the difference in measured COD if measured on a total, settled or filtered sample.

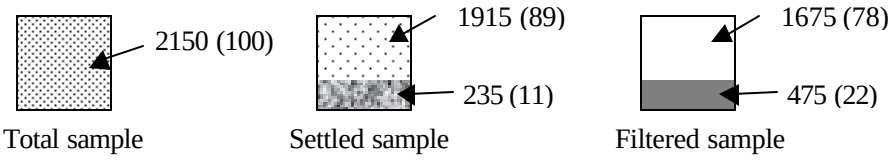

Figure 4.8. Description of COD in water from Ana. Numbers in ( ) are in percent of total COD.

Equation 4.2 is used to calculate, i_{NS}.

$$COD_{sed} = COD_{filt} + i_{NS}*COD_{part}$$
$$1915 = 1675 + i_{NS}*(2150-1675)$$
$$i_{NS} = 0.51$$

For soluble matter, values from Table 4.1 give:

$S_I / COD_{tot} = (COD_{filt} - BOD_{inf,filt}) / COD_{tot} = 875/2150 = 0.407$
$S_S / COD_{tot} = (BOD_{7,filt}) / COD_{tot} = 560/2150 = 0.260$
$S_R / COD_{tot} = (BOD_{inf,filt} - BOD_{7,filt}) / COD_{tot} = 240/2150 = 0.112$

For particulate matter two sets of X_I and X_S will be calculated with equal total COD. Different fractionation is reached if COD_{part} is calculated as $COD_{tot} - COD_{filt}$ or if COD_{part} is measured as COD_{tot} in the filtrated cake.

COD in particulate part calculated as: $COD_{part} = COD_{tot} - COD_{filt} = 2150 - 1675 = 475$

$X_I / COD_{part} = 225/475 = 0.474$
$X_S / COD_{part} = (1-0.474) = 0.526$

$COD_{part} / COD_{tot} = 475/2150 = 0.221$

$X_I / COD_{tot} = 0.474*0.221 = 0.105$
$X_S / COD_{tot} = 0.526*0.221 = 0.116$

COD in particulate part measured

$X_I / COD_{part} = 209/339 = 0.617$
$X_S / COD_{part} = (1-0.617) = 0.383$

For relation to COD_{tot} is all COD_{part} used
$COD_{part} / COD_{tot} = 475/2150 = 0.221$

$X_I / COD_{tot} = 0.617*0.221 = 0.136$
$X_S / COD_{tot} = 0.383*0.221 = 0.085$

Table 4.4 presents the fractionation for use in ASM1. Values are in percent of measured COD_{tot}.

Table 4.4. Fractionation of COD_{tot} in water from anaerobic treatment.

X_I	X_S	S_I	S_S	S_R	
22.1			77.9		Sum
		40.7	26	11.2	
10.5	11.6				Calculated particulate
13.6	8.5				Measured particulate

4.1.5 Effluent water from AS2 sedimentation

It is necessary to be able to compare the model's predictions with actual measurements. Since actual measurements show COD measured on a settled sample, and the model predicts the total COD in the sample, a recalculation of either one must be done. Detailed measurements on the water from the effluent from AS2 sedimentation were performed on 2000-10-23, and presented in Table 4.5.

Table 4.5. Detailed measurements on the effluent water from AS2 sedimentation

Effluent AS2 sedimentation	mg/L
Suspended solids	120
COD_{tot}	815
COD_{sed}	687
COD_{filt}	522
N_{tot}	12
N_{sed}	5.9
N_{filt}	2.7

The link between the measured and the predicted concentrations is the non-settling fraction, described in Equation 4.2.

$$COD_{sed,meas} = COD_{filt} + i_{NS}*COD_{part}$$
$$687 = 522 + i_{NS}*(815-522)$$
$$i_{NS} = 0.56$$

4.1.6 Recalculation of S_I and S_R

The calculations on the influent wastewater to AS2 gave the inert soluble fractions in waters from Bio and Ana as 33 and 40.7 percent of the total COD, respectively. These percentages give the following concentrations of S_I in the waters, when the results from the detailed measurements in Table 4.1 are used:

In water from Bio: $S_I = 0.244*COD_{tot} = 0.244*2050 = 500$ mg/L
In water from Ana: $S_I = 0.407*COD_{tot} = 0.407*2150 = 875$ mg/L

These concentrations are higher than the one found in the effluent water from the final sedimentation, which is impossible, since no soluble material is permanently withdrawn. The soluble inert material in the effluent from the final settler is calculated using results from the detailed measurements. Since BOD_7 is used a maximum concentration is found. The calculations below uses values from the campaign, presented in Table A3.1.

$$S_I = COD_{filt} - BOD_{7,filt} = 384 - 43 = 341 \text{ mg/L}$$

Thus the factors relating S_I to the measured COD must be recalculated to give lower estimations of the soluble inert material. In order to maintain the same total amount of COD, S_R will have to be increased. This assumption can be justified by recognizing S_I as consisting of both an inert and a very slowly degradable part. When adjusting the concentrations of S_I it is assumed that the ratio $S_{I,Ana}$:$S_{I,Bio}$ will be the same as the one already calculated. In the calculations, the results from the detailed measurements in Table 4.1 are used.

For Bio: $S_I = (COD_{filt} - BOD_{inf,filt})/COD_{tot} = (1200 - 700)/2050*COD_{tot}$
$= 24.4*COD_{tot}$
For Ana: $S_I = (COD_{filt} - BOD_{inf,filt})/COD_{tot} = (1675 - 800)/2150*COD_{tot}$
$= 40.7*COD_{tot}$
$S_{I,Bio} / S_{I,Ana} = 24.4/40.7 = 0.600$

Setting x as the concentration of S_I in water from Ana and solving for a concentration in the combined influent of 341 mg/L (flow rates are through AS2 based on yearly averages presented in Table 3.4):

$(Q_{Bio+PS}*x*0.6 + Q_{Ana}*x)/(Q_{Bio+PS} + Q_{Ana}) = 341$
$(8490*x*0.6 + 2910*x)/11400 = 341$

=> x = 485.7 mg/L (concentration of soluble inert material in the anaerobic water)

This gives the new estimation of the inert fraction:

S_I Bio = 485.7*0.6 mg/L
S_I Ana = 485.7 mg/L

For Bio: $S_I / COD_{sed} = 485.7*0.6/1515 = 0.192$ (older was 0.33)
For Ana: $S_I / COD_{tot} = 485.7/2150 = 0.226$ (older was 0.407)

New fraction of S_R in water from Bio (in % of measured COD_{sed}, concentrations from Table 4.1):

$S_R = COD_{filt}/COD_{sed} - S_S/COD_{sed} - S_I/COD_{sed} = 1200/1515 - 420/1515 - 0.192 = 0.322*COD_{sed}$ (old estimation 0.185 in Table 4.3)

New S_R Ana (in % of measured COD_{tot}):

$S_R = COD_{filt}/COD_{tot} - S_S/COD_{tot} - S_I/COD_{tot} = 1675/2150 - 560/2150 - 0.226 = 0.293*COD_{tot}$ (old estimation 0.112 in Table 4.4)

S_S is considered unchanged in the final fractionation of the soluble COD, and the fractions presented in Table 4.3 and Table 4.4 will be used. Due to lack of actual measurements on the water from the primary sedimentation, the above method of re-fractionation is not likely to produce more reliable data regarding this water.

Table 4.6. Final fractionation of soluble components in percent of measured COD, COD_{sed} for Bio and COD_{tot} for Ana, compared with old values (in paranthesis).

	S_I	S_S	S_R
Bio	19.2 (33)	27.7 (27.7)	32.2 (18.5)
Ana	22.6 (41)	26 (26)	29.3 (11.2)

4.1.7 Correlation of suspended solids to particulate COD

The ratios of suspended solids to particulate COD were determined by dividing the measured suspended solids concentration with the calculated concentration of particulate COD. Only a lumped parameter will be achieved in this way, but since the influent most likely is low on bacteria the value will apply to X_I and X_S. In the water in AS2, calculations were performed using the yearly average of the concentration of suspended solids. For all other calculations the results from the detailed measurements were used.

Water from Ana:
Particulate COD: 2150-1675 = 475 mg/L

Suspended solids: 240 mg/L
Ratio = 240/475 = 0.51 mgTSS/mgCOD_{part}

Water from Bio + PS:
Particulate COD: 2050-1200 = 850 mg/L
Suspended solids: 480 mg/L
Ratio = 480/850 = 0.56 mgTSS/mgCOD_{part}

Activated sludge:
Particulate COD: (8512-613) = 7900 mg/L
Suspended solids (yearly average) = 5100 mg/L
Ratio = 5100/7900 = 0.65 mgTSS/mgCOD_{part}

Effluent from AS2 sedimentation:
Particulate COD: (815-522) = 293 mg/L
Suspended solids = 120 mg/L
Ratio = 120/293 = 0.41 mgTSS/mgCOD_{part}

4.1.8 Final fractionation of COD

Fractionation of the particulate material was done using the calculated COD_{part}. This value is believed to be more reliable since the measured value lacks a substantial amount of COD. A sum of fractions over 100% in the water from Bio and from PS means that the model also must consider the COD that is not detected in the measurements. The non-settling fraction, i_{NS}, describes how much of the particulate material that does not settle, and is used to correlate the measured settled COD_{sed} to the total COD. The ratio TSS/COD_{part} is used to express particulate COD as suspended solids that are not modelled explicitly. The non-settling fraction and TSS/COD are also estimated in the effluent water from AS2 sedimentation. These are used when comparing the model's predictions with the observed reality. Table 4.7 presents the results derived in Chapter 4, regarding COD.

Table 4.7. COD in influent to AS2 and effluent from AS2 sedimentation. (Reservation is made for rounding errors).

Water from	Variables (in % of measured COD)					Sum	i_{NS}	TSS/COD_{part}
	X_I	X_S	S_I	S_S	S_R			
Bio	39.6	16.6	19.2	27.7	32.2	135.3	0.37	0.56
PS	21.4	12	19.2	27	55.4	135.3	0.37	0.56
Ana	10.5	11.6	22.6	26	29.3	100	0.51	0.51
Effluent AS2 sedimentation							0.56	0.41

4.2 Measurements of nitrogen

Nitrogen is present as soluble and particulate matter. The nitrogen contents in the various particulate fractions must be calculated in order to predict the effect of influent total nitrogen concentration on bacterial growth. The procedure for nitrogen determination is the same as for COD, with the exception that nitrate is measured both before and after oxidation. In general, all particulate components are believed to partly consist of nitrogen but the nitrogen content in soluble COD components is normally neglected. Soluble nitrogen compounds invisible in COD measurements are considered

to consist of free ammonia. In Figure 4.9, the nitrogen present in particulate substrate ($i_{XS}*X_S$) is in the simulations interpreted as organic nitrogen, X_{ND}. The nitrogen content in each particulate fraction of COD is determined by the factors i_{Xi}. These factors have the unit mg N/mg COD.

