Thesis Systems and Control

Quantifying the greenhouse gas emissions of wastewater treatment plants

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August 2009-December 2009

WAGENINGEN UNIVERSITY
AGROTECHNOLOGY AND
FOOD SCIENCES

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Name course	:	Thesis project Systems and Control
Number	:	SCO-80424
Study load	:	24 ects
Date	:	April 2010
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Registration number	:	85-05-17-781-100
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Summary

There is an interest to determine the carbon footprints of wastewater treatment plants (WWTPs) due to global warming. The greenhouse gases (GHG) that are emitted in a WWTP are carbon dioxide, CO_2, methane, CH_4, and nitrous oxide, N_2O. The global warming potential of N_2O is 296 kg equivalent CO_2. To model the GHGs of a WWTP it is therefore important to take the N_2O emissions into account. There are empirical static models available to describe the GHG emissions of a WWTP and there are detailed mechanistic models to describe the performance of a WWTP. These models can be combined to estimate the GHG emissions of a WWTP.

The boundaries chosen for the estimation of the carbon footprint are according to Scope 2 the direct GHG emissions during the processes of the treatment, the indirect GHG emissions due to the use of energy, the production of biogas, the indirect GHG emissions due to sludge disposal, the power credit due to the biogas usage, and the indirect GHG emissions due to chemicals usage. The GHG N_2O can be produced during the processes denitrification, nitrification and during chemical reactions that take place in the WWTP. Only the N_2O produced during denitrification will be taken into account in this study.

The empirical model used in this thesis for the estimation of the GHG emissions of a WWTP was a model created by Bridle Consulting. In this model the GHGs according to the chosen boundaries are calculated. These calculations are divided in 6 different processes, namely biotreatment, sludge digestion, sludge reuse, chemical usage, power consumption and biogas usage. The model uses measured influent and effluent data and mostly conversion factors to estimate the GHGs.

To create a dynamic model the Petersen matrix is used. The Activated Sludge Model no. 1 (ASM1) was extended with processes of denitrification and nitrification to include the production of N_2O. The model of Hiatt and Grady was the basis for the extension. This new model was named ASM_2N_4DN and was verified by comparing the results of this model with the results of Hiatt & Grady when using the same configurations and parameters. To get the model working the parameter K_{FNA} had to be changed from $1 * 10^{-4}$ to $1 * 10^{-6}$. After the verification with the Hiatt & Grady model was done, the ASM_2N4DN was compared with the ASM1. After these verifications it was assumed that the model realistically predicts the performance of a WWTP. The process of anaerobic digestion has the largest contribution to the GHGs.

Within this model different PI anti windup controllers were implemented to see the effect of different oxygen, ammonia and nitrate concentrations on the production of GHGs. At an oxygen level below 1 mg/L the X_{ANO} are inhibited and at high O_2 concentrations the aeration gives a high total production of GHGs. The N_2O production was the most sensitive to the ammonia concentration. The nitrate concentration did not have much effect on the performance of the WWTP.

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1. Introduction

Due to the increased concern on global warming there is more awareness about emissions of greenhouse gases (GHGs) worldwide. These gases obstruct the radiation of heat from the Earth back into the atmosphere, resulting in increased temperatures on the Earth's surface. They are mainly expressed in kg CO_2. For these gases a carbon trade market is being developed that will control pollution by providing economic incentives for achieving reductions in the emissions of those gases.

There is considerable interest to determine carbon footprints of Wastewater Treatment Plants (WWTPs) with respect to greenhouse gas emissions, energy usage, energy production, and carbon credits. In order to estimate GHG emissions in a WWTP an inventory of all GHGs emitted has to be conducted and the appropriate global warming potential (GWP) for each gas has to be applied. The GWP of a GHG is the ratio of heat trapped by one unit mass of the gas compared to one unit mass of CO_2 over a specified time period (typically 100 years). The GWP values for some of the gases are listed in the next table (IPCC, 2001).

Table 1.1. The GWP of GHGs produced in WWTPs

Gas	Chemical Name	2001 IPCC GWP
Carbon Dioxide	CO_2	1
Methane	CH_4	23
Nitrous Oxide	N_2O	296

As shown in the table, the GWP varies significantly, depending on the type of gas. Therefore, a small quantity of gas emitted with a high GWP has a greater effect on the atmosphere than a gas with low GWP. For example one kilogram (kg) of N_2O emitted will have the same heat trapping potential as 296 kg of CO_2.

There are different types of models available to estimate the GHG emissions. On the one hand there are empirical static models available ((Bridle Consulting, 2007), (National Greenhouse Gas Inventory Committee, 2007) (Monteith, Sahely, MacLean, & Bagley, 2005)) that estimate the emissions as an average value for a given period. On the other hand, detailed mechanistic models that dynamically describe the behavior of activated sludge systems are available (e.g. Activated Sludge Model 1 (IAWPRC Task Group, 1986)). These models can be extended to include the GHGs as state variables.

1.1 Boundaries to estimate GHG emissions in a WWTP

There are three Scopes defined by the United Nations to look at emissions of an industrial plant. **Scope 1** includes the direct greenhouse gas emissions, "Direct GHG emissions occur from sources that are owned or controlled by the company" (The Greenhouse Gas Protocol Initiative, 2004). The CO_2 emissions from combustion of biomass are not included in this scope. **Scope 2** includes beside the direct GHG emissions from Scope 1 also the GHG emissions that occur from the use of electricity. By the Greenhouse Gas Protocol Initiative, 2004 the extra emissions are described as: “GHG emissions from the generation of purchased electricity consumed by the company”. The purchased electricity is the electricity bought by the plant or brought into the organizational boundary of the plant. The actual GHG emissions occur during electricity generation and thus not at the plant. However due to the use of electricity of the plant these emissions need to be added to the emissions of the plant according to Scope 2. For a WWTP this would include for example the emissions of the power used for aeration. **Scope 3** includes besides the GHG emissions of Scope 1 and 2, also other indirect GHG’s. This is applicable to emissions from “sources not owned or controlled by the company” (World Business Council for Sustainable Development). For WWTP this is for example the GHG emissions that occur during the production of the chemicals that are used in the WWTP.

To estimate the GHG emissions of the wastewater treatment plants (WWTP) in a comparable way the considered emissions have to be listed. The selected boundaries are from Scope3 and are listed below (Bridle Consulting, 2007):

1. CO_2 and N_2O emissions at biotreatment, endogenous respiration, BOD oxidation nitrification CO_2 credit and nitrogen removal
2. Energy use of plant, for aeration, mixing and pumping which leads to CO_2 emissions
3. Sludge digestion, biogas CH_4 and CO_2
4. Sludge disposal, truck emissions trip to reuse/disposal site, CO_2 emissions mineralization
5. Power credit by use of biogas
6. GHG emissions from chemical use

In figure 1 a WWTP is schematically displayed. The different boxes show the treatment processes. The GHGs that can be released during the treatment processes are given in the circles. The numbers in the figure correspond with the numbers of the list of boundaries. Emissions that are not taken into account are indirect emissions from employers that occur when they travel towards work, thus for example the emissions of the car that is used by an employee. This is not taken into account as it is very specific for each WWTP and will be small compared to the other sources.

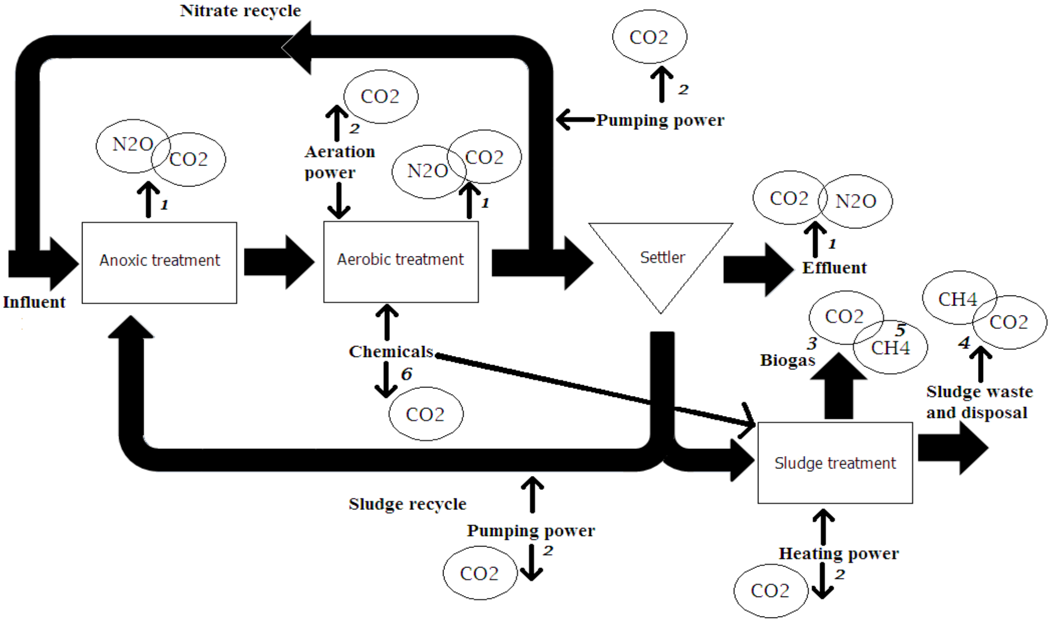

Figure 1.1. Greenhouse gas emissions of a wastewater treatment plant that are taken into account

1.2 Nitrous oxide production in wastewater treatment plants

As mentioned before the GWP of N_2O is 296 times bigger than for CO_2. This is the reason why processes that generate N_2O in a wastewater treatment plant are being investigated in the last years. The different processes in a WWTP that can produce N_2O will be presented in this chapter.

Nitrogen can occur in different forms in the environment. In figure 1.2 the different forms in which nitrogen can be formed microbially are shown.