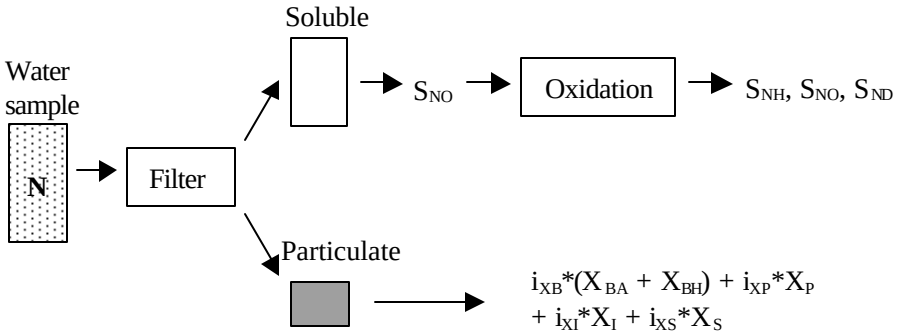

Figure 4.9. Scheme for determination of nitrogen fractions.

Nitrogen is an especially important variable in this work since the water is reported to be nitrogen deficient. A first step would be to determine if all nitrogen is detected with the current measurements. Nitrogen hiding in particulate material may provide a useful source of cheap nitrogen. Nitrogen must be continuously supplied as it is incorporated in the biomass that partly is lost with the effluent and with the waste sludge. Nitrogen availability for bacterial growth is determined by its location. If present in inert components, nitrogen is detected but is unavailable for the bacteria. Makinia *et al.*, (2000) found nitrogen in soluble inert components, where it is usually neglected. The amount was, in a municipal wastewater, about 3% of the total Kjeldahl nitrogen.

From the results of the detailed measurements presented in Table 4.8 it is seen that nitrogen is present in both particulate and soluble material. Calculations on the effluent water from AS2 sedimentation reveal that the nitrogen content in the non-settling particulate COD, COD_{NS}, is different from that in the total particulate COD:

$COD_{NS} = COD_{sed} - COD_{filt} = 687 - 522 = 165$ mg COD/L
$N_{sed} - N_{filt} = 5.9 - 2.65 = 3.25$ mg N/L
=> % N in particulate non-settling fraction = 3.25/165 = 2.0%

$COD_{part} = COD_{tot} - COD_{filt} = 815 - 522 = 293$ mg COD/L
$N_{tot} - N_{filt} = 12 - 2.65 = 9.35$ mg N/L
=> % N in particulate COD = 9.35/293 = 3.2%

The lower nitrogen content in the non-settling fraction could be the result of nitrogen release during hydrolysis. This process would also give smaller particulate components less likely to settle well.

Table 4.8. Results from nitrogen measurements.
(From Table 4.1, Table 4.2, Table 4.5 and Table A3.1)

	Final sedimentation	Bio + PS	Ana	AS2 reactor	Effluent AS2 sedimentation
Suspended solids	45	480	240		120
CODtot	437.5	2050	2150	8512	815
CODsed		1515	1915		687
CODfilt	384	1200	1675	613	522
Ntot	4.15	34.5	28.5	325	12
Nsed	2.45	9.15	16.5		5.9
Nfilt				3.0	2.65

When analysing the concentrations and artificial additions of nitrogen an inconsistency was found. Nitrogen is added as pure urea (46w% N, 750 kg/m³) and as a N-P salt (26w% N, 1000 kg/m³). On an average 111 kg N/d is added as urea to 2900 m³/d prior to the anaerobic treatment, giving an inlet concentration at minimum 38 mg N/L (111000/2900). However, the yearly average of the measured nitrogen concentration in this water is at Hylte 25 mg N/L, which is less than the theoretical. An explanation could be that the sample for measurement is withdrawn before the addition of urea or that the salt is not immediately dissolved and does not show in the measurements.

Mass balances are used to track nitrogen in the waste sludge and in the influent water from Bio where nitrogen is not measured. For correlation of measured data on settled samples to the total nitrogen the results from the fractionation of COD are used. The detailed measurements, presented in Table 4.8, indicate that the concentration of nitrogen in soluble compounds is about 3 mg/L.

A typical fractionation of COD in the reactor achieved from the simulations was used for determination of the total nitrogen in the waste sludge. The nitrogen fractions in the particulate COD are assumptions partly based on literature data and partly from the correlations between TSS and COD found for the current water. TSS is taken as the yearly average. From the detailed measurements, presented in Table 4.8, it was found that the soluble nitrogen is about 3 mg/L in the reactor. In Table 4.9 the assumptions made for determination of nitrogen in particulate material are presented.

Table 4.9. Tracking nitrogen.

	COD	% of COD_{part}	% N/COD	TSS/COD
X_I	4245	57.8	0.5	0.45
X_S	17	0	1	0.45
X_{BH}	2385	32.5	8.6	0.9
X_P	693	9.4	6	0.9

With the same fractionation of COD in the waste sludge as in the reactor, the nitrogen concentrations arising from the particulate fractions are calculated as:

$$\text{TSS (in wastesludge flow)} \cdot \frac{\text{COD}}{\text{TSS}} \cdot \frac{\text{COD}_i}{\text{COD}} \cdot \frac{\text{N}}{\text{COD}_i} = \text{N} \quad \left[\frac{\text{mg}}{\text{L}}\right]$$

COD_i is a particulate fraction of COD, for instance X_I.

N content in X_I: 7900*0.578/0.45*0.005 = 50.7 mg N/L
N content in X_{BH}: 7900*0.325/0.9*0.086 = 245.3 mg N/L
N content in X_P: 7900*0.094/0.9*0.06 = 49.5 mg N/L

N in particulate = 345.5 mg/L
N_{sol} = 3 mg N/L

=> N in waste sludge = 348.5 mg N/L

The total nitrogen in the effluent from AS2 sedimentation is calculated in the same way. In this water is the yearly average of TSS 290 mg/L, and the median 210 mg/L. The high average may be a result of many peaks that could be the results of faulty measurements. Using 250 mg/L the concentrations are calculated as the concentrations in the waste sludge*250/7900:

N content in X_I: 50.7*250/7900 = 1.606 mg N/L
N content in X_{BH}: 245.3*250/7900 = 7.763 mg N/L
N content in X_P: 49.5*250/7900 = 1.567 mg N/L

N in particulate = 10.94 mg/L
N_{sol} = 3 mg N/L

=> N in effluent from AS2 sedimentation = 13.94 mg N/L

This value was compared with the yearly average of nitrogen (measured on settled samples) in the water. The non-settling fraction is estimated to 0.56, the same as for COD presented in Table 4.7.

Predicted measured N on total sample: 3 + 0.56*10.94 = 9.1
Measured N on settled sample: 9.7

The calculated value indicates, with all assumptions put together, that the estimation of nitrogen concentrations are valid. It is now possible to estimate the not measured concentration of influent nitrogen. From Ana the yearly average of nitrogen in the raw sample was 17.3 mg/L (Appendix III). From Bio (with water from PS) are no measurements taken. The following mass balance was used for various estimations of Q_W, where it is assumed that no denitrification occurs. The flows are from Table 3.4.

$Q_{Bio+PS}*N_{Bio+PS} + Q_{Ana}*N_{Ana} = Q_E*N_E + Q_W*N_W$
$8438*N_{Bio+PS} + 2910*17.3 = (8438+2910-Q_W)*13.94 + Q_W*348.5$

Q_W = 550 => N_{Bio+PS} = 34.6 mg/L
Q_W = 600 => N_{Bio+PS} = 36.6 mg/L
Q_W = 650 => N_{Bio+PS} = 38.5 mg/L

These values are close to the one determined in the detailed measurements, see Table 4.8, which was 34.5 mg/L.

Since the above estimation uses the nitrogen content in the particulate material, and the particulate material depends on the total influent nitrogen, the calculations must be run with the reached inlet concentration. This iteration proceeded until the assumed nitrogen concentration and the one calculated from the computed fractionation were equal, giving the result above.

For validation the minimum total nitrogen concentration in the effluent from Bio was calculated as the concentration increase arising from the salt addition in the water coming from the primary sedimentation. Estimating this concentration is difficult, as some of the water in the influent to Bio originates from other sources. Of the

12950 m³/d influent to Bio, one part comes from the primary sedimentation already mentioned, and the rest from another primary sedimentation where no measurements exists. The effluent 7100 m³/d from the already mentioned primary sedimentation is divided between Ana and Bio. Assuming that all water to Ana is withdrawn from the 7100 and that the nitrogen concentration in the water from the other primary sedimentation is zero, an under estimate is assured using the measured settled value.

Nitrogen concentration in water from primary sedimentation (in settled sample): 23.3 mg/L

Concentration after dilution (in settled sample):
((7100-2910)*23.3 + (12950 – (7100-2910))*0)/12950 = 7.53 mg/L

Added salt: 180.6 L/d (1 kg/L) to 12950 m³/d
=> 13.95 mg/L

Minimum total nitrogen concentration in effluent water from Bio:
7.53 + 13.95 = 21.5 mg/L

If N_{tot}/N_{sed} = 2 in the water from PS the minimum concentration becomes 29 mg/L. (23.3*2 mg N/L in water from PS).

4.2.1 Final fractionation of nitrogen

Nitrogen enters AS2 as fractions of soluble and particulate organic material as well as pure nitrogen compounds. Moreover, some of the nitrogen is bound in non-biodegradable substances and will never be available for microbial growth. The nitrogen content in the various fractions, expressed as mg N/mg COD, was estimated using both values from literature and values specific for this water. The latter were found using mass balances in combinations with fractionations of COD determined by simulations. The values presented in Table 4.10 of mg N/mg COD were found to apply:

Table 4.10. Nitrogen content in particulate fractions of COD.

N in COD S_I	0.5%
N in COD X_I	1.0%
N in COD X_{BH}	7.0%
N in COD X_P	5.0%

These values give for the typical day a concentration of soluble nitrogen in the effluent of about 3 mg N/L, the measured value.

The influent nitrogen in the flow from PS and Bio+PS is determined as:

Total N is *a* times higher than measured on settled sample:
$PS_{N,tot} = a*PS_{N,meas}$

Effluent from Bio is the sum of added salt + influent flow from PS diluted 1/*b* times due to the flow from the other primary sedimentation:
$BioPS_{N,tot} = N_{salt} + b*PS_{N,tot}$

Constants *a* and *b* were iteratively determined using mass balances with fractionation achieved by simulations. Constant *a* were in the detailed measurements found to be about 2 in all waters.

The yearly average of total nitrogen concentration in the water from Bio, where no measurements of nitrogen were performed, was determined by mass balances to be about 33 mg N/L. To reach this concentration the flow from PS was diluted 40% and the ratio of N_{tot} to N_{sed} in the water from PS was set to 2.35.

The nitrogen remaining after the above fractionation is assumed to be both soluble as well as a part of X_S. The reason that X_S is not considered to contain any nitrogen in the above fractionation is that X_S later is formed from biomass decay and has its nitrogen content expressed in the variable X_{ND}. The physical difference between X_S in the incoming water and X_S formed by biomass decay is also a reason not to use the same nitrogen content. The nitrogen content of X_S was estimated to 1% in the incoming water and expressed as X_{ND}. Nitrogen fractionation is in the waters performed as:

S_{NH} = total nitrogen - $i_{SI}*S_I$ - $i_{XI}*X_I$ - $i_{XS}*X_S$
$X_{ND} = i_{XS}*X_S$ (only in influent)

Available nitrogen = total nitrogen - $i_{SI}*S_I$ - $i_{XI}*X_I$

Where: i_{XI} = mg N/mg COD_{XI}

No nitrate, S_{NO}, or organic soluble nitrogen, S_{ND}, is considered to exist in the influent. This assumption does not affect the total amount of influent nitrogen, and is considered to be valid. In Table 4.11 the measured and calculated nitrogen concentrations in the waters are presented. Measured values are yearly averages found in Appendix III. The particulate nitrogen is calculated using the fractionation of COD from Table 4.7 together with the information of the nitrogen content in these fractions presented in Table 4.10. The soluble nitrogen is calculated as the total nitrogen minus the particulate nitrogen.

Calculations for water from trickling filters (Bio):
Calculated settled nitrogen concentration: 34.3 mg N/L
Nitrogen in particulate COD (X_I, X_S) calculated as: $N/COD_i*COD_{sed,meas}$
(0.396+0.166)*0.01*1290 = 7.3 mg N/L

Calculations for the anaerobic water:
Measured total nitrogen concentration: 17.3 mg N/L
Nitrogen in particulate COD calculated as: $COD_i/COD_{tot}*N/COD_i*COD_{tot,meas}$
(0.105+0.116)*0.01*1490 = 3.3 mg N/L

Calculations for water from PS
Calculated settled nitrogen concentration: 28.4 mg N/L
Nitrogen in particulate COD calculated as: $COD_i/COD_{sed}*N/COD_i*COD_{sed,meas}$
(0.214+0.12*0.01*2540 = 8.5 mg N/L

Table 4.11. Measured and used nitrogen concentrations in the influent waters.

	N_{tot} used (soluble + particulate) mg N/L	Measured N mg N /L
Trickling filters	34.3 (27 + 7.3)	-
Anaerobic treatment	17.3 (14 + 3.3)	17.0 (tot)
Primary sedimentation	28.4 (19.9 + 8.5)	12.3 (sed)

5 Simulation

The plant was simulated in Simulink, an extension to Matlab. Matlab is a calculation software by MathWorks that can be used for almost any application. It has a high level language that makes programming fast, but some calculations slow. A large number of application-specific toolboxes that extend the Matlab environment in order to solve particular classes of problems are available. These toolboxes include signal processing, control system design, system identification, optimisation, neural networks, fuzzy logic, statistics, partial differential equations, symbolic math, etc.

Simulink is an interactive system for simulating dynamic systems. It is a graphical, mouse-driven program that allows the user to model a system by drawing a block diagram in a graphical editor. It handles linear, non-linear, continuous-time, discrete-time, multi-variable and multi-rate systems. A large number of predefined building blocks is included in the program and it is easy for the user to extend this library with blocks of his own. Hierarchical models are recommended since blocks may include other blocks and allows for 'information zooming'. Results are numerically and graphically available in numerous ways.

Measurements were imported as text-files from Excel. This operation was facilitated by macros in Excel as well as by special scripts in Matlab.

5.1 The simulated part of the plant

The simulated part of the plant is the activated sludge basin no 2, AS2, with subsequent sedimentation. The simulated settler is a combination of the two settlers that receive water from the activated sludge basin. Outlet concentrations used for validation are those from AS2's primary settler. The AS2 basin is modelled as three CSTR's and the settler as a ten layer model.

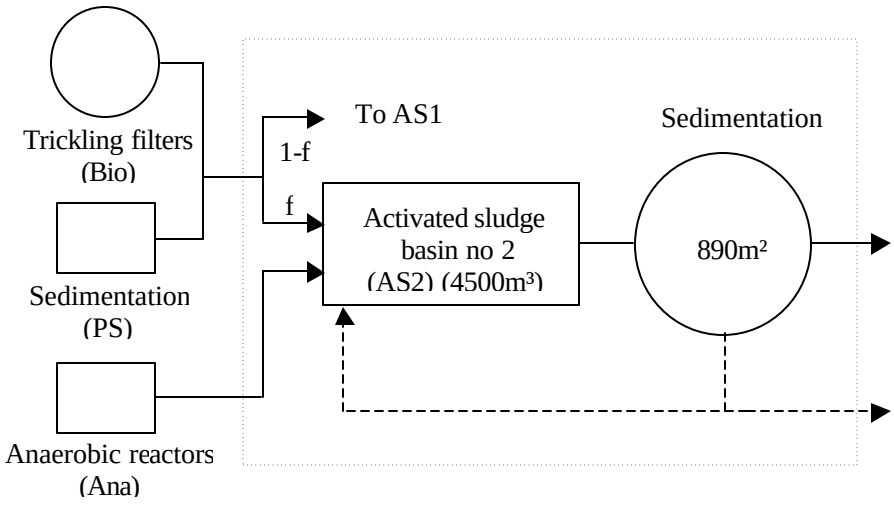

Figure 5.1. The simulated part of the plant (dotted square).

In Simulink the model in Figure 5.2 is set up. The basin is assumed to consist of three CSTR's. This is an estimate, but anything above one is reasonable. Each part of the "whole" basin is connected with arrows. These arrows transmit the number of variables written next to it, which in this case are 16 (13 from ASM1 + S_R + flow + TSS). Other

inputs to the blocks are parameters for oxygen transfer and the return and waste sludge flow. These are constants in this model, but may easily be made variables if some sort of regulator is included. The input block in the lower left supplies input concentrations and flows. This block contains a matrix where the value of each variable is given at different times.

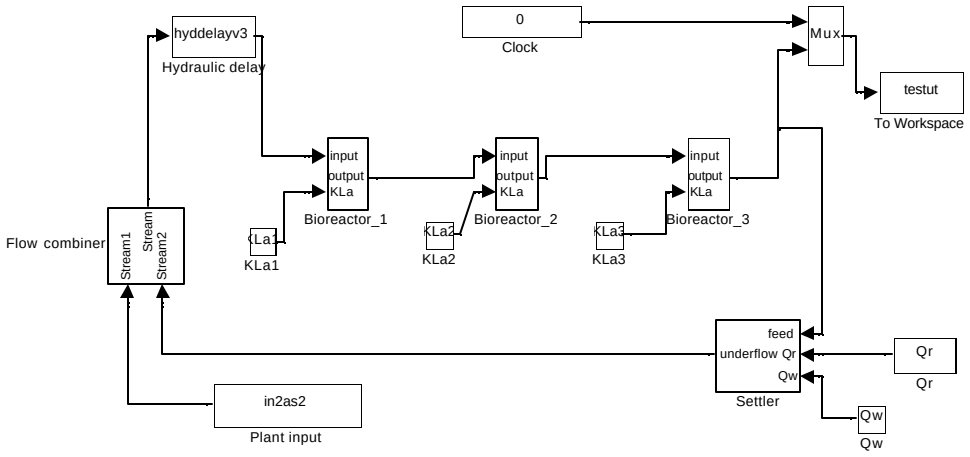

Figure 5.2. The plant as described in the Simulink environment.

5.1.1 Sedimentation models and parameters

An ideal settler has a great advantage in its high computational speed but does not describe dynamics, which could prove fatal in a dynamic simulation. Both an ideal settler and a layer model were used to describe the sedimentation process and a sensitivity study of the thickening factor and the return sludge flow rate was performed. Numerical problems occurred with the ideal settler with certain combinations of flows and thickening factors.

5.2 Pulp and paper waters in ASM1

5.2.1 Ammonium

Negative concentrations of ammonium are calculated partly as a result of large growth rates. Since ammonium is not growth limiting for heterotrophs in ASM1, large growth rates may result in too large an uptake. This problem is not likely observed when working with municipal wastewaters where ammonium is present in high concentrations. Solving the problem was accomplished by adding a growth limiting Monod expression for ammonium to the ærobic heterotrophic growth. The same conclusion was reached in ASM2 (Henze *et al.*, 1995), and the improved aerobic heterotrophic growth rate becomes:

$$\hat{\mu}_H \left(\frac{S_{NH}}{K_{NH} + S_{NH}} \right) \left(\frac{S_S}{K_S + S_S} \right) \left(\frac{S_O}{K_{O,H} + S_O} \right) X_{BH}$$

5.2.2 Soluble BOD

To better describe the heterogeneous water another soluble biodegradable fraction was added (S_R), which is hydrolysed to S_S in a similar fashion as X_S. To keep changes in ASM1 to a minimum, S_R is not considered to be formed by biological decay.

5.2.3 Temperature

Many of the biological parameters are temperature dependent. Some are not, but will still have values that differ from the ones in literature covering municipal wastewaters. All kinetic parameters are more or less temperature dependent and increase with increasing temperature up to a limit. Such behaviour is often described with an Arrhenius function with unique parameters for every kinetic parameter to be described (Makinia *et al.,* 2000 e.g.). Also half-saturation coefficients vary with temperature, but in different and more unpredictable ways (Henze *et al.,* 1987). Temperature dependencies described by Arrhenius equations are only valid for the same type of biomass. This is probably not the case for the temperatures 10 and 40 degrees, thus the kinetic parameters should be estimated at the operating temperature.

5.2.4 Suspended solids

In the detailed measurements, the COD content in the particulate fraction of the samples was determined as well as the COD in the water before and after filtration. From this experiment the lumped TSS-factor is calculated in water from Ana to 0.41 - 0.63 and in water from Bio to 0.53 - 0.62. Using the ratio between total and particulate COD determined during the campaign and the yearly average of suspended solids, also the factor for the activated sludge could be determined and found to be 0.65. These values lower than the recommended ones in ASM1. In the activated sludge model no 2 (Henze *et al.,* 1995) are the ratios for biomass increased to 0.9. These are also used in this work to match the high sludge concentration. Determination of the individual factors is difficult with laboratory experiments only, as the particulate fractions are difficult to separate. Laboratory work in combination with numerical simulations of plant behaviour could be a better way.

5.3 Influent wastewater described by detailed measurements

In Chapter 3 and Chapter 4, flow rates and concentrations in the influent were determined. This section discusses all input to the model presented in the next section, which also presents the results from the simulations.

Fractionation of COD was done according to the results of the detailed measurements. The ratio between S_R and S_S is still an open question, and may still be chosen to achieve good results.

Volumetric flow rates of the influents are used as described by the flow analysis. Q_W will be altered around 600 m³/d and used to reach sufficient suspended solids concentrations in the reactor.

- Q_R: ~17000 m³/d
- Q_W: ~600 m³/d
- Q_{IN}: ~11000 m³/d

For the nitrogen dependency of the heterotrophic growth is the half saturation coefficient estimated to 0.05. This value is recommended in ASM2 where this

dependency is implemented. The maximum specific growth rate, among others, may be increased to reach higher sludge concentrations.

The ratio of suspended solids to COD is fairly free to modify in order to change the apparent sludge concentration. A plot of the load of the measured suspended solids is seen in Figure 5.3. Bio is the dominating influent. The variation in the load from Bio is big, partly because of a four times larger flow than from Ana.