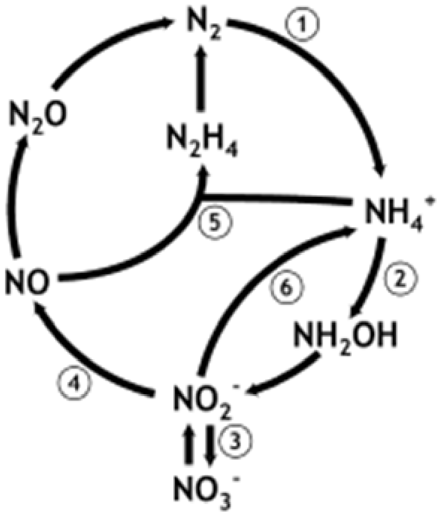

Figure 1.2. The microbial nitrogen cycle (Jetten, 2008)

Process 1 is dinitrogen fixation, process 2 is aerobic ammonium oxidation by bacteria and archaea, process 3 is aerobic nitrate oxidation, process 4 is the denitrification, process 5 is anaerobic ammonium oxidation and process 6 is dissimilatory nitrate and nitrite reduction to ammonium (Jetten, 2008). The main processes used in WWTP for the removal of nitrogen are aerobic ammonium oxidation in combination with aerobic nitrate oxidation which is also called nitrification and denitrification. There are different processes in WWTP that can produce N_2O, namely denitrification, nitrification and chemical reactions (Kampschreur, Temmink, Kleerebezem, Jetten, & van Loosdrecht, 2009)

Production of N_2O during denitrification. Denitrification is done by anoxic growth of heterotrophs. Anoxic growth occurs when there is no oxygen to use as an electron acceptor and the bacteria are able to use nitrogen instead. Denitrification is a four step process, as heterotrophic bacteria can us nitrate, nitrite, nitric oxide, and nitrous oxide as an electron acceptor. The denitrification follows the four steps according to:

$$\mathbf{NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2}$$

As can be seen N_2O is an intermediate in this process. Thus, N_2O can be produced and released to the atmosphere due to incomplete denitrification.

Production of N_2O during nitrification. Another way N_2O can be produced in a WWTP is by the bacteria that perform the nitrification process. During nitrification ammonia reacts to nitrite and then to nitrate. This is done by two different autotrophic bacteria, nitrite oxidizing and ammonia oxidizing bacteria. Autotrophic bacteria are bacteria that use a different substrate than carbon to grow on. The nitrite oxidizing bacteria use free nitrous acid as a substrate and the ammonia oxidizing bacteria use free ammonia. There are ammonia oxidizing bacteria that can produce N_2O although it is not an intermediate in the nitrification (Colliver, 2000). The process done by ammonia oxidizing bacteria in which N_2O can occur is called aerobic denitrification. This is the reverse of the nitrification of the bacteria in which the ammonia is converted into nitrite. The mechanism of this process is needs further research.

Production of N_2O due to chemical reactions. Nitrous oxide can also be produced during a chemical reaction between nitrite and hydroxylamine, NH_2OH (Cleemput, 1998). The hydroxylamine is an intermediate from the ammonia oxidizing bacteria. It is not know how large the contribution of this reaction to the total N_2O formation is. Therefore this also needs further research. For the model that should include the N_2O production during the biological treatment only the process of denitrification is included.

The objective of this work is to quantify GHG emissions in WWTPs using model-based approaches. The static model presented in Bridle Consulting, 2007 is combined with a dynamic deterministic model that describes N_2O production. These models are implemented and used for two different applications. In the first application the static model is used to quantify GHG emissions of the Benchmark plant nº2 (Jeppsson *et al.*, 2007). In a second application the deterministic model together with the static model are used to quantify the emissions of the Benchmark plant nº1 (Copp *et al.*, 2002) and to evaluate the effect of different operating conditions (i.e. dissolved oxygen levels, different nitrate levels and different ammonia levels) on the production of GHGs.

In this project first an existing static model to calculate the greenhouse gas emissions will be examined. The calculation of N_2O in that model will be replaced by a mathematical model that predicts the N_2O formation. Different existing models that include a two step nitrification and four step denitrification are compared for that. After this literature review the static model will be adjusted. The results of the Benchmark Simulation Model 2 which uses the Activated Sludge Model 1 and Anaerobic Digestion Model 1 to describe the performance of the WWTP can replace some of the calculations done in the static model. The estimated GHG production will then be compared with literature estimations. Then to replace the N_2O production calculation of the static model, one of the reviewed models with two step nitrification and four step denitrification will be adjusted. This model will then be checked and verified to ensure the performance. Finally, the effects of the concentrations of oxygen, ammonia and nitrate on the production of N_2O and the production on the GHG in total will be examined. This way the optimal conditions for minimizing the production of GHGs can be chosen.

2. The calculations of the Bridle model for the GHG production of a WWTP

Different models to calculate the greenhouse gas emissions of WWTP already exists as mentioned before in the introduction. For this project the model created by Bridle was used as this model has implemented the GHG according to the boundaries chosen in the chapter 1.1.

Bridle has distinguished five parts where greenhouse gases are emitted, namely the biotreatment, the sludge treatment, the chemical usage, the power consumption and the biogas produced (Bridle Consulting, 2007). For each part it calculates the greenhouse gases that are emitted in the unit kg CO_2/day. Here for measured influents and effluents are used, the performance of a sludge digester is estimated and a large number of parameters to simulate the biological processes are determined. Then with formulas and conversion factors the amount of kg CO_2 emitted per day from a wastewater treatment plant is estimated. The inputs used for this estimation can be seen in figure 2.1.

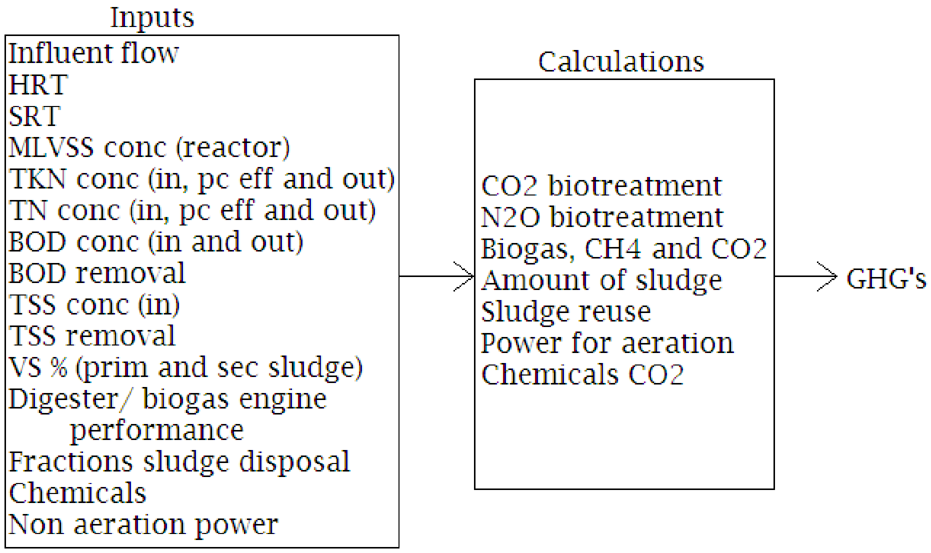

Figure 2.1. The schematic overview of the inputs used in the Bridle model to calculate the GHG according to different processes.

In Fig. 2 the following abbreviations are used:

HRT is the hydraulic retention time
SRT is the sludge retention time
MLVSS are the mixed liquor volatile suspended solids
TKN is the total Kjeldahl nitrogen, which is the ammonia and ammonium together
TN is the total nitrogen which is nitrate, nitrite with the TKN
BOD is the biological oxygen demand
TSS are the total suspended solids
VS are the volatile solids

Bridle has created an Excel sheet to perform the calculations. In this Excel sheet the calculations are applied onto three case studies. The sheet has implemented two models to calculate the emissions, namely the comprehensive model and the WSAA model. The WSAA model is created by the Water Services Association of Australia and the comprehensive model by Bridle Consulting. There are two big differences between those models. The first difference is the way the emissions of the biotreatment are calculated. The WSAA model only takes the N_2O emissions into account and converts it to CO_2 with the global warming potential. In the comprehensive model the biotreatment is divided in three processes where GHG production can take place, namely endogenous biomass decay, BOD oxidation, and nitrogen removal. In those processes organic matter is oxidized which results in CO_2 emissions. The other difference between the models is that the comprehensive model also includes the emissions due to the use of chemicals. Looking at the boundaries that are chosen for the assessment of the greenhouse gases in the previous chapter 1.1; the comprehensive model is a better choice to use instead of the WSAA model. The comprehensive model will be named the Bridle model in the rest of the thesis.

In the following subchapters the different calculations used by Bridle are explained. It is divided over 6 subchapters, biotreatment, sludge digestion, sludge reuse, chemical usage, power consumption and biogas usage. The different subchapters are the processes of a WWTP where GHG emissions occur.

2.1 GHG calculations of Bridle model process biotreatment

The biotreatment of the wastewater is performed through three processes, namely endogenous decay, the BOD oxidation and the nitrogen removal, as mentioned before. In these processes CO_2 is produced, consumed, and N_2O is produced.

The Bridle model calculates the biomass decayed by:

$$\mathbf{X_{decayed} = Q_{influent} * HRT * MLVSS * k_D}$$

$X_{decayed}$ is the biomass decayed per day	[kgVSS/day]
$Q_{influent}$ is the average daily flow	[m^3/day]
HRT is the hydraulic retention time	[days]
MLVSS is the concentration of mixed liquid volatile suspended solids	[kg/m^3]
k_D is the endogenous decay coefficient	[1/day]

The average daily flow, hydraulic retention time and the MLVSS are measured. The endogenous decay coefficient comes from Black & Veatch as included in the Bridle model.