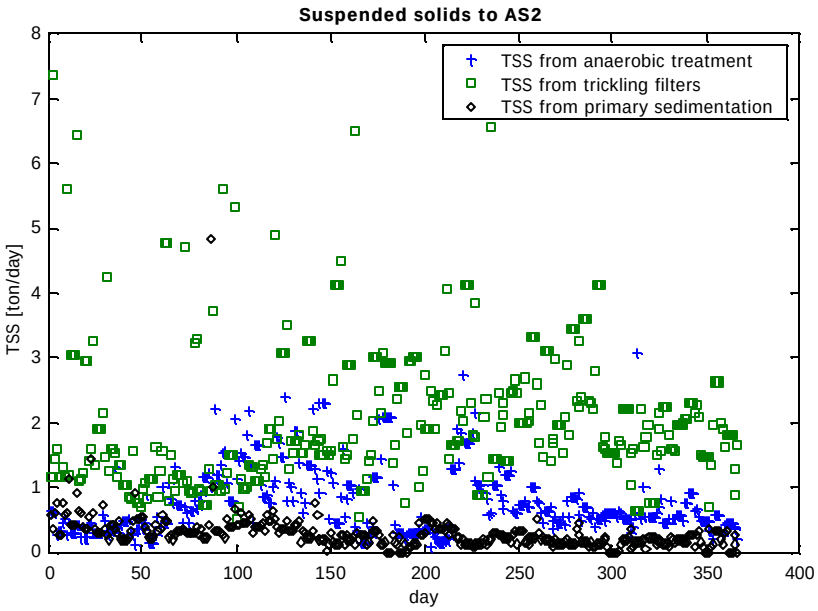

Figure 5.3. The load of suspended solids from the three flows leading to AS2.

A rough estimation of the influent was performed in the early stages of the work, prior to any detailed measurements. Some of its simplifications are:

- Measured, not total, COD are used for calculation and evaluation
- Fractionation of the influent is estimated to give good predictions of the effluent only.
- Alterations of ASM1 parameters likely to be constant, such as Y_H

With these simplifications it was possible to describe the measured effluent COD, but other variables were less accurately predicted. The original biological model was abandoned with the assumptions made of parameter values and influent fractionation.

5.4 Results

The non-settling fraction in the effluent water is used to recalculate the predicted total concentrations to the measured settled.

Table 5.1 presents parameters used to describe biological reactions and the wastewater. Biological parameters that differ from the ones in the original ASM1 are in italic.

Table 5.1. Parameter values and average flow rates used in the simulation.

ASM1 parameters	used	default	Other parameters	
mu_H	*9.000*	6.000	TSS / X_I	0.450
K_S	20.000	20.000	TSS / X_S	0.450
K_OH	0.200	0.200	TSS / X_{BH}	0.900
K_NO	0.500	0.500	TSS / X_{BA}	0.900
b_H	*0.930*	0.620	TSS / X_P	0.900
mu_A	0.800	0.800		
K_NH	1.000	1.000	i_{NS} in AS2 effluent	0.5
K_OA	0.400	0.400		
b_A	0.200	0.200	Nitrogen fraction of particulate COD	
ny_g	0.800	0.800		
k_a	0.080	0.080		
k_h	*6.000*	3.000	i_XI	0.01
K_X	0.030	0.030	i_XS	0.01
ny_h	0.400	0.400	i_SI	0.005
Y_H	0.670	0.670		
Y_A	0.240	0.240	Settler parameters	
f_P	0.080	0.080		
i_XB	*0.070*	0.086	v0_max	100
i_X_P	*0.050*	0.060	v0	145
K_NH2	0.050	0.050	r_h	0.00042
k_h2	3.000	3.000	r_p	0.00500
K_X2	0.030	0.030	f_ns	0.04500
ny_h2	0.400	0.400	X_t	3000
Q_{IN}	11352		Area	890
Q_R	17500		Height	4
Q_W	450			

In Table 5.2 the predicted concentrations of the model variables are presented. Since the reactor is divided into three compartments, the result from each compartment is shown. COD components are presented in mg COD/L and nitrogen components in mg N/L. Only inert components maintain their concentrations in the three compartments.

Table 5.2. Average concentration of model variables in the influent, effluent and along the reactor.

	Influent mg/L	Reactor(s) mg/L			Effluent mg/L
S_I	305.0	305.0	305.0	305.0	305.0
S_S	412.3	246.7	283.8	268.6	268.8
X_I	428.9	4075	4074	4074	183.4
X_S	217.5	109.3	56.2	29.8	1.34
X_{BH}	0	2410	2439	2453	110.4
X_{BA}	0	0	0	0	0
X_P	0	659.7	669.0	678.5	30.5
S_O	0	0.21	1.15	1.75	1.75
S_{NO}	0	0	0	0	0
S_{NH}	21.0	1.38	0.40	0.40	0.40
S_{ND}	0	0.53	0.91	0.90	0.90
X_{ND}	2.18	5.26	3.36	1.98	0.09
S_{al}	7.00	5.60	5.53	5.53	5.53
TSS	271.3	4645	4656	4665	209.9
S_R	559.6	160.0	65.3	19.7	19.7

Table 5.3 presents the easiest observable variables. Effluent predicted concentrations from AS2 sedimentation might be compared directly to the measured. The concentrations of suspended solids in each layer of the modelled settler are presented, showing a sludge blanket level about 1 meter from the bottom of the basin. Predictions from the model are almost equal to the averages of the measured concentrations.

Table 5.3. Predicted and measured concentrations of COD, TSS and nitrogen.

TSS in the settler mg/L			Predicted mg/L	Measured mg/L
TOP		**COD in effluent**	756	750
Layer 1	210	**TSS in reactor**	4656	5060
Layer 2	211	**TSS in effluent**	210	210
Layer 3	218	**TSS in waste sludge**	7378	7930
Layer 4	303	**Thickening factor**	1.58	1.6
Layer 5	1398			
Layer 6	1468	**Particulate COD**	326	
Layer 7	1714	**Soluble COD**	594	
Layer 8	2802			
Layer 9	4718	**Soluble nitrogen**	2.82	
Layer 10	7378	**Particulate nitrogen**	12.06	
BOTTOM		**Settled nitrogen**	8.85	9.7

Of greater importance than similar average concentrations is the dynamic behaviour. When observing the graphs that display the predicted and measured values for the whole year, one must observe that the plant is shut down during the Christmas and Easter holidays. This results in low measurement frequency and dramatic changes in flow rates around days 180 and 310.

Effluent COD from the AS2 settler is well predicted, as seen in Figure 5.4. The more part of the extreme errors coincide with periods of either high or low ratios of COD to nitrogen in the influent. These errors could be the result of bad measurements or due to few detailed measurements.

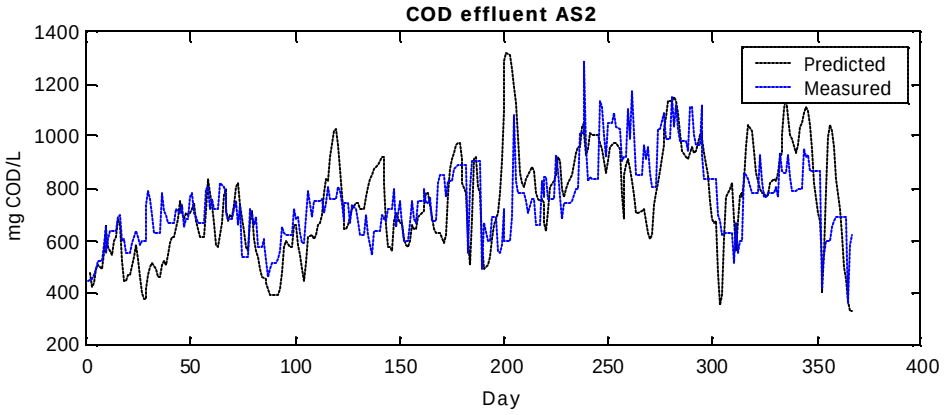

Figure 5.4. Predicted and measured effluent COD.
Predicted values are presented as if they were measured as COD_{sed}.

The concentration of suspended solids in the reactor is not as accurately predicted as the effluent COD, as seen in Figure 5.5. On most occasions the average and the rate of change coincide, but at some occasions the model predicts an opposite rate of change than the measured.

Two periods where the model and reality disagree are at days 120 and 170, where the measured sludge concentrations decrease at a dangerous rate. The decrease at day 150 is preceded by a period of a high concentration of effluent suspended solids, and the problem is most likely solved at Hylte by a change in operating conditions, as the sludge concentration increases rapidly to higher levels. The decrease at day 170, however, is not preceded by periods of high concentrations of effluent suspended solids. It is also not the result of too little incoming COD or nutrients, proven by the predicted increase in biomass. The decrease is hence unknown in origin, perhaps are the bacteria poisoned.

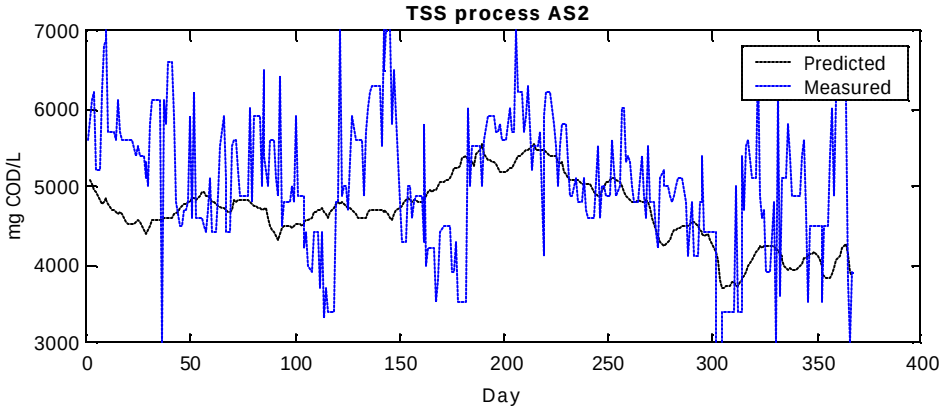

Figure 5.5. Predicted and measured concentrations of suspended solids in the reactor.

Effluent suspended solids is the least accurately predicted variable of the COD-components, as seen in Figure 5.6. Although the average concentration is equal to the measured, the dynamic behaviour is not well predicted, since hydraulic effects are neglected. The huge variation in measured values may be the result of not modelled sludge specific variables, or not modelled hydraulic shocks in the settler.

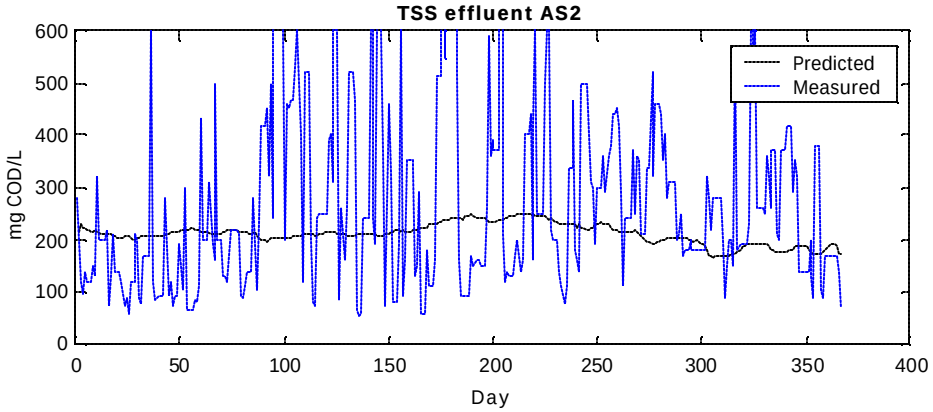

Figure 5.6. Predicted and measured concentrations of effluent suspended solids from AS2 sedimentation.

Influent suspended solids, see Figure 5.7, are accurately predicted, proving only that the estimated ratios of suspended solids to particulate COD are valid for the influent water.

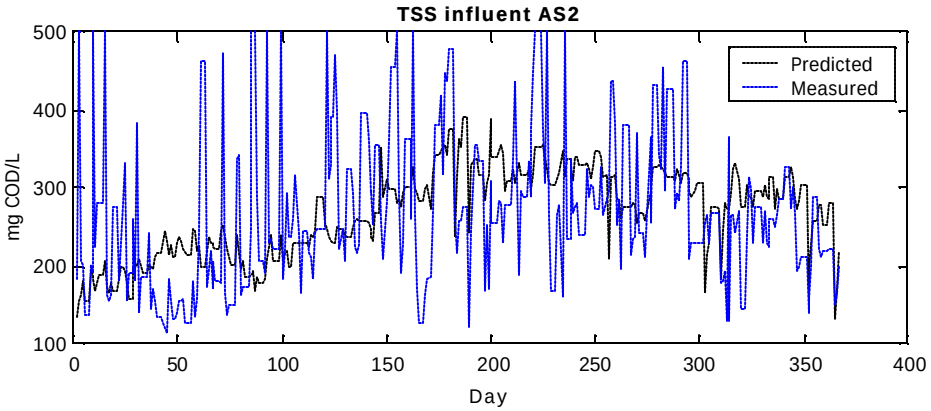

Figure 5.7. Predicted and measured concentrations of influent suspended solids to AS2

Effluent nitrogen is predicted to be more constant than measurements reveal, as seen in Figure 5.8. Average values are equal, but the model tends to predict higher values than the measured during the first 150 days. Predicted nitrogen concentrations are highly correlated to the effluent suspended solids, as these species contain nitrogen. To determine if the erroneous predictions at day 250 are a result of poorly described effluent suspended solids, measured concentrations of suspended solids were compared with measured concentrations of nitrogen. Figure 5.9 shows the normalized concentrations of effluent nitrogen and suspended solids, which are correlated. However, from day 150 to 325 measured effluent nitrogen concentrations are elevated.

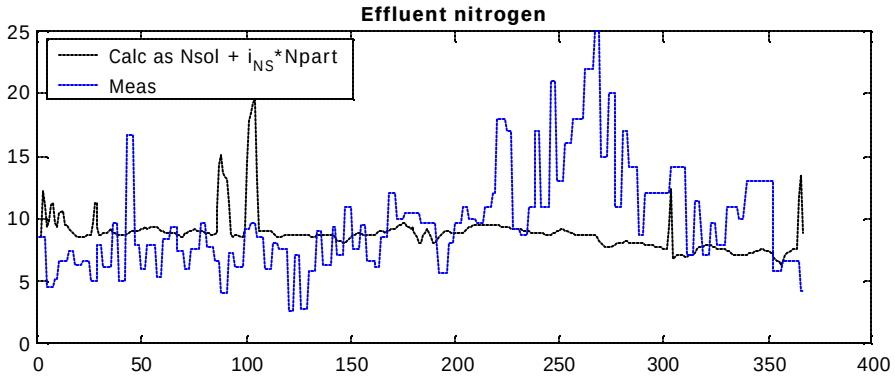

Figure 5.8. Predicted and measured effluent nitrogen.

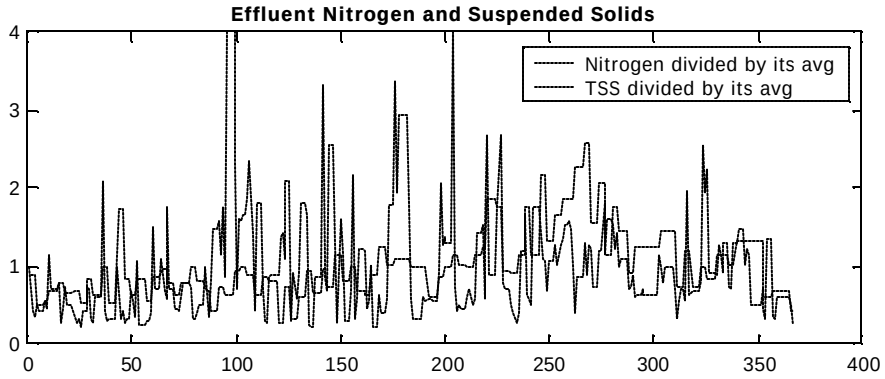

Figure 5.9. Measured concentrations of nitrogen and suspended solids in the effluent.

The predicted concentration of soluble effluent nitrogen is presented in Figure 5.10.

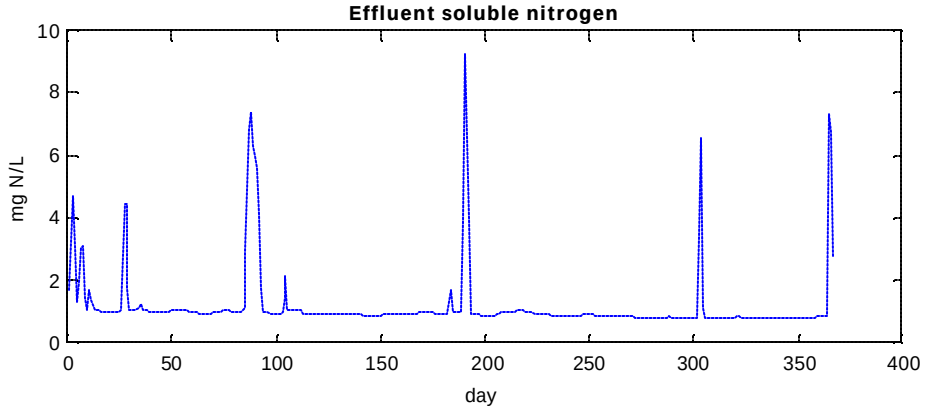

Figure 5.10. Effluent soluble nitrogen.

The not measured oxygen concentration is predicted and shown in Figure 5.11. Since aeration is constant, the variation reflects the conditions in the reactor and the influent COD and nitrogen. This will give a curve showing the dynamic behaviour, with an unknown level of the baseline. Three periods with different oxygen concentrations are seen, with a drastic change at day 270. In order to maintain the COD balance, oxygen is expressed in units of negative COD.

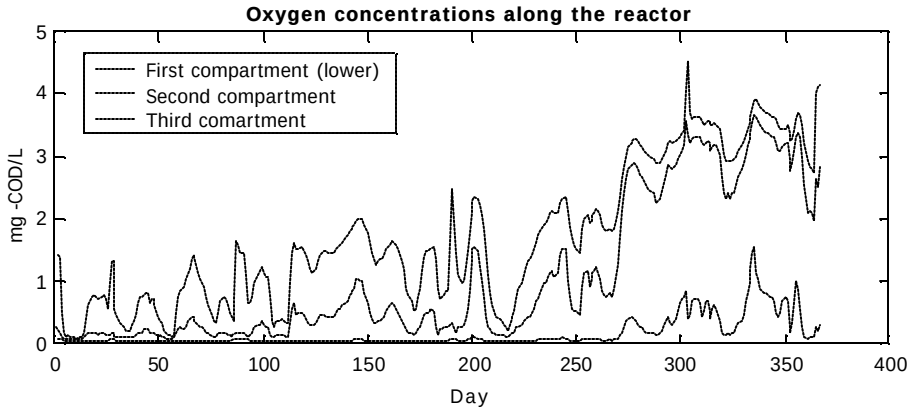

Figure 5.11. Oxygen concentrations in the three compartments.

An attempt to understand the predic ted variations is facilitated by knowledge of the influent. Figure 5.12 shows the load of influent biodegradable nitrogen and Figure 5.13 the load of influent COD. In Figure 5.13, Christmas, day 180, New Years Eve, day 190, and Easter, day 310, are seen as short periods with little influent COD.

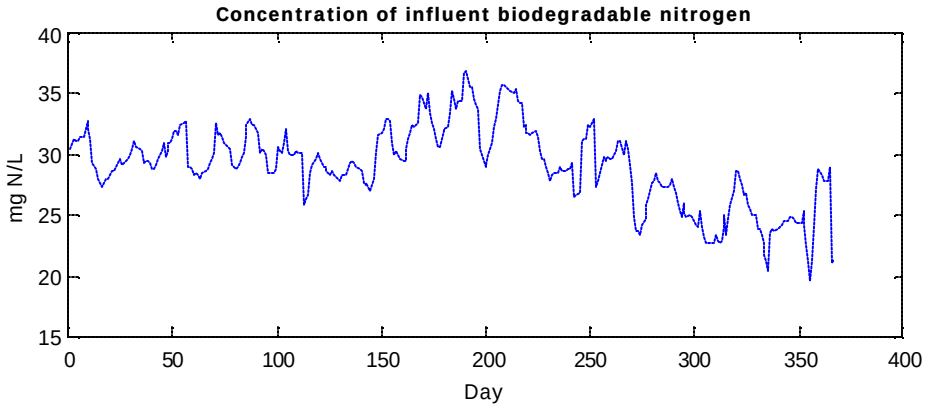

Figure 5.12. Influent biodegradable nitrogen.

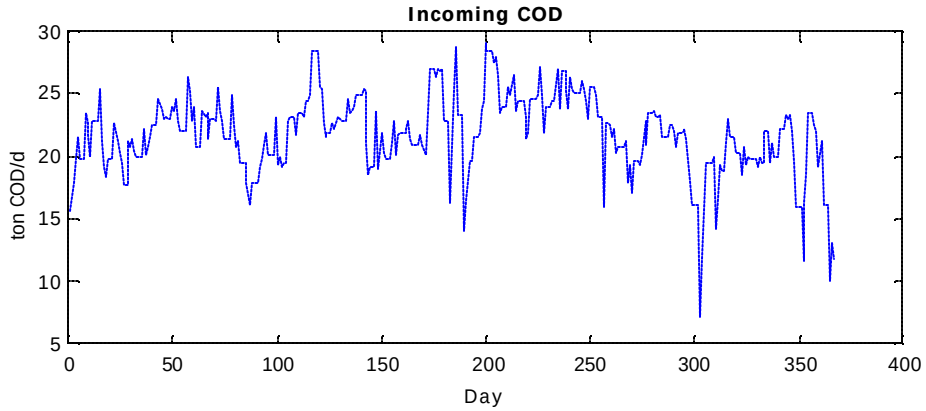

Figure 5.13. Influent COD.

Figure 5.14 shows the influent flow rate to AS2.