To go from the biomass decayed to the CO_2 produced the chemical reaction describing the biomass decay is needed. The elemental composition of biomass is $C_5H_7O_2N$ (Bridle Consulting, 2007).

$$\mathbf{C_5H_7O_2N + 5\ O_2 \rightarrow 5\ CO_2 + 2\ H_2O + NH_3}$$

The biomass to CO_2 ratio is 113 : 5*44 which equals 1 : 1.947. This means that for the decay of one kg of biomass 1.947 kg of CO_2 is produced.

$$CO_{2,decay} = X_{decayed} * 1{,}947$$

Also, during biomass production CO_2 is emitted. The Bridle model first calculates the observed biomass yield.

$$Y_{obs} = Y / (1 + k_D * SRT)$$

Y_{obs} is the observed biomass yield	[kg VSS/kg $BOD_{removed}$]
Y is yield set in the Bridle model	[kg VSS/kg $BOD_{removed}$]
SRT is the sludge retention time given in	[days]

The net biomass produced is calculated from:

$$X_{net,produced} = Y_{obs} * BOD_{ox}$$

$X_{net,produced}$ is the net biomass produced per day	[kg VSS/day]

The oxidized BOD is calculated from:

$$BOD_{ox} = Q_{influent} * ((100\%-BOD_{rem})/100\% * BOD_{influent} - BOD_{effluent})$$

BOD_{ox} is the BOD oxidized by the biomass	[kg BOD/day]
BOD_{rem} is the BOD removal efficiency of the primary clarifier	[%]
$BOD_{influent}$ is the influent BOD	[kg BOD/m^3]
$BOD_{effluent}$ is the effluent BOD	[kg BOD/m^3]

With the net biomass produced the rate of oxygen used can be calculated:

$$R_{O2} = BOD_{ox} / (f) - 1{,}42 * X_{net,produced}$$

R_{O2} is the rate at which oxygen is used by the biomass	[kg O_2/day]
f is the BOD_5_BOD_u ratio, a fraction set in the Bridle model	[-]

When the rate of oxygen used is known the amount of CO_2 produced per day can be calculated.

$$CO_{2,\ BODox} = R_{O2} * CO_2fromBODox$$

$CO_{2,\ BODox}$ is the amount of CO_2 produced per day by BOD oxidation	[kg CO_2/day]

CO_2fromBODox is a conversion factor which comes from the chemical reaction in which $C_{10}H_{19}O_3N$ is the elemental composition of BOD:

$$2\ C_{10}H_{19}O_3N + 25\ O_2 \rightarrow 20\ CO_2 + 16\ H_2O + 2\ NH_3$$

The ratio between O_2 and CO_2 is then 25 * 32 : 20 * 44 which is 1 : 1.1. Thus for 1 kg of O_2 1.1 kg of CO_2 is produced.

The last step in the biotreatment part is the nitrogen removal. By removing ammonia, CO_2 is consumed leading to a CO_2 credit. When nitrate is denitrified CO_2 and N_2O are emitted.

The amount of N in the biomass is calculated from the elemental composition. The molar weight of N is 14 and that of biomass 113 as seen above. Thus the amount of N incorporated in the net produced biomass is:

$$N_{biomass} = X_{net,produced} * 14/113$$

$N_{biomass}$ is the amount of nitrogen in the biomass [kg N/day]

The amount of ammonia oxidized is calculated by the following equation:

$$NH_{ox} = Q_{influent} * (TKN_{p.c.\ effluent} - TKN_{effluent}) - N_{biomass}$$

$TKN_{p.c.\ effluent}$ is the total nitrogen in the effluent of the primary clarifier [kg N/m^3]
$TKN_{effluent}$ is the total nitrogen in the effluent [kg N/m^3]

The CO_2 credit from the ammonia that is oxidized is calculated with:

$$CO_{2,\ credit} = NH_{ox} * CO_{2,\ consumed}$$

The $CO_{2,\ consumed}$ is set by stoichiometry

$$20\ CO_2 + 14\ NH_4^+ \leftrightarrow 10\ NO_3^- + 4\ C_5H_7O_2N + 24H^+ + 2H_2O$$

The CO_2 to N ratio is 20 * 44 : 14 * 14 which leads to 4.49 : 1 and thus the amount of $CO_{2,consumed}$ is 4,49 kg per kg of N nitrified.

The amount of CO_2 formed by biotreatment is calculated by first calculating the amount of nitrogen removed.

$$N_{removed} = Q_{influent} * (TN_{p.c.\ effluent} - TN_{effluent}) - N_{biomass}$$

$N_{removed}$ is the nitrogen removed by the bacteria [kg N/day]
$TN_{p.c.\ effluent}$ is the total nitrogen in the effluent of the primary clarifier [kg/m^3]
$TN_{effluent}$ is the total nitrogen that leaves the plant [kg/m^3]

With stoichiometry the amount of CO_2 that is formed during nitrogen removal can be calculated, assuming methanol is the carbon source.

$$6\ NO_3^- + 5\ CH_3OH \leftrightarrow 3\ N_2 + 5\ CO_2 + 7\ H_2O + 6\ OH^-$$

The N to CO_2 ratio is 6 * 14 : 5 * 44, which equals 1 : 2.62. However this is not included in the calculation because the denitrifiers use BOD as a carbon source. So, the calculation of the CO_2 produced is already included in the calculation for BOD oxidation.

The N_2O emitted during nitrogen removal is calculated with the following equation:

$$N_2O_{emission} = Q_{influent} * TN_{p.c.\ effluent} * R_{N2O,\ generation}$$

$N_2O_{emission}$ is the amount of N_2O emitted [kg N_2O /day]
$R_{N2O,\ generation}$ is the conversion factor of N in the feed to N_2O in kg N_2O/ kg N feed, the value comes from data of Lee Walker as included in the Bridle model. This factor has to be measured for each wastewater treatment plant.

With the global warming potential as calculated by the IPCC, the CO_2 equivalent of N_2O can be calculated:

$$CO_{2,\ equivalent} = N_2O_{emission} * GWP_{N2O}$$

GWP_{N2O} is the global warming potential of N_2O (IPCC, 2001) [kg CO_2/ kg N_2O]
$CO_{2,equivalent}$ is the equivalent of CO_2 of the N_2O emissions in [kg CO_2/day]

The total amount of CO_2 emissions in kgCO_2/day is:

$$\mathbf{CO_{2,biotreatment} = CO_{2,decay} + CO_{2,BODox} - CO_{2,credit} + CO_{2,equivalent}.}$$

2.2 GHG calculations of Bridle model process sludge digestion

After the calculation of the CO_2 produced in the biotreatment during the endogenous decay, BOD oxidation and nitrogen removal the CO_2 produced during the sludge treatment is calculated. The sludge treatment process is divided in two parts, the digestion part which is explained in this subchapter and the sludge reuse part which will be explained in the next subchapter.

With the digestion of sludge CO_2 and CH_4 are emitted. The Bridle model starts with calculating the amount of sludge formed in the wastewater treatment plant. The amount of sludge that is digested can then be calculated and from that the biogas that is formed is calculated. With the amount of biogas known the production of CO_2 and CH_4 can be calculated.

$$\mathbf{Sludge_{primary\ mass} = Q_{influent} * TSS_{influent} * TSS_{rem}}$$

$Sludge_{primary\ mass}$ is the amount of sludge. Primary sludge comes from the particles that are in the influent of the wastewater treatment plant. [kg sludge/day]
$TSS_{influent}$ is the amount of total suspended solids that are in the influent of the wastewater treatment plant [kg/m^3]
TSS_{rem} is the fraction of total suspended solids that is removed [-]

The secondary sludge from the biomass formed is then calculated

$$\mathbf{Sludge_{secondary\ mass} = X_{net,produced} / VS_{secondary\ sludge} - Q_{influent} * TSS_{effluent} + TSS_{influent} * Q_{influent} * (1-TSS_{rem}) * 0.27}$$

$Sludge_{secondary\ mass}$ is the sludge [kg/day]
$VS_{secondary\ sludge}$ is a parameter describing the VSS fraction in the secondary sludge [-]
$TSS_{effluent}$ is the amount of total suspended solids in the effluent [kg TSS/m^3]
0.27 is the fraction of the sludge that is not recycled. [-]

The sludge that goes to the digester, $Sludge_{total}$ is the primary sludge and the secondary sludge together. Of the total sludge the VSS present is calculated from:

$$\mathbf{VS_{combined\ sludge} = (Sludge_{primary\ mass} * VS_{primary\ sludge} + Sludge_{secondary\ mass} * VS_{secondary\ sludge}) / Sludge_{total}}$$

$VS_{combined\ sludge}$ is the VS present in the sludge expressed as fraction of TS [-]
$VS_{primary\ sludge}$ is the fraction of VSS in the primary sludge [-]

The VS that goes to the digestion is [kg VS/day]

$$\mathbf{VS_{digestion} = Sludge_{total} * VS_{combined\ sludge}}$$

The fraction of $VS_{digestion}$ that is destroyed is

$$\mathbf{VS_{destroyed} = VS_{digestion} * VS_{destruction}}$$

$VS_{destroyed}$ is the part of VS that is destroyed	[kg/day]
$VS_{destruction}$ is the fraction of the VS that is destroyed	[-]

The sludge that is digested is calculated

$$\mathbf{Sludge_{digested} = Sludge_{total} – VS_{destroyed}}$$

$Sludge_{digested}$ is the digested sludge	[kg/day]
Then the biogas mass can be calculated	[kg/day]

$$\mathbf{Biogas_{mass} = Sludge_{total} - Sludge_{digested}}$$

To go from sludge to biogas a conversion factor should be used. Bridle assumes that 1 kg of sludge equals 1 kg of biogas.