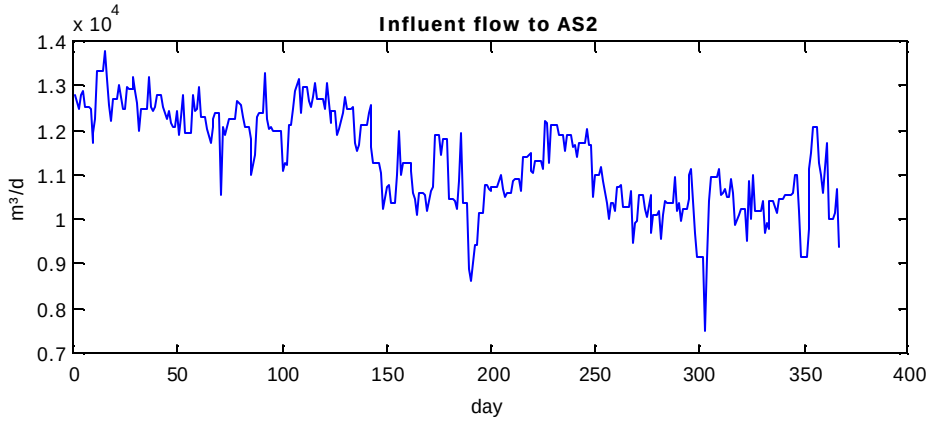

Figure 5.14. Influent flow rate to AS2.

One purpose with the model is to predict the result of hypothetical modifications in the plant.

With the return sludge flow lowered to 5000 m³/d from 17500 m³/d, a much lower concentration of sludge is reached in the reactor, 3000 mg/L instead of 5000 mg/L. The effluent COD, however, is only increased to 810 mg COD/L from 750 mg COD/L. Due to the lower concentration of sludge in the reactor, the particulate part of the effluent COD is lower than before. The concentration of the thickened sludge is increased, due to the lower flow rate to the settler, to 9100 mg/L from 7400 mg/L. A return sludge flow rate of 10000 m³/d will increase effluent COD with 1.7% and increase the concentration of the thickened sludge with 10%. The sludge blanket level is left relatively unchanged in the two cases.

The waste sludge flow rate has great impact on the sludge concentration in the reactor, as mentioned earlier in the work. With the waste sludge flow rate reduced to 200 m³/d from 450 m³/d, the settler is filled with sludge. Sludge concentrations in the reactor and the effluent increase significantly. Given the nature of the process, a variable waste sludge flow rate would be beneficial.

A doubling of the added nitrogen salt results in increased growth (suspended solids increased 10%) and lower levels of effluent COD (decreased 17%). At this point, it is the aeration that is growth limiting. As this prediction contradicts the observed behaviour of the plant, more information is needed regarding the reactions in which nitrogen is involved.

6 Conclusions

With the modified ASM1 it is possible to predict the performance an activated sludge plant treating water from the pulp and paper industry.

Of paramount importance for model validation are the performed measurements. The many steps involved in sampling and measuring must be understood perfectly or the measurements' informational value is lost. The fundamental questions "how?", "what?", "where?", "when?", and "why?" should be answered, evaluated and documented for every link in the chain of data collection. For instance, what is oxidized when measuring COD? Is it only organic material and if so, all organic material?

It was found that a model using measurements already implemented at Hylte could describe the effluent COD accurately. The COD used is measured on a settled sample, resulting in a lower value than the actual total COD. This has several drawbacks, which calls for several unrealistic parameter values. The most obvious impact of less influent COD is that the concentration of biomass will be lower than in reality. This demands that parameters describing oxygenation and sedimentation must be other than the actual ones, and that any attempt to determine these parameters will be in vain. Also other biological parameters must be altered, in some cases to unrealistic values. Determining these values by reasoning and trial and error was hard, since a true biological model was no longer used.

As oxygen is included in the model, the effect of another kind of aeration can be evaluated. With knowledge of electricity costs, the cost of adding more aerators may be compared with what is gained with the assumed reduction in effluent concentrations of COD. Alternative ways of adding oxygen may be evaluated with knowledge of the hydraulic and biological model.

How flow variations affects the sludge concentration and effluent COD might be studied to determine the best obtainable variation in influent flow rates. It has also been shown that the assumed division of flow between the basins is not valid, and should be determined.

The cost of sludge disposal might be compared with the cost of more effluent COD as the result of lower concentrations of suspended solids in the reactor.

Future work includes a more detailed model of the settler in order to predict the actual variations of the effluent suspended solids. These are affected by hydraulic shocks and by the characteristics of the sludge. Including an estimation of the sludge settling characteristics in the model could improve the predictions of the effluent solids in a short time frame.

Appendix I IAWQ Activated sludge model No 1

This model is a result of the work of an IAWQ task group that started in 1983. Their goal was to review current models and to find the simplest mathematical model describing the performance of sludge systems carrying out oxidation, nitrification and denitrification. The many possible models have all advantages and disadvantages, and in the final model a compromise between simplicity and accuracy had to be made. Henze *et al.*, (1987) presented the final model 1987, and it has been the basis of both more complex and reduced models.

ASM1 uses 13 state variables of different fractions of COD and nitrogen, presented in Table A1.1. The biological cycles are described in Figure A1.1 Carbonaceous material is divided into biodegradable, non-biodegradable and active mass COD. Biodegradable COD is divided into two groups: the soluble (S_S) and the particulate (X_S) COD. Soluble COD are assumed to be small molecules that easily diffuse through the bacterial membranes for digestion, whereas particulate COD requires enzymatic breakdown, hydrolysis, prior to assimilation. Non-biodegradable COD is inert material and considered unaffected by any biological reactions that take place. It may be soluble (S_I), or particulate (X_I). Also inert products from biomass decay (X_P), are included. Active mass COD is the biomass COD. This is divided into the heterotrophic biomass (X_{BH}) and the autotrophic biomass (X_{BA}). Biodegradable COD exists in the model either as substrate or biomass. Death and decay of organisms result in a shift from biomass COD to particulate COD. This concept is called the death-regeneration hypothesis.

Nitrogenous material exists in the model as free and saline ammonia (S_{NH}), organically bound nitrogen (S_{ND}), active mass nitrogen (X_{ND}) and nitrate and nitrite combined in (S_{NO}). Organically bound nitrogen may be soluble or particulate, both with an inert fraction. In the model only the biodegradable fractions of nitrogen, S_{ND} and X_{ND} are explicitly included. Active mass nitrogen is the nitrogen bound in biomass, mainly as proteins and DNA. It is included to describe an increase in organically bound nitrogen with biomass decay. The last two variables are the dissolved oxygen (S_O), expressed as negative COD, and the alkalinity (S_{ALK}). The alkalinity is only monitored in order to predict changes in pH.

Table A1.1. Variables used in the ASM1.

Variable	Description	Unit
S_I	Soluble inert organic material	mg COD/L
S_S	Soluble organic biodegradable material	mg COD/L
X_I	Particulate inert organic material	mg COD/L
X_S	Particulate organic biodegradable material	mg COD/L
X_{BH}	Heterotrophic biomass	mg COD/L
X_{BA}	Autotrophic biomass	mg COD/L
X_P	Inert products arising from biomass decay	mg COD/L
S_O	Dissolved oxygen	mg -COD/L
S_{NO}	Nitrate nitrogen	mg N/L
S_{NH}	Ammonium nitrogen	mg N/L
S_{ND}	Soluble organically bound nitrogen	mg N/L
X_{ND}	Particulate organic nitrogen	mg N/L
S_{ALK}	Alkalinity	mol $CaCO_3$/L

The IAWQ Activated Sludge Model No 1, ASM1, uses eight differential equations to describe the biological reactions:

1. Aerobic growth of heterotrophs

2. Anoxic growth of heterotrophs
3. Aerobic growth of autotrophs
4. Decay of heterotrophs
5. Decay of autotrophs
6. Ammonification of soluble organic nitrogen
7. Hydrolysis of entrapped organics
8. Hydrolysis of entrapped organic nitrogen

These do not necessarily have a physical or biological meaning, but together they describe reality well. The equations affect many variables and hence the reactions of a variable are described by a combination of rates. Accumulation of heterotrophic biomass uses, for example, equation 1, 2 and 4. In the eight equations the 19 parameters presented in Table A1.2 are used. They are not all explicitly identifiable, with the consequence that different sets of parameters may give the same result. This makes it hard to extract parameter values based on one model to use in another model, and is a drawback of ASM1. Additional parameters are needed to describe oxygenation, sedimentation and the hydraulics of the modelled environment.

Table A1.2. Typical parameter values at neutral pH.

		20°C	10°C
Stoichiometric parameters			
Y_A	Autotrophic yield [g cell COD / g N]	0.24	0.24
Y_H	Heterotrophic yield [g cell COD / g S_S]	0.67	0.67
f_P	Fraction of inert products from biomass decay [ ]	0.08	0.08
i_{XB}	Nitrogen fraction of COD in biomass [ ]	0.086	0.086
i_{XP}	Nitrogen fraction of COD in endogenous mass [g N / g COD]	0.06	0.06
Kinetic parameters			
μ_H	Heterotrophic maximum specific growth rate [1 / day]	6.0	3.0
K_S	Half saturation constant for assimilation of carbon [g COD / m³]	20	20
K_{OH}	Heterotrophic oxygen half saturation constant [g O_2 / m³]	0.20	0.20
K_{NH}	Half saturation constant for ammonium [g NH_4-N / m³]	1.0	1.0
K_{NO}	Half saturation constant for nitrate [g NO_3-N / m³]	0.50	0.50
K_{OA}	Autotrophic oxygen half saturation constant [g O_2 / m³]	0.4	0.4
μ_A	Autotrophic maximum specific growth rate [1 / day]	0.80	0.3
b_H	Heterotrophic decay rate [1 / day]	0.62	0.20
b_A	Autotrophic decay rate [1 / day]		
k_a	Specific ammonification rate [m³ / (g COD day)]	0.08	0.04
k_h	Maximum specific hydrolysis rate [g COD / (g cell COD day)]	3.0	1.0
K_X	Hydrolysis half saturation constant [g COD / (g cell COD)]	0.03	0.01
η_h	Correction factor for anoxic hydrolysis [-]	0.4	0.4
η_g	Correction factor for anoxic growth of heterotrophs [-]	0.8	0.8

Aerobic growth of heterotrophs. In the presence of air, heterotrophs use one part of the biodegradable COD they assimilate to produce biomass. The other is oxidized to convert energy, creating an oxygen demand. Only substrate and oxygen are rate limiting

$$\text{rate1} = \hat{\mu}_H \left(\frac{S_S}{K_S + S_S} \right) \left(\frac{S_O}{K_{O,H} + S_O} \right) X_{BH}$$

Anoxic growth of heterotrophs. In the absence of air, heterotrophs use nitrate as the terminal electron acceptor instead of oxygen. This energetically less favourable reaction is described by multiplying the growth rate with a factor η_g (<1), which means that less

biomass is produced. The cause of the lower apparent growth rate is not specified. Possible explanations are a lower growth rate during anoxic conditions or that only a part of the heterotrophic community is able to live under anoxic conditions. The nitrate consumed is primarily reduced into nitrogen gas, but also the greenhouse gas dinitrogen oxide (N_2O) is formed. Nitrogen used for cell synthesis is in the form of ammonia, NH_4-N.

$$\text{rate } 2 = \hat{\mu}_H \left(\frac{S_S}{K_S + S_S} \right) \left(\frac{K_{O,H}}{K_{O,H} + S_O} \right) \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) ?_g X_{BH}$$

Aerobic growth of autotrophs. Autotrophs rely on ammonia as their energy source, not carbon. Since ammonia is also used for biomass growth, autotrophs have significantly lower growth rates than heterotrophs. The ammonia is oxidized to nitrate in a process called nitrification. This process is far more oxygen consuming than the oxidation of carbon.

$$\text{rate } 3 = \hat{\mu}_A \left(\frac{S_{NH}}{K_{NH} + S_{NH}} \right) \left(\frac{S_O}{K_{O,A} + S_O} \right) X_A$$

Decay of heterotrophs. The organisms are believed to decay at a rate proportional to the amount of biomass.

$$\text{rate } 4 = b_H X_{BH}$$

Decay of autotrophs. Modelled as decay of heterotrophs.

$$\text{rate } 5 = b_A X_{BA}$$

Ammonification of soluble organic nitrogen. Soluble organic nitrogen is converted into free and saline ammonia by a first-order process mediated by the heterotrophs.

$$\text{rate } 6 = k_a S_{ND} X_{BH}$$

Hydrolysis of entrapped organics. It is the heterotrophic genera that are able to hydrolyse organic material, and subsequently this is done in both aerobic and anoxic environments. The rate of hydrolysis is reduced under anoxic conditions. Hydrolysis is modelled with a Monod expression.

$$\text{rate } 7 = k_h \left(\frac{X_S / X_{BH}}{K_X + X_S / X_{BH}} \right) \left[\left(\frac{S_O}{K_{O,H} + S_O} \right) + ?_h \left(\frac{K_{O,H} + S_O}{S_O} \right) \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) \right] X_{BH}$$

Hydrolysis of entrapped organic nitrogen. Biodegradable organic nitrogen is hydrolysed to soluble organic nitrogen at a rate defined by the hydrolysis reaction for entrapped organics.

$$\text{rate } 8 = k_h \left(\frac{X_S / X_{BH}}{K_X + X_S / X_{BH}} \right) \left(\frac{X_{ND}}{X_S} \right) \left[\left(\frac{S_O}{K_{O,H} + S_O} \right) + ?_h \left(\frac{K_{O,H} + S_O}{S_O} \right) \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) \right] X_{BH}$$

In Figure A1.1 the biological pathways associated with heterotrophic growth are presented. The outer loop describes organic carbon, and the inner describes nitrogen

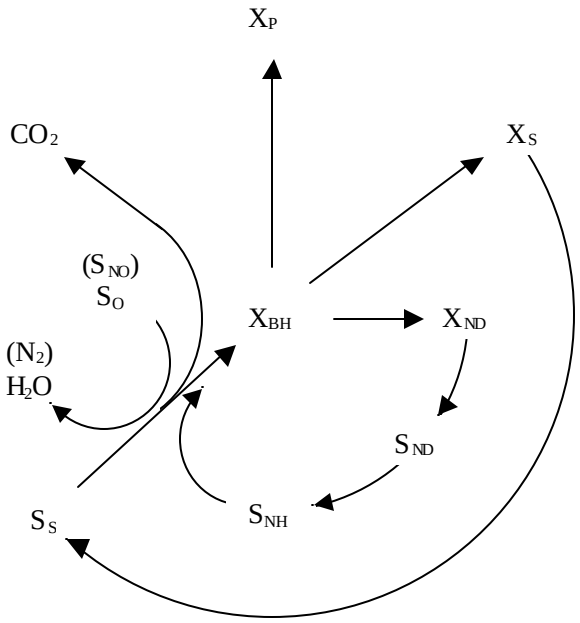

Figure A1.1. Variables in ASM1 as affected by aerobic and (anoxic) heterotrophic growth.

Figure A1.2 presents the biological pathways associated with autotrophic growth. Due to the low concentrations of nitrogen, autotrophs will not exist in the current plant.

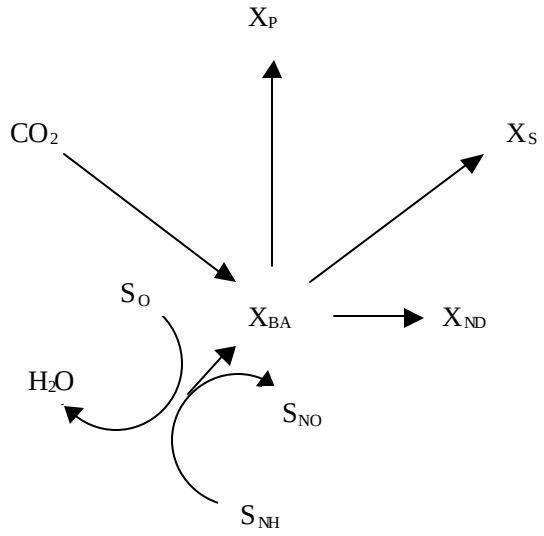

Figure A1.2. Variables in ASM1 as affected by autotrophic growth.

Appendix II Monod kinetics

Microbial growth is often described by a relationship derived by Monod 1942. It is based on the observation that the growth rate will not exceed a certain limit regardless of the concentration of the limiting substrate. The equation describes the growth rate as a function of substrate concentration using two parameters, a half-saturation coefficient and a maximum growth rate. Its use in the IAWQ model also comes from the fact that it is numerically stable (the denominator is never zero). An example of Monod kinetics describing the growth rate is shown in Figure A2.1.

$$\mu = \mu_{max}\left(\frac{S}{hsc + S}\right)$$

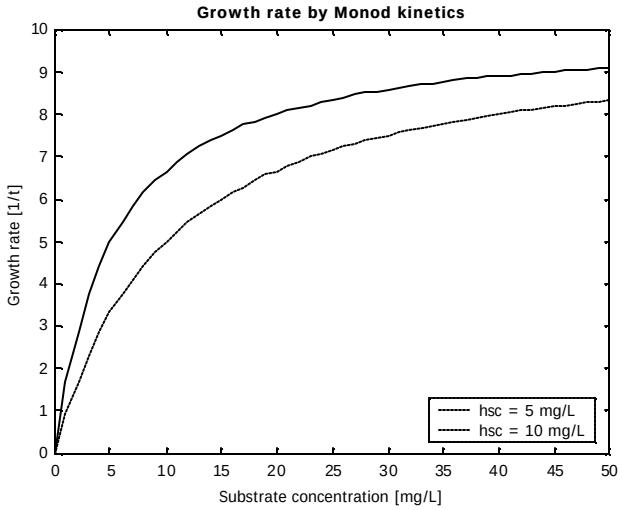

Figure A2.1. An example of Monod kinetics describing the growth rate. Maximum specific growth rate is 10.

Appendix III Data and calculations

Detailed measurements

Samples submitted to a higher degree of scrutiny were extracted at 2000-08-15 and 2000-08-23. Table A3.1 presents the results from the measurements on the influent water to AS2 and on the effluent water from the final sedimentation.

Table A3.1. Results from detailed measurements on water entering AS2.

		Final sedimentation			Bio + PS			Ana		
		15/8	23/8	avg	15/8	23/8	avg	15/8	23/8	avg
TSS	mg/L	58	32	45	520	440	480	260	220	240
COD_{tot}	mg COD/L	487	388	437.5	2220	1880	2050	2175	2125	2150
COD_{sed}	mg COD/L				1620	1410	1515	1970	1860	1915
COD_{filt}	mg COD/L	422	346	384	1230	1170	1200	1760	1590	1675
P_{tot}	mg P/L	0.64	0.32	0.48	5.8	5.1	5.45	1.3	1.3	1.3
P_{filt}	mg P/L	0.25	0.19	0.22	1.3	1.8	1.55	0.5	0.5	0.5
N_{tot}	mg N/L	5	3.3	4.15	44	25	34.5	29	28	28.5
N_{sed}	mg N/L	2.6	2.3	2.45	8.3	10	9.15	21	12	16.5
$BOD_{7,tot}$	mg BOD/L	61	52	56.5	650	570	610	670	630	650
$BOD_{7,filt}$	mg BOD/L	44	42	43	440	400	420	620	500	560
$BOD_{21,tot}$	mg BOD/L				930	810	870	940	820	880
$BOD_{21,filt}$	mg BOD/L				620	580	600	780	650	715
$BOD_{42,tot}$	mg BOD/L				1000	880	940	1100	920	1010
Only cake*										
COD_{tot}	mg COD/L				516	572	544	282	396	339
$BOD_{7,tot}$	mg BOD/L				160	130	145	58	70	64
$BOD_{21,tot}$	mg BOD/L				200	190	195	96	110	103

	Samples from AS2						Averages		
	15/8			23/8			15/8	23/8	Both
	1	2	3	1	2	3			
CODtot	8200	8220	8370	8810	9760	7710	8263	8760	8512
CODfilt	665	628	647	600	582	554	647	579	613
Ntot	314	295	301	376	361	302	303	346	325
Nfilt	3.1	3.2	3.3	3.0	2.6	2.7	3.2	2.8	3.0

* Lower COD_{tot} than from measurements on whole sample ($COD_{tot} - COD_{filt}$). The origin of this gross error is unknown.

Table A3.2 presents the results from the measurements on the effluent water from the AS2 settler. These measurements are from a sample collected on 2000-10-23.

Table A3.2. Results from measurements on effluent from AS2 sedimentation.

	Samples from AS2 sedimentation			
	23/10			Averages
TSS	120			
CODtot	814	818	814	815
CODsed	690	684	688	687
CODfilt	522	520	523	522
Ntot	11	13		
Nsed	5.9			
Nfilt	2.7	2.6		

Yearly averages of daily averages

In Table A3.3 to Table A3.7, the yearly averages of the measurements performed at Hylte are presented. The average concentrations from the trickling filters and the primary sedimentation are similar to the ones found by the detailed measurements. Concentrations from the anaerobic treatment experience a larger variation, and thus the results from the detailed measurements differ significantly from the yearly averages.

Table A3.3. Measurements from AS.

Tag	Description	Value	Unit
AS1	SVI AS1	170	mL/g
in reactor	TSS in AS1	5900	mg/L
	TSS in Q_R AS1	10100	mg/L
	Aerated AS1	7645	m³/d
From AS1	BOD_7	87	mg BOD/L
after settler	COD	660	mg COD/L
	Flow	5623	m³/d
	N	8.2	mg N/L
	P	1.4	mg P/L
	pH	7.9	-
	TSS	270	mg/L
AS2	SVI AS2	192	mL/g
in reactor	TSS in AS2	5063	mg/L
	TSS in Q_R AS2	7900	mg/L
	Aerated AS2	11393	m³/d
From AS2	BOD_7	117	mg BOD/L
after settler	COD	752	mg COD/L
	Flow	8054	m³/d
	N	9.7	mg N/L
	P	1.5	mg P/L
	pH	8.1	-
	TSS	287	mg/L
From AS3	BOD_7	102	mg BOD/L
after settler	COD	696	mg COD/L
	Flow	4000	m³/d
	N	9.5	mg N/L
	P	1.6	mg N/L
	pH	8.1	-
	TSS	218	mg/L

All tests on clear phase of sedimented sample

Table A3.4. Measurements from aerobic treatment (Bio).