The methane concentration in mass percentage is then calculated

$$\mathbf{Conc_{CH4\ biogas} = (100 * Biogas_{CH4\ content} * MW_{CH4} / MV) / (Biogas_{CH4\ content} * MW_{CH4} / MV + (100 - Biogas_{CH4\ content}) * MW_{CO2} / MV)}$$

$Conc_{CH4\ biogas}$ is the mass percentage of methane in the biogas	[%]
$Biogas_{CH4\ content}$ is the volume percentage of methane in the biogas	[%]
MW_{CH4} is the molar weight of methane	[g/mole]
MV is the volume of 1 mole at a temperature of 20 °C	[m^3/mole]
MW_{CO2} is the molar weight of carbon dioxide	[g/mole]

With the mass percentage of methane known the amount of methane gas can be calculated [kg CH_4/day]

$$\mathbf{Biogas_{CH4} = Biogas_{mass} * Conc_{CH4\ biogas}/100\ \%}$$

Then the CO_2 gas is assumed to be the rest of the biogas, thus

$$\mathbf{Biogas_{CO2} = Biogas_{mass} – Biogas_{CH4}}$$

$Biogas_{CO2}$ is the amount of CO_2	[kg CO_2/day]

In the Bridle model a part of the biogas is combusted. Hereby CO_2 will be emitted as well

$$\mathbf{CO_{2\ combustion} = (Biogas_{boiler} + Biogas_{flare}) * (Biogas_{CO2} + Biogas_{CH4} * MW_{CO2}/MW_{CH4}) /100\%}$$

$CO_{2\ combustion}$ is the CO_2 that is produced during combustion	[kg CO_2/day]
$Biogas_{boiler}$ is a percentage of the biogas volume that goes to the boiler	[%]
$Biogas_{flare}$ is a percentage of the biogas volume that goes to the flare	[%]

Another part is going to an engine

$$\mathbf{CO_{2\,engine} = Biogas_{engine} * (Biogas_{CO2} + Biogas_{CH4} * MW_{CO2}/MW_{CH4})\ /100\%}$$

$CO_{2\,\text{engine}}$ is the amount of CO_2 that is produced the engine [kg CO_2/day]
$\text{Biogas}_{\text{engine}}$ is a percentage of the biogas volume that goes to the engine [%]

Bridle also assumes that a part of the biogas is leaked.

$$\mathbf{CO_{2\,leak} = Biogas_{leak} * (Biogas_{CO2} + Biogas_{CH4} * GWP_{CH4})\ /100\%}$$

$CO_{2\,\text{leak}}$ is the amount of CO_2 that is assumed to be leaking [kg CO_2/day]
$\text{Biogas}_{\text{leak}}$ is a percentage of the volume that is assumed to leak [%]
GWP_{CH4} is the global warming potential of methane, 23 (IPCC, 2001) [kg CO_2/kg CH_4]

2.3 GHG calculations of Bridle model process sludge reuse

After the treatment of the sludge, the sludge can be reused in different ways. The Bridle model gives four different options, reuse for agriculture, reuse for composting, reuse for forestry and reuse for other options. For each wastewater treatment plant different fractions of the reuse of the sludge may be given. First, the amount of sludge that can be reused needs to be calculated. Then, the amount of carbon in the sludge is needed, to calculate how much carbon will be converted to CO_2.

The fraction of VS in the digested sludge is: [-]

$$\mathbf{Fraction_{VSS,digested\ sludge} = (VS_{digestion} – VS_{destroyed})\ /\ Sludge_{digested}}$$

Then the carbon in the sludge is evaluated from an empirical relationship to calculate how much CO_2 can be formed.

$$\mathbf{C_{sludge} = 0.3962 * VS_{digested\ sludge} * 100\% + 9.4548}$$

C_{sludge} is the amount of carbon in sludge [%]
The values 0.3962 and 9.4548 are from the Bridle consulting data

With the amount of carbon in the sludge known the CO_2 emissions from the different reuse options can be calculated:

$$\mathbf{CO_{2\ carbonsludge\ agri} = MW_{CO2}/MW_{C} * C_{sludge} * Sludge_{digested} * Carbon\ mineralization * Fraction_{agriculture}\ /\ 1000\,000}$$

$CO_{2\,\text{carbonsludge agri}}$ is the CO_2 emissions through reuse in agriculture [kg CO_2/day]
MW_C is the molar weight of carbon [g/mol]
Carbon mineralization is the sludge carbon that is mineralized to CO_2 [%]
$\text{Fraction}_{\text{agriculture}}$ is the fraction of sludge that is reused for agriculture purposes [-]

The sludge needs to be transported from the wastewater treatment plant to the agricultural site. Trucks are used to transport the sludge and CO_2 is emitted with the combustion of the fuel.

$$\mathbf{CO_{2\,trucking\ agri} = Sludge_{digested\ mass} * Fraction_{agriculture} * Trucking\ emissions * distance_{agriculture\ site} * 2 * 100 / (V_{truck} * solids_{cake} * 100\,000)}$$

$CO_{2\ \mathrm{trucking\ agri}}$ is the amount of CO_2 emissions from truck use to the agriculture site and back [kg CO_2/day]
Trucking emissions is the amount of kg CO_2 emitted per kilometer [kg CO_2/km]
Distance$_{\mathrm{agriculture\ site}}$ is the distance of the wastewater treatment plant to the agriculture site [km]
V_{truck} is the volume of sludge the truck can transport [m^3]
Solids$_{\mathrm{cake}}$ is the percentage of the solids in the sludge [%]
The extra 1000 by which the sludge$_{\mathrm{digested\ mass}}$ is divided is the density of the sludge [kg/m3]

These calculations are also performed for the other options of reuse

$$\mathbf{CO_{2\,carbonsludge\ composting} = MW_{CO2}/MW_C * C_{sludge} * Sludge_{digested} * Carbon\ mineralization * Fraction_{composting} / 1000\,000}$$

$CO_{2\ \mathrm{carbonsludge\ composting}}$ is the amount of CO_2 emitted by composting sludge [kg CO_2/day]
Fraction$_{\mathrm{composting}}$ is the fraction of sludge that is reused for composting purposes [-]

$$\mathbf{CO_{2\,trucking\ composting} = Sludge_{digested\ mass} * Fraction_{composting} * Trucking\ emissions * distance_{composting\ site} * 2 * 100 / (V_{truck} * solids_{cake} * 100\,000)}$$

$CO_{2\ \mathrm{trucking\ composting}}$ is the amount of CO_2 emissions from truck use to the composting site and back [kg CO_2/day]
Distance$_{\mathrm{composting\ site}}$ is the distance of the wastewater treatment plant to the composting site [km]

$$\mathbf{CO_{2\,carbonsludge\ forestry} = MW_{CO2}/MW_C * C_{sludge} * Sludge_{digested} * Carbon\ mineralization * Fraction_{forestry} / 1000\,000}$$

$CO_{2\ \mathrm{carbonsludge\ forestry}}$ is the amount CO_2 emitted by forestry [kg CO_2/day]
Fraction$_{\mathrm{forestry}}$ is the fraction of sludge that is reused for forestry purposes [-]

$$\mathbf{CO_{2\,trucking\ forestry} = Sludge_{digested\ mass} * Fraction_{forestry} * Trucking\ emissions * distance_{forestry\ site} * 2 * 100 / (V_{truck} * solids_{cake} * 100\,000)}$$

$CO_{2\ \mathrm{trucking\ forestry}}$ is the amount of CO_2 emissions from truck use to the forestry site and back [kg CO_2/day]
Distance$_{\mathrm{forestry\ site}}$ is the distance of the wastewater treatment plant to the forestry site [km]

$$\mathbf{CO_{2\,carbonsludge\ other\ reuse} = MW_{CO2}/MW_C * C_{sludge} * Sludge_{digested} * Carbon\ mineralization * Fraction_{other\ reuse} / 1000\,000}$$

$CO_{2\ \mathrm{carbonsludge\ other\ reuse}}$ is the amount of CO_2 emitted by reusing the sludge for other purposes [kg CO_2/day]

$\text{Fraction}_{\text{other reuse}}$ is the fraction of sludge that is reused for other purposes [-]

$$\mathbf{CO_{2\ trucking\ other\ reuse} = Sludge_{digested\ mass} * Fraction_{other\ reuse} * Trucking\ emissions * distance_{other\ reuse\ site} * 2 * 100 / (V_{truck} * solids_{cake} * 100\,000)}$$

$\text{CO}_{2\text{ trucking other reuse}}$ is the amount of CO_2 emissions from truck use to the other reuse site and back [kg CO_2/day]
$\text{Distance}_{\text{other reuse site}}$ is the distance of the wastewater treatment plant to the other reuse site [km]

The total CO_2 emissions from the sludge process treatment is

$$\mathbf{CO_{2\ total\ sludge} = CO_{2\ combustion} + CO_{2\ engine} + CO_{2\ leak} + CO_{2\ carbonsludge\ agri} + CO_{2\ trucking\ agri} + CO_{2\ carbonsludge\ composting} + CO_{2\ trucking\ composting} + CO_{2\ carbonsludge\ forestry} + CO_{2\ trucking\ forestry} + CO_{2\ carbonsludge\ other\ reuse} + CO_{2\ trucking\ other\ reuse}}$$

2.4 GHG calculations of Bridle model during chemical usage

The scope used for the boundaries included besides the offsite emissions due to sludge reuse as mentioned before also the offsite emissions due to the use of chemical. When chemicals are added to the wastewater treatment plant, they have an impact on the CO_2 emissions. With the production of the chemicals CO_2 is emitted. This is thus not done at the WWTP but included in the emissions because of the boundaries chosen. The Bridle model calculates the CO_2 emissions for five different chemicals: lime, chlorine, caustic, hypochlorite, and polymers.

$$\mathbf{CO_{2\ lime} = Lime_{added} * Sludge_{total} * Lime_{CO2} / 1000}$$

$\text{CO}_{2\text{ lime}}$ is the CO_2 emitted because of the use of lime [kg CO_2/day]
$\text{Lime}_{\text{added}}$ is the amount of lime added to the wastewater treatment plant [kg lime/kg dry solids]
Lime_{CO2} is the amount of kg CO_2 emitted when a tonne of lime is used [kg CO_2/tonne lime]

For chlorine the amount of CO_2 emitted is calculated by:

$$\mathbf{CO_{2\ chlorine} = Chlorine_{use} * Chlorine_{CO2} / 1000}$$

$\text{CO}_{2\text{ chlorine}}$ is the CO_2 emitted because of the use of chlorine [kg CO_2/day]
$\text{Chlorine}_{\text{use}}$ is the amount of chlorine used [kg chlorine/day]
$\text{Chlorine}_{\text{CO2}}$ is the amount of kg CO_2 emitted when a tonne of chlorine is used [kg CO_2/tonne chlorine]

For the chemicals caustic and hypochlorite the calculations are the same as for chlorine but different parameters are used.

The CO_2 emissions due to polymer addition are calculated differently as the chemical is used in the sludge.

$$\mathbf{CO_{2\ polymer} = Polymer_{added} * Sludge_{digested\ mass} * Polymer_{CO2} / 1000\,000}$$

$\text{CO}_{2\text{ polymer}}$ is the CO_2 emitted because of the use of polymers [kg CO_2/day]

$Polymer_{added}$ is the amount of polymer added to the wastewater treatment plant
[kg polymer/kg dry solids]
$Polymer_{CO2}$ is the amount of kg CO_2 emitted when a tonne of polymer is used
[kg CO_2/tonne polymer]

2.5 GHG calculations of Bridle model for power consumption

The offsite emissions for the use of power are also included in the boundaries. The Bridle model only calculates the amount of energy needed for the aeration. The non aeration power is quantifed in the Bridle model. The amount of kW is converted in CO_2 with a conversion factor. To calculate the aeration power, the amount of oxygen needed in the tank is calculated.

$$\mathbf{O_{2\ respiration} = X_{decayed} * O_{2\ VSS}}$$

$O_{2\ respiration}$ is the amount of O_2 needed for the respiration of the decayed biomass [kg O_2]
$O_{2\ VSS}$ is the stoichiometry factor of O_2 per kg VSS [kg O_2/kg VSS]

$\mathbf{C_5H_7O_2N + 5\ O_2 \rightarrow 5\ CO_2 + 2\ H_2O + NH_3}$
113 : 5*32 equals 1 : 1.416.

The oxygen needed for BOD oxidation is already calculated in the biotreatment part. Next, also the oxygen needed for nitrification is calculated.

$$\mathbf{O_{2\ nitrification} = NH_{ox} * O_{2NH}}$$

$O_{2\ nitrification}$ is the amount of O_2 needed for the nitrification [kg O_2/day]
NH_{ox} is the amount of ammonia oxidized [kg N/day]
O_{2NH} is the stoichiometric factor for oxygen needed per ammonia oxidized [kg O_2/kg N]

$$\mathbf{NH_4^+ + 1.83O_2 + 1.98HCO_3^- \rightarrow 0.021C_5H_7NO_2 + 1.041H_2O + 0.98\ NO_3^- + 1.88H_2CO_3}$$

As can be seen from the reaction, the amount of kg O_2 consumed per kg N nitrified is 1.83 * 32 : 14 which leads to 4.18 kg O_2/kg N. However, according to Bridle the amount of O_2 consumed is set to be 4.32 and therefore that value is used.

There is also an oxygen credit from denitrification to consider:

$$\mathbf{O_{2\ denitrification} = N_{removed} * O_{2\ N}}$$

$O_{2\ denitrification}$ is the amount of O_2 consumed in denitrification [kg O_2/day]
$O_{2\ N}$ is the stoichiometric factor of the oxygen consumed per nitrogen [kg O_2/kg N]
The total O_2 needed is [kg O_2/day]

$$\mathbf{O_{2,\ total} = O_{2\ respiration} + O_{2\ nitrification} - O_{2\ denitrification}}$$

The amount of oxygen the organisms need is not the same as the amount of oxygen supplied to the tanks. More oxygen is supplied:

$$\mathbf{O_{2\ sat\ coef} = 51.6 * C_{s20} / (31.6 + T)}$$

$O_{2\,\text{sat coef}}$ is the oxygen saturation coefficient	[mg/l]
C_{s20} is the O_2 saturation coefficient for pure water at 20°C	[mg/l]
T is the temperature	[°C]

$$\textbf{Field oxygen transfer coefficient} = \text{SOTR} * \alpha * (\beta * O_{2\,\text{sat coef}} - \text{Conc}_{O2\,\text{in basin}}) * C_{s20}$$

SOTR is standard oxygen transfer rate	[kg O_2/kWh]
α is an aeration efficiency	[-]
β is a correction factor for the oxygen solubility	[-]
$\text{Conc}_{O2\,\text{in basin}}$ is the concentration of oxygen in the tank	[mg/L]

The amount of power needed is then calculated from:

$$P_{\text{aeration}} = O_{2\,\text{total}} / (\text{field oxygen transfer coefficient} * 24)$$

P_{aeration} is the power needed for the aeration	[kW]

With the amount of power needed known the amount of CO_2 emissions can be calculated. The power used in the case studies of Bridle comes from a coal-fired power station with an emission of 0.94 kg CO_2/kWh. Coal is the most polluting fuel that can be used for the production of electricity. In the papers of Bani Shahabadi *et al.*, 2009 and Keller & Hartley, 2003 a same value can be found for the kg CO_2 equivalent/kWh of a coal fired power station. The paper of Bani Shahabadi *et al.*, 2009 also conversion factors for different types of energy generation can be found.

$$CO_{2\,\text{aeration}} = P_{\text{aeration}} * CO_{2\,\text{kWh}} * 24$$

$CO_{2\,\text{aeration}}$ is the amount of CO_2 that is emitted by using aeration power	[kg CO_2/day]
$CO_{2\,\text{kWh}}$ is the conversion factor	[kg CO_2/kWh]

Power is also used for other purposes than aeration. In the Bridle model this is given with the input data.

$$CO_{2\,\text{non aeration}} = P_{\text{non aeration}} * CO_{2\,\text{kWh}} * 24$$

$CO_{2\,\text{non aeration}}$ is the CO_2 that is emitted by using power for other purposes than aeration	[kg CO_2/ day]
$P_{\text{non aeration}}$ is the power used for other purposes than aeration	[kW]

The total CO_2 emission through power use is then the amount of $CO_{2\,\text{aeration}}$ plus the amount of the $CO_{2\,\text{non aeration}}$.

2.6 GHG calculations of Bridle model for biogas usage

Besides CO_2 production also CO_2 credit is calculated in the model. By using the biogas created during the sludge digestion a CO_2 credit can be gained. The biogas can be used to generate power instead of getting the power from the grid. To calculate the amount of power that can be generated with the formed biogas, the gross calorific value needs to be calculated.

The gross calorific value of the combined sludge is given by the equation provided in the Bridle model:

$$\mathbf{GCV_{combined\ sludge} = VS_{combined\ sludge} * 0.263 - 1.535}$$

$GCV_{combined\ sludge}$ is the gross calorific value of the combined sludge [MJ/kg]
The numbers 0.263 – 1.535 come from Bridle Consulting Data as mentioned in the Bridle model.

The gross calorific value of the digested sludge is [MJ/kg]

$$\mathbf{GCV_{digested\ sludge} = VS_{digested\ sludge} * 0.263 - 1.535}$$

The amount of power that can be generated is then calculated from:

$$\mathbf{P_{generated} = (Sludge_{total} * GCV_{combined\ sludge} - Sludge_{digested} * GCV_{digested\ sludge}) * 11.57 * efficiency_{gas\ engine} * Biogas_{engine} /(100*1000)}$$

$P_{generated}$ is the amount of power that can be generated [kW]
$Efficiency_{gas\ engine}$ is the efficiency of the gas engine [%]

With the power generated the amount of potential renewable energy can be calculated

$$\mathbf{REC = P_{generated} *24}$$

The CO_2 credit from using the biogas is [kg CO_2/day]

$$\mathbf{CO_{2\ credit\ biogas} = P_{generated} * CO_{2kWh} * 24}$$

3. The implementation of two step nitrification and four step denitrification in the mathematical model ASM1

As mentioned in the introduction the mathematical models that predict the performance of a WWTP have not included the production of N_2O. The nitrification and denitrification are included both as a one step process. Nitrification has two steps that are done by two autotrophic bacteria and denitrification has four steps done by heterotrophic bacteria. To predict realistically the production of N_2O with a mathematical model, the two step nitrification and four step nitrification should be included. This model can then replace the calculations in the Bridle model as can be seen in figure 3.1.

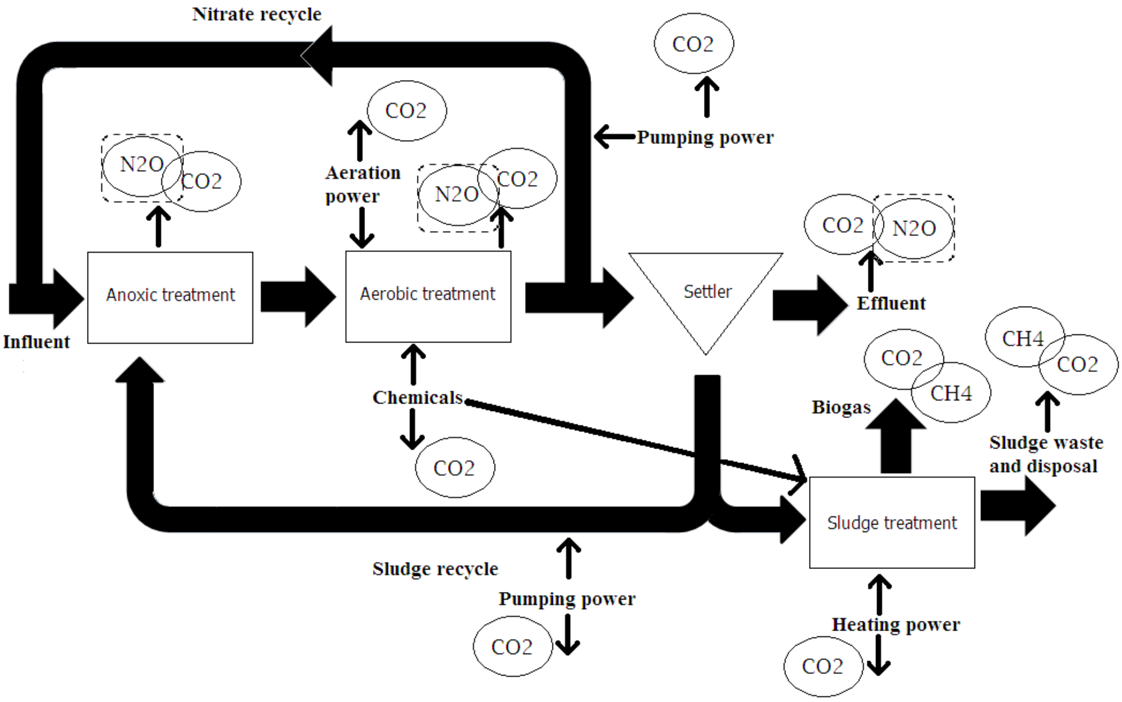

Figure 3.1. The replacement of the two step nitrification, four step denitrification model in the calculations for the GHG's of Bridle indicated in the dotted boxes.

In this chapter first the mathematical model Activated Sludge Model No. 1 will be explained. Then a comparison will be made of different models with two step nitrification and four step denitrification. Finally a method to check a model will be described.

3.1 The Activated Sludge Model No. 1

The Activated Sludge Model No. 1 (ASM1) was designed to have a consensus on a model to use for the design and operation of biological wastewater treatment plants (IAWPRC Task Group, 1986). This model is simple but nevertheless it also realistically predicts the performance of a single sludge system, which carries out carbon oxidation, nitrification and denitrification.