Tag	Description	Value	Unit
To Bio	BOD7	648	mg BOD/L
	COD	1573	mg COD/L
	Flow	12930	m³/d
	pH	7.3	-
	TSS	229	mg/L
From Bio	BOD7	470	mg BOD/L
	COD	1290	mg COD/L
	Flow	12950	mg/L
	pH	7.5	mg/L
	TSS	297	m³/d

All tests on clear phase of sedimented sample

Table A3.5. Measurements from primary sedimentation (PS).

Tag	Description	Value	Unit
From PS	BOD7	1170	mg BOD/L
	COD	2540	mg COD/L
	Flow	7060	m³/d
	N	12.3	mg N/L
	P	1.9	mg P/L
	pH	7.3	-
	TSS	177	mg/L
	Shunt to AS	3032	m³/d

All tests on clear phase of sedimented sample

Table A3.6. Measurements from anaerobic treatment (Ana).

Tag	Description	Value	Unit
To Ana	BOD7	1456	mg BOD/L
	COD	2900	mg COD/L
	Flow	2914	m³/d
	N	25	mg N/L
	P	2	mg P/L
	pH	7.3	-
	TSS	100	mg/L
	Temp	40	C
From Ana1	SVI	94	mL/g
	TSS in Ana1	2.5	mg/L
	TSS in Q_R		
	BOD7	570	mg BOD/L
	COD	1500	mg COD/L
	Flow	1327	m³/d
	N	18.1	mg N/L
	P	1.1	mg P/L
	pH	8.1	-
	Susp solids	238	mg/L
	Temp	40	C
From Ana2	SVI	86	mL/g
	TSS in Ana2	2600	mg/L
	TSS in Q_R		
	BOD7	550	mg BOD/L
	COD	1480	mg COD/L
	Flow	1582	m³/d
	N	16.9	mg N/L
	P	1	mg P/L
	pH	8.0	-
	TSS	238	mg/L
Combined effluent	SVI		mL/g
	TSS in Ana2		mg/L
	TSS in Q_R		
	BOD7	560	mg BOD/L
	COD	1490	mg COD/L
	Flow	2910	m³/d
	N	17.3	mg N/L
	P	1.0	mg P/L
	pH		-
	TSS	254	mg/L

All tests on shaken (raw) sample

Table A3.7. Measurements from final sedimentation.

Tag	Description	Value	Unit
From FS	BOD7	60	mg BOD/L
	COD	450	mg COD/L
	Flow	17324	m³/d
	N	4.1	mg N/L
	P	0.41	mg P/L
	pH	7.6	-
	Susp solids	45	mg/L

All tests on shaken (raw) sample

A warning regarding average values

In this work many calculated average values as well as ratios between values have been used. When an average of ratios is calculated the average of the terms must not be used, or an erroneous result will be reached. An example using two vectors, a and b, will show the different results reached.

$$\frac{a_1 + a_2}{b_1 + b_2} \neq \frac{a_1 / b_1 + a_2 / b_2}{2}$$

Methods used for the detailed measurements

Estimation of COD in particulate material

A 100 mL aliquot was filtered through a Whatman GF/A 1µ filter. The cake was washed in a small beaker, transferred to a larger and diluted to 200 mL. Measurements of COD and nitrogen were performed according to standards at Hylte.

Nomenclature

Name	Description	Unit
A	Area	m^2
AS	Activated sludge	-
AS1	Activated sludge basin no 1 at Hylte	-
AS2	Activated sludge basin no 2 at Hylte	-
AS3	Shared settler between AS1 and AS2 at Hylte	-
ASM1	Activated Sludge Model no 1 by IAWPRC	-
ASM2	Activated Sludge Model no 2 by IAWQ	-
Ana	The anaerobic treatment at Hylte	-
b_A	Autotrophic decay rate	1/day
b_H	Heterotrophic decay rate	1/day
Bio	The trickling filters at Hylte	-
BOD	Biological oxygen demand	mg BOD/L
c	Concentration	mg/L
BOD_{filt}	BOD measured after sample is filtrated	mg BOD/L
BOD_{inf}	Accumulated oxygen demand after a very long time	mg BOD/L
BOD_{meas}	Measured BOD	mg BOD/L
BOD_i	Accumulated oxygen demand for biological growth after i days	mg BOD/L
BOD_{sed}	BOD measured after sample has settled	mg BOD/L
BOD_{tot}	BOD measured on raw sample	mg BOD/L
CSTR	Continuously stirred tank reactor	-
COD	Chemical oxygen demand –oxygen equivalent required for complete oxidation of all organic material and other material possible to oxidize	mg COD/L
COD_{bd}	Biodegradable part of all COD	mg COD/L
COD_{filt}	COD measured after sample is filtered	mg COD/L
COD_{meas}	Measured COD	mg COD/L
COD_{sed}	COD measured after sample has settled	mg COD/L
COD_{tot}	COD measured on raw sample	mg COD/L
D_p	Diameter of spherical particle	m
DO	Dissolved oxygen	mg O_2/L
f	Factor used in various calculations	-
f_{ns}	non-settling fraction of sludge (used in settler calculations)	-
f_P	Fraction of inert products from biomass decay	-
FS	Final sedimentation at Hylte	-
HRT	Hydraulic Retention Time – unit volume per unit flow	day
i_{NS}	Non-settling fraction of particulate material	-
IAWPRC	International Association on Water Pollution Research and Control, now IWA	-
IAWQ	International Association on Water Quality, now IWA	-
IWA	International Water Association	-
i_{XB}	Nitrogen fraction of COD in biomass	g N/ g COD
i_{XP}	Nitrogen fraction of COD in endogenous mass, X_P	g N / g COD
i_{XI}	Nitrogen fraction of COD X_I	g N/ g COD
i_{XS}	Nitrogen fraction of COD X_S	g N/ g COD
i_{SI}	Nitrogen fraction of COD S_I	g N/ g COD
J	Flux	kg/(m^2.day)
k_a	Specific ammonification rate	m^3/(g COD. day)
k_h	Maximum specific hydrolysis rate	g COD/(g cell COD. day)]
K_{NH}	Half saturation constant for ammonium	g NH_4-N/ m^3]
K_{NO}	Half saturation constant for nitrate	g NO_3-N/ m^3]
K_{OA}	Autotrophic oxygen half saturation constant	g O_2/m^3

K_{OH}	Heterotrophic oxygen half saturation constant	g O_2/m^3
K_S	Half saturation constant for assimilation of carbon	g COD/m^3
K_X	Hydrolysis half saturation constant	g COD/(g cell COD)
μ	Kinematic viscosity	kg/(m.s)
μ_A	Autotrophic maximum specific growth rate	1/day
μ_H	Heterotrophic maximum specific growth rate	1/day
N	Nitrogen	mg N/L
η_g	Correction factor for anoxic growth of heterotrophs	-
η_h	Correction factor for anoxic hydrolysis	-
P	Phosphorous	mg P/L
PS	Primary sedimentation at Hylte	-
PFR	Plug flow reactor	-
Q	Volumetric flow	m^3/d
ρ	Density	kg/m^3
r_h	settling characteristic of the hindered settling zone	-
rsx_i	Ratio of suspended solids to component i of particulate COD	kg TSS/COD
r_p	settling characteristic at low concentrations of suspended solids	-
SA	Sludge age, same as SRT	day
S_{ALK}	Alkalinity	mol $CaCO_3$/L
S_I	Soluble inert organic material	mg COD/L
S_{ND}	Soluble organicaly bound nitrogen	mg N/L
S_{NH}	Ammonium nitrogen	mg N/L
S_{NO}	Nitrate nitrogen	mg N/L
S_O	Dissolved oxygen	mg -COD/L
SRT	Sludge retention time, same as SA	day
S_S	Soluble organic biodegradable material	mg COD/L
V	Volume	m^3
v	Velocity	m/s
v_0	maximum theoretical settling velocity	m/day
v_i	settling velocity	m/day
v_{max}	maximum practical settling velocity	m/day
X_{BA}	Autotrophic biomass	mg COD/L
X_{BH}	Heterotrophic biomass	mg COD/L
X_I	Particulate inert organic material	mg COD/L
X_F	Concentration of suspended solids in feed to settler	mg/L
X_{ND}	Particulate organic nitrogen	mg N/L
X_P	Inert products arising from biomass decay	mg COD/L
X_S	Particulate organic biodegradable material	mg COD/L
Y_A	Autotrophic yield	g cell COD/g N
Y_H	Heterotrophic yield	g cell COD/g S_S

Literature

van Ginkel, C. G., Kester H., Stroo C. A. and van Haperen A. M. (1999). Biodegradation of EDTA in pulp and paper mill effluents by activated sludge. *Wat. Sci. Tech.*, **40**(11-12).

Henze, M., Grady Jr, C. P. L., Gujer, W., Marais, G. v. R., Matsuo, T. (1986). *Activated sludge model no 1.* International Association on Water Pollution Research and Control. Scientific and Technical Reports No 1. ISSN: 1010-707X.

Henze, M., Gujer, W., Mino, T., Matsuo, T., Wentzel, M. C., Marais, G. v. R., Van Loosdrecht, M. C. M. (1995). *Activated sludge model no 2*. Scientific and Technical Reports No 3. IAWQ.

Houbron, E., Torrijos, M. and Capdeville, B. (1999). An alternative use of biogas applied at the water denitrificaton. *Wat. Sci. Tech*., **40**(8).

Lopetegui, J. and Sancho, L. (2000). Thermophilic aerobic microorganisms - determination of kinetics on paper mill effluents. (Unpublished).

Makinia, J. and Wells, S. A. (2000). A general model of the activated sludge reactor with dispersive flow. *Wat. Res*., **34**(16).

MathWorks (1999). *Matlab®- user's guide*. The Mathworks Inc., www.mathworks.com.

MathWorks (1999). *Simulink® – dynamic system simulation software, User's guide*, The Mathworks Inc., www.mathworks.com.

Monod, J. (1942). Recherche sur la Croissance des Cultures Bacteriennes. *Herman et Cie*, Paris, France

Olsson G. (1999). Effektstyrning kan bli sparbössa i VA-systemet. *VAV-Nytt* 5/99.

Skogsindustrins Utbildning i Markaryd AB (1997). *Yttre miljöskydd i massa och pappersindustrin*. ISBN 91-7322-228-3.

Tacács, I., Patry, G. G., Nolasco, D. (1991). A dynamic model of the clarification-thickening process. *Wat. Res.*, **25**(10), pp 1263-1271.

Virtapohja, J. and Alén, R. (1998). Accelerated degradation of EDTA in an activated sludge plant. *Pulp and Paper Canada*, November 1998.

Vitasovic, Z. Z. (1989). Continuous settler operation: a dynamic model. *Dynamic modelling and expert systems in wastewater engineering.* (G. G. Patry and D. Chapman eds.), Lewis Publishers Inc, Chelsea, Michigan, USA, pp. 59-81.

Weijers, S. (2000). *Modelling, identification and control of activated sludge plants for nitrogen removal.* PhD thesis, Technische Universiteit Eindhoven, The Netherlands. ISBN 90-386-0997-3