The model is based on mass balances. The basic mass balance is

Input – Output + Reaction = Accumulation

Input and Output are transportation terms and the Reaction term is in the stoichiometric matrix which is also called Petersen matrix. An example of the Petersen matrix can be seen in table 3.1. The Petersen matrix consists of different rows and columns. The different rows represent the processes that take place in the wastewater treatment plant, like in the example Growth and Decay. The different columns represent the components that are in the wastewater treatment plant and that are of importance in the processes, for example X_{OHO}. Via stoichiometry the components are linked to a process, as can be seen in the following reaction:

$$\mathbf{a\ O_2 + b\ NH_3 + c\ CO_2 \rightarrow d\ NO_3^- + 1\ X_{OHO} + e\ H^+}$$

The letters a, b, c, d, and e are the stoichiometric parameters.

When setting up a matrix, as shown in table 3.1, the first step is to identify the relevant components, the state variables for example the heterotrophic biomass X_{OHO} and substrate S_B. These components are named via a standard notation. Soluble components have the symbol S and insoluble components have the symbol X. The subscripts are used to specify the component. According to Corominas *et al.* the subscripts are as follow. The first symbol for a subscript that can be given is a symbol for the degradability of the component. There are three different symbols to describe the degradability, B for biodegradable, U for undegradable and A for abiotically degradable. The next subscript that can be added to the component is a symbol for organic or inorganic matter, Org or Ig. The last symbol that can be added is to specify the name of the component. For example dissolved oxygen this is S_{O2} and for inert particulate organic material X_U. In the Petersen matrix the components have the index *i.* The components are represented in the columns in the middle of the matrix.

The second step in setting up the Petersen matrix is to identify the occurring processes, for example heterotrophic biomass growth. These processes are listed in the leftmost column and are applicable to the row it is in. The processes have the index *j*, thus for growth it is 1 and decay 2. The rate of the process is in the rightmost column of the matrix in the same row and is denoted by ρ_j, for growth this is $(\mu_{max} * S_B)/ (K_{SB} + S_B) * X_{OHO}$. The kinetic parameters that are used in the rates are defined below the table.

Finally, the elements within the matrix describe the relationship between the components in a process. When the element has a negative value the component in the column is consumed and when it has a positive value the component is produced. Looking at the process growth the component X_{OHO} has the value 1, which indicates that the component is formed during that process. Component S_B has a value of -1/Y and is thus consumed during the process. The elements are denoted by denoted by ν_{ij} and made of the comprised stoichiometry coefficients. These coefficients are simplified by working in constituent units, COD. The stoichiometric parameters are also defined below the table.

The mass balance of a component without the transport can then be found by summing the products of the stoichiometric coefficients and the process rates. For the heterotrophic biomass X_{OHO} this is then:

$$\mathbf{dX_{OHO}/dt = 1 * (\mu_{max} * S_B)/ (K_{SB} + S_B) * X_{OHO} \ \ -1* b* X_{OHO}}$$

This is also described in the row of observed conversion rates.

Table 3.1. Petersen Matrix for heterotrophic biomass growth and decay

Component → *i* *j* Process ↓	1 X_{OHO}	2 $S_{B,Org}$	3 S_{O2}	Process rate, ρ_j [$ML^{-3}T^{-1}$]
1 Growth	1	-1/Y	-(1-Y)/Y	$(\mu_{max} * S_{B,Org})/ (K_{SB} + S_{B,Org}) * X_{OHO}$
2 Decay	-1		-1	$b* X_{OHO}$
Observed Conversion Rates $ML^{-3}T^{-1}$	$r_i = \sum_j r_{ij} = \sum_j v_{ij}\rho_j$			
	Biomass [$M(COD)L^{-3}$]	Substrate [$M(COD)L^{-3}$]	Oxygen (negative COD) [$M(-COD)L^{-3}$]	

The symbols used in table 3.1 are:

Y is the true growth yield,
μ_{max} is the maximum specific growth rate,
K_{SB} is half saturation constant,
b is the specific decay rate,
The stoichiometric parameters can be found in the columns in the middle and the kinetic parameters can be found in the last column with the process rates.

The advantages of presenting the ASM1 in a Petersen Matrix compared to a state space model is that it easily shows which state variables play a role in a process and in which process a state variable is consumed or produced. Also in the Petersen Matrix the rates can be checked to see if there are errors in it. This is done with the continuity check which is explained in section 3.3. An disadvantage of the Petersen Matrix is that it is not possible to design a controller or observer easily. For systems represented in a state space model structure many controller and observer design methods are available in the literature. For the ASM1 the Petersen Matrix is a better form of notation as it is important to see the interactions of the state variables in the different processes. The Petersen Matrix only shows the reactions and not the transport thus for the mass balance of a state variable the transport should be taken into account as was stated before. In a state space model representation this is included. To go from the Petersen Matrix to the state space model the equations in the column of a state variable should be summed up and the transport terms should be included. Thus to go from the Petersen Matrix to a state space model could be easily done, if the transportation rates are known.

3.2 The comparison between different models with two step nitrification and four step denitrification

The Activated Sludge Model no. 1 (ASM1) has eight processes and thirteen components. In these processes the nitrification and denitrification are included as a one step process as was mentioned before. In this chapter different mathematical models based on ASM with multiple nitrification and denitrification steps will be compared.

There are different models with the extension of the multiply nitrification and denitrification steps indentified, namely the models described in the papers of Hiatt & Grady (2008), von Schulthess & Gujer (1996), and Alinsafi (2008). In the paper of Sin *et al.* (2008) different models that made an extension with nitrification and denitrification are described. Kaelin *et al.* (2009) extended the ASM3 which has storage as extra processes included (Gujer *et al.*, 1999). To have the two different steps of nitrification included, the components S_{NHx}, S_{NO3}, and S_{NO2} should be included as they are formed or consumed. Also the two autrotrophic bacteria should be included, X_{NNO} and X_{ANO} that perform the nitrification. For the denitrification the components S_{NO3}, S_{NO2}, S_{NO}, S_{N2O}, and S_{N2} should be included as can be seen in figure 1.2. in the introduction. In table 3.2 the components used in the different models are shown. They are named according to the new nomenclature (Corominas, *et al.*, accepted). As mentioned before Kaelin *et al.* extended the ASM 3 and thus has also components concerning the storage in their model, however those are not included in the table. The goal is to extend the ASM 1 and therefore the storage is of no importance. The components of importance for the two step nitrification and four step denitrification are at the bottom of the table S_{NO3}.

The different components in table 3.2 are S_U soluble inert organic matter, $S_{B,Org}$ readily biodegradable substrate, X_U particulate inert organic matter, XC_B slowly biodegradable substrate, X_{OHO} active heterotrophic biomass, X_{ANO} active autotrophic biomass, X_P particulate products arising from biomass decay, S_{O2} oxygen (negative COD), $S_{NO3}{}^1$ nitrate and nitrite nitrogen, S_{NHx} NH_4^+ + NH_3 nitrogen, S_{BN} soluble biodegradable organic nitrogen, X_{BN} particulate biodegradable organic nitrogen, S_{ALK} alkalinity, S_{NO3} nitrate, S_{NO2} nitrite, S_{NO} nitric oxide, S_{N2O} nitrous oxide, S_{N2} dinitrogen, X_{ANO} ammonia nitrifying organisms, X_{NNO} nitrite nitrifying organisms.

Table 3.2. The components used in the different papers for the extension of nitrification and denitrification.

Component (new nomenclature)	ASM1	Hiatt & Grady	Kaelin *et al.*	Von Schulthess & Gujer	Alinsafi *et al.*	Sin *et al.*
S_U	X	X	X	X	X	X
$S_{B,Org}$	X	X	X	X	X	X
X_U	X	X	X	X	X	X
XC_B	X	X	X	X	X	X
X_{OHO}	X	X	X	X	X	X
X_{ANO}^1	X			X	X	X
X_P	X	X	X	X	X	X
S_{O2}	X	X	X	X	X	X
S_{NO3}^1	X					
S_{NHx}	X	X	X	X	X	X
S_{BN}	X	X	X	X	X	X
X_{BN}	X	X	X	X	X	X
S_{ALK}	X	X	X	X	X	X
S_{NO3}		X	X	X	X	X
S_{NO2}		X	X	X	X	X
S_{NO}		X				
S_{N2O}		X		X	X	
S_{N2}			X		X	X
X_{ANO}		X	X			X
X_{NNO}		X	X			X

Looking at the implemented components for the four step denitrification none of the models have included them all. The models in the papers of Hiatt & Grady and Alinsafi *et al.* miss one component and are therefore the best option. The papers of Kaelin *et al.* and Sin *et al.* neglected the intermediates NO and N_2O in their models. Because the goal is to model the production of N_2O, this intermediate needs to be included. Therefore the model in the paper of Kaelin *et al.* and models compared in the paper of Sin, are not useful in that point. Looking at the processes only the model in the paper of Hiatt & Grady has included them.

For the nitrification two autotrophic bacteria had to be included and the models in the papers of Hiatt & Grady, Kaelin *et al.* and Sin *et al.* have done that. However only Hiatt & Grady have included the two autotrophic growth processes.

3.3 The continuity check of a Petersen matrix

As mentioned before there is a method to check the Petersen matrix. This can be done with the continuity check (Gujer & Larsen, 1995) (IAWPRC Task Group, 1986). The continuity check is based on the principle of the conservation of matter. There is no matter created or destroyed. The continuity check is done by making different balances, a charge, COD and nitrogen balance, over the components that are involved. The values in the balances are then multiplied with the stoichiometric value of the components. This is done for all components involved in that process. Those multiplications are summed up and the sum has to be zero. If the sum is not zero, either the matrix or the balance or both of them are not correct. First it will be explained how the COD, N and charge balances are made. Then an example will be given on how to check the continuity. The balances can be found in appendix A.

3.3.1 Making the COD balance for the continuity check

In the COD balance the theoretical oxygen demand is given. This is the amount of oxygen needed to oxidize the component to its final oxidation state. For biomass this is 1 and for oxygen this is -1 because it delivers oxygen. The components S_{NO3} till S_{N2} can be oxidized further to NH_3 . The ammonia can not be further oxidized and therefore has no value in the COD balance. The unit in the COD balance is gCOD/gN. The amount of oxygen the nitrogen components need to form ammonia, multiplied by the molar weight of oxygen and then divided by the molar weight of nitrogen is the value in the COD balance in the right unit. For example the component NO_3^- needs 8 electrons to form NH_3

$$\mathbf{NO_3^- + 8\,e^- + 9\,H^+ \rightarrow NH_3 + 3H_2O}$$

These 8 electrons are formed by the reaction of water into oxygen and protons.

$$\mathbf{2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-}$$

By the formation of 1 oxygen 2 electrons are formed. Thus the 8 electrons should be divided by 2, which means 4 O mole is needed. The molar weight of an O atom is 16 and of a N atom 14. The value in COD balance is then - (4*16)/14 is -4.57. To prevent errors in the continuity check the numbers should not be rounded.

3.3.2 Making the N balance for the continuity check

The next balance to make is the N balance. Check for every component if it contains nitrogen. For example biomass, thus X_H has a fraction of N. This value is not calculated but measured. The components like S_{NO} are concentrations of mole N thus are always 1, also the component S_{N2O}. The same reasoning applies for the P balance.

3.3.3 Making the charge balance for the continuity check

After making the COD balance and the N balance, the charge balance is made. This is done by checking which components have a charge, for example component NH_4^+ has a charge of +1. The unit in which the continuity check for charge is done is charge/gN. Thus the charge needs to be divided by the molar weight of the nitrogen. Thus +1/14. For NO_3^- it is - 1/14.

3.3.4 An example of the continuity check

An example is given with aerobic growth of heterotrophs. The process and the components involved are given in table 3.3 with the values for the elements within the matrix. The values for the components involved in the three balances are given in table 3.4.

Table 3.3. Petersen Matrix for aerobic growth of heterotrophs

	$S_{B,Org}$	X_{OHO}	S_{O2}	S_{NH}	S_{ALK}	**Process rate**
Aerobic growth of heterotrophs	-1.67	1	-0.67	-0.086	-0.086*1/14	$\mu_{max,H} * X_{OHO} * (S_{O2}/(S_{O2}+K_{OH1})) * (S_S/(S_S+K_{S1}))$

Table 3.4. The balance of the components involved in the process aerobic growth of heterotrophs

Component	**COD**	**N**	**Charge**
$S_{B,Org}$	1	0	0
X_{OHO}	1	0.086	0
S_{O2}	-1	0	0
S_{NH}	0	1	1/14
S_{ALK}	0	0	-1

For COD the multiplication is ($S_{B,Org}$) -1.67*1 + (X_{OHO}) 1*1 + (S_{O2}) -0.67 * -1 + (S_{NH}) -0.086 * 0 + (S_{ALK}) -0.086*1/14* 0 = 0. Thus for COD the process is correct.

For N the multiplication is -1.67 * 0 + 1*0.086 + -0.67 * 0 + -0.086 * 1 + -0.086*1/14* 0 = 0. Also for N the process is correct.

For charge the multiplication is -1.67 * 0 + 1*0 + -0.67 * 0 + -0.086 * 1/14 + -0.086*1/14* -1 = 0. Also for N the process is correct.

When the values are rounded in the matrix or in the balances the continuity check can give an error. For example if the value of the N of X_{OHO} is 0.09 instead of 0.086 the check for the N will give an error of $4*10^{-3}$.

4. BSM2 replacements in the Bridle model for calculation of the GHG production

After analyzing the calculations used in the Bridle model, these are applied to the WWTP of the Benchmark Simulation Model 2 (BSM2). This will make it possible to calculate the GHGs dynamically. First an explanation of the BSM2 will be given. Then the results with the calculations of Bridle will be provided.

A standard platform was selected to evaluate different control strategies. This model, the IWA Benchmark Simulation Model no 1 (BSM1) (Copp 2002) is a standardized simulation and evaluation procedure. It includes a plant layout, simulation models and model parameters, a detailed description of disturbances that needs to be applied during the testing and evaluation criteria for testing the relative effectiveness of simulated control strategies. The plant layout is comprised of five bioreactors in series followed by a circular secondary settler This model was then further developed to BSM2, including additional units such as primary settler, thickeners, anaerobic digestion, dehydration and several recycle and bypass options. The BSM2 evaluates the control strategies taking both the water and sludge line into account (Jeppsson, *et al.*, 2007). This model is available for different simulation platforms, for example WEST, Fortran, GPS-X and Matlab. It is then possible to compare the results of different control strategies among different simulation platforms. The BSM2 consists also of standard models that describe the processes in the WWTP, for example ASM1, a standard configuration with parameters and a standard influent. By using the same configuration, models, parameters, and influents, the same results should be obtained in different simulation platforms. This way control strategies can be easily compared. The BSM2 consists of five tanks of which the first two are anoxic and the last three aerobic.

The model of Bridle was implemented into a Matlab file to work with the BSM2 Matlab/Simulink implementation given in appendix D. Thus, it is possible to calculate the GHG emissions with a dynamic influent. This will also give a more realistic description of the performance of a WWTP as the BSM2 uses the models ASM1 and ADM1, Anaerobic Digestion Model 1 (Batstone, *et al.*, 2002), to describe the biological processes. The BSM2 results will replace some of the conversion factors used in the Bridle model. Figure 4.1 shows which GHG emissions are calculated by the Bridle model and which by the BSM2. The calculations done by BSM2 are in the black boxes and the calculations done by the Bridle model are in the dotted boxes. The adjustments to the Bridle model are further explained in this chapter and can also be seen in figure 4.2. In figure 4.2 the inputs that are not needed in the BSM2 model are crossed out and the processes calculated by BSM2 are circled blue. Besides the adjustments also a comparison with the Bridle model and with data found in literature is made per subchapter. The same subchapters are used as in the previous chapter “The Bridle model”, namely biotreatment, sludge treatment, sludge reuse, chemical usage, power consumption and biogas usage.

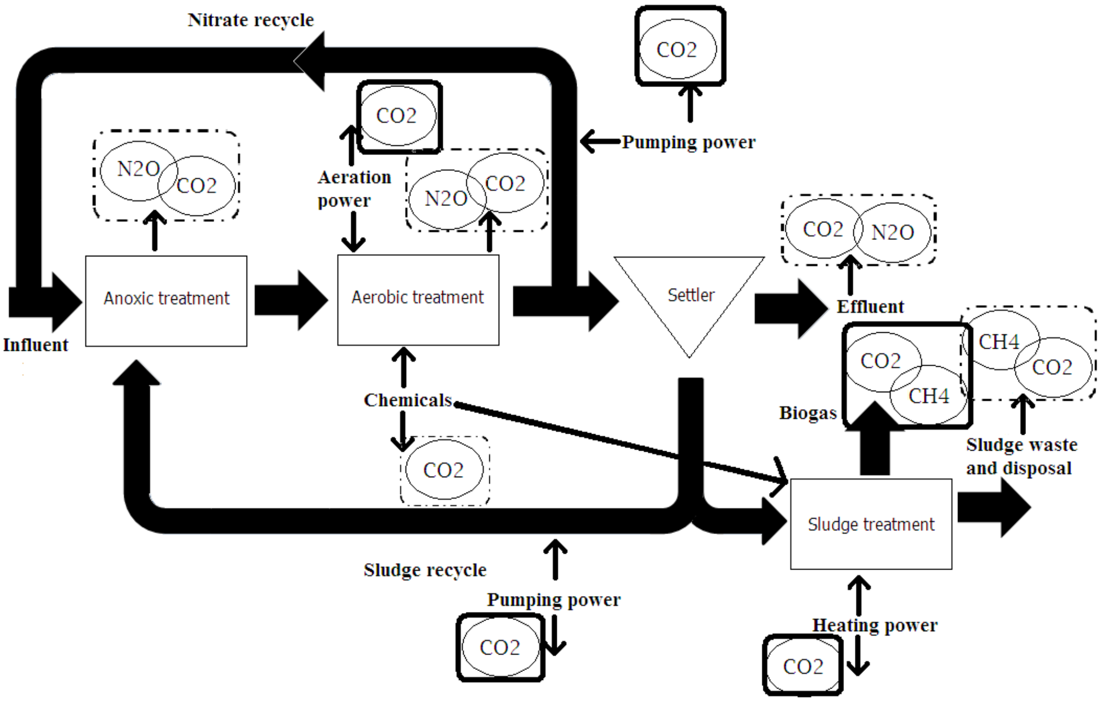

Figure 4.1. The greenhouse gas emissions, produced in a WWTP, calculated by the BSM2 are in the boxes and the greenhouse gas emissions calculated by the Bridle model are in the dotted boxes.

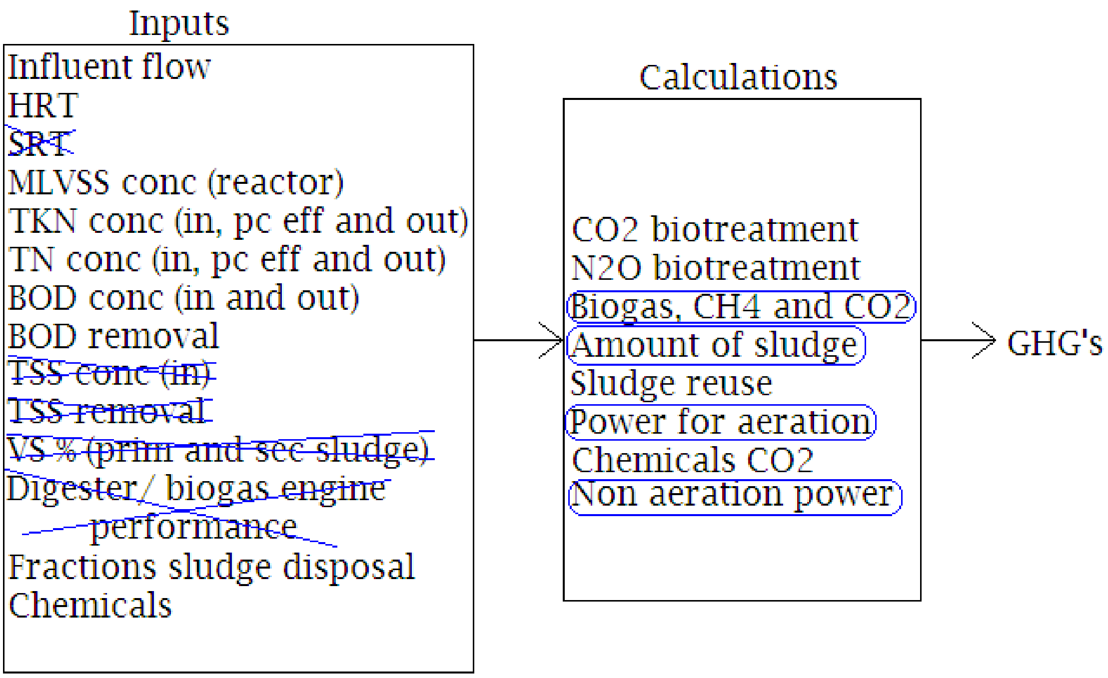

Figure 4.2. The replacements of BSM2 (blue) in the Bridle model.

4.1 GHG calculations for the BSM2 biotreatment process

As mentioned in chapter 2.1 the GHG emissions are calculated in three different processes, the endogenous decay, the BOD oxidation and the nitrogen removal. The influent data to calculate the GHG production, comes from the BSM2 following the principles outlined by Gernaey *et al.* (2007). The endogenous decay is quantified using the conversion factors given in the Bridle model, which estimates potential GHG formation from decomposed cell products. For the estimation of the GHGs produced during BOD oxidation the conversion factors of Bridle are used. Finally, a similar approach is used to calculate the CO_2 credit and N_2O production of the nitrogen removal. The conversion factor for the generation of N_2O comes from the first WWTP of the Bridle model, Beenyup.

To compare the results of different wastewater treatment plants the unit kg CO_2 equivalent / m^3 treated water is used. Thus, the results of the BSM2 that are in kg CO_2/day are divided by the total influent flow. The results from the biotreatment of the BSM2 are in the same range as the results from Monteith *et al.* (2005) (0,153 to 0,280 kg CO_2e/m^3). For the BSM2 the CO_2 emissions are 0,214 kg CO_2e/m^3, which is thus within the range. The amount of kg CO_2e/m^3 of the first WWTP in the Bridle model, Beenyup, is 0.07, which is 3 times lower than the BSM2. This is due to a lower concentration of MLVSS than the BSM2 has. As was shown in the chapter 2.1, the emissions due to biomass decay use MLVSS as a variable. The other two WWTP used by Bridle have a higher emission value for the biotreatment namely 0.16 and 1.33 kg/m^3. Again, the differences between the BSM2 and these two plants come from the different MLVSS concentrations. Also the Beenyup WWTP has a lower HRT than those two WWTP. The HRT also has a role in the calculation for the GHG production in the biomass decay. However, the large emissions of the third WWTP is caused by the higher generation rate of N_2O. According to the measurements on which the generation rate is based, the third WWTP generates 0.06 kg N_2O per kg N feed while the other two only generate 0,004 kg N_2O / kg N feed. The conversion factor used for the BSM2 emissions is 0.004 kg N_2O / kg N feed.

4.2 GHG calculations for the BSM2 sludge digestion process

The sludge treatment has two parts, sludge digestion and sludge reuse. First the sludge digestion will be explained. Biogas is produced during sludge digestion which consists mainly of CH_4 and CO_2. The internationally accepted ADM1 is used in the BSM2 to describe the performance of the digester and to predict the amount of sludge produced in kg TSS/day. Also the composition of the biogas can be given by ADM1 in the concentrations of CH_4 and CO_2. The only calculation left to calculate the GHG production is then the conversion of CH_4 to CO_2 equivalent.

If the results are compared with the calculations of the Bridle model, it can be seen that the values are slightly different. The mean values of the Bridle model and the BSM2 model are 1085.8 kg CH_4/day and 1059.5 kg CH_4/day respectively. The average difference between the productions of CO_2 calculated by the two models is higher, namely 80.3 kgCO_2/day with again a higher value for the Bridle model, 1607.8 kg CO_2/day. Comparing the values of the CO_2 emissions of the Beenyup WWTP with the BSM2 values, these have to be changed into kg CO_2e/m^3 as mentioned in the previous subchapter. The total amount of GHG production for the Beenyup is 1.82 kgCO_2e/m^3, which is higher than the 1.59 kg CO_2e/m^3 of the BSM2, but in the same range. The higher results of the Bridle model can be explained as follows. In the Bridle model it is assumed that there are no other gases in the biogas than methane and carbon dioxide. The BSM2 model also calculates that there is hydrogen in the biogas and therefore the values for methane and carbon dioxide are lower. Another explanation is that in the Bridle model it is also assumed that the total sludge in kg/day minus the digested sludge in kg/day is the biogas in kg/day. This implies that the conversion factor from sludge to biogas is 1. The reality is probably that the biogas produced is lower and therefore the amount of methane and carbon dioxide is also lower.

In the paper of Bani Shahabadi *et al.* (2008) a value could be found for the GHG production of the biotreatment and sludge digestion together. For the BSM2 this is 1.806 kg CO_2e/m^3. The paper mentions the value of 1.759 kg CO_2e/m^3 for aerobic treatment, thus it is in the same range.

4.3 GHG calculations for the BSM2 sludge reuse process

The digested sludge can be reused in different ways. The four options mentioned in the Bridle model are for agriculture, compost, forestry and other options as mentioned before in section 2.3. The BSM2 does not take sludge reuse into account. Therefore the fractions of reuse from the first WWTP of the Excel sheet from Bridle are used. As mentioned in the previous subchapter, the produced amount of sludge is provided by the BSM2. To calculate the CO_2 production due to sludge reuse, it is necessary to know the amount of carbon in the sludge, as a fraction of that carbon is converted to CO_2. The carbon in the sludge is calculated using a stoichiometric factor obtained from the following reaction:

$$\mathbf{C_5H_7O_2N + 5\ O_2 \rightarrow 5\ CO_2 + NH_3 + 2\ H_2O}$$

The elemental composition for sludge is $\mathbf{C_5H_7O_2N}$ (Bridle Consulting, 2007). From the total COD provided by the BSM2 the quantity of carbon in the sludge can be estimated. The COD used in the reaction is 5*32 and the carbon in the sludge is 5*12. This leads to the ratio 160/60 which equals 2.67. Thus the carbon in the sludge is calculated by dividing the COD with 2.67. With the carbon content known the CO_2 emissions can be calculated. The fractions for the different reuse options and the trucking emissions are calculated in the same manner as is done in the Bridle model.

The sludge reuse is difficult to compare with other papers as the amount of kg CO_2 produced is dependent on a large number of variables, for example the distance to the reuse site and the fraction that is reused. The amount of kg CO_2 e/ m^3 treated water in the Bridle model is in the range of 0.167 to 0.429 for the three WWTP. For the BSM2 with the same factors used as in the Beenyup WWTP the amount of kg CO_2e/m^3 is 0.134 which is almost the same as calculated for the Beenyup WWTP, namely 0.167. Bani Shahabadi *et al.* (2009) mentioned a value of $6 * 10^{-3}$ of kg CO_2/m^3 treated water with an aerobic treatment. This is a lower value, but as mentioned before, it is difficult to compare because of the values for the variables used can be different.

4.4 GHG calculations for chemical usage in BSM2

The Bridle model takes the GHG emissions occurring during the production of chemicals that are used in a WWTP into account. Nevertheless the BSM2 does not use the chemicals proposed by Bridle. Therefore this part is not taken into account.

In the paper of Bani Shahabadi *et al.* (2009) conversion factors for the use of methanol and alkalinity can be found, respectively 1.54 g CO_2e/g methanol and 1.74 g CO_2e / g alkalinity. The use of alkalinity in the WWTP of Bani Shahabadi *et al.* (2009) leads to a production of 0.206 kg CO_2e/m^3. The Beenyup WWTP has a production of 0.06 kg CO_2e/m^3 because of the use of different chemicals. The amount of chemicals used in the Beenyup WWTP is lower than the amount used in the paper of Bani Shahabadi *et al.* (2009) which explains the large difference in this production of CO_2.

4.5 GHG calculations for power consumption in BSM2

The energy consumption in the BSM2 involves aeration, pumping, mixing and heating energy. The Bridle model calculates the power used for aeration and measures the power used for other purposes. The power used for aeration in the BSM2 model running in steady state uses a static K_La and thus the power needed stays constant. The amount of CO_2 emissions for power for aeration according to the BSM2 model is 3760 kg CO_2/day when using the same conversion factor from kWh to CO_2. With the calculations of the Bridle model the CO_2 emissions range from 1831 kg CO_2/day to 3614 kg CO_2/day. The amount of oxygen needed for the different processes changes with the different influent concentrations and therefore the CO_2 emissions of the power needed in the Bridle model change.

The CO_2 produced in the BSM2 model for all the power used is 0.392 kg CO_2e / m^3 treated water. This value is in range with the kg CO_2 e /m^3 treated water in the paper of Bani Shahabadi *et al.* namely 0.512 kg CO_2e/m^3. The value for the first WWTP in the Excel sheet is 0.353 kg CO_2e/m^3.

4.6 GHG calculations for biogas usage in BSM2

The biogas produced during sludge digestion can be used for generation of power as mentioned in subchapter 2.6. The BSM2 uses the biogas for heating the sludge digester. As the sludge digestion uses most of the energy that is brought into the WWTP, this is a good solution to reduce the power consumption. For the calculation of the power consumption the power needed for heating is not taken into account in the sum for the total GHG production of the BSM2.

4.7 Overall GHG emissions for BSM2

The most GHGs are produced during the anaerobic digestion and the sludge reuse, shown in figure 4.3. According to the calculation the N_2O produced is only responsible for 1% of the GHG produced. As mentioned before the methane produced by the anaerobic digestion in the BSM2 plant is used for the heating. This would indicate that the sludge reuse contributes the most to the GHG production. However, as stated in the subchapter 4.3 it is difficult to compare the sludge reuse because it is depended on a large number of variables. Table 4.1 gives an overview of the amount of CO_2 equivalent produced per m^3 treated wastewater for the Bridle WWTP, the BSM2 plant and values found in literature.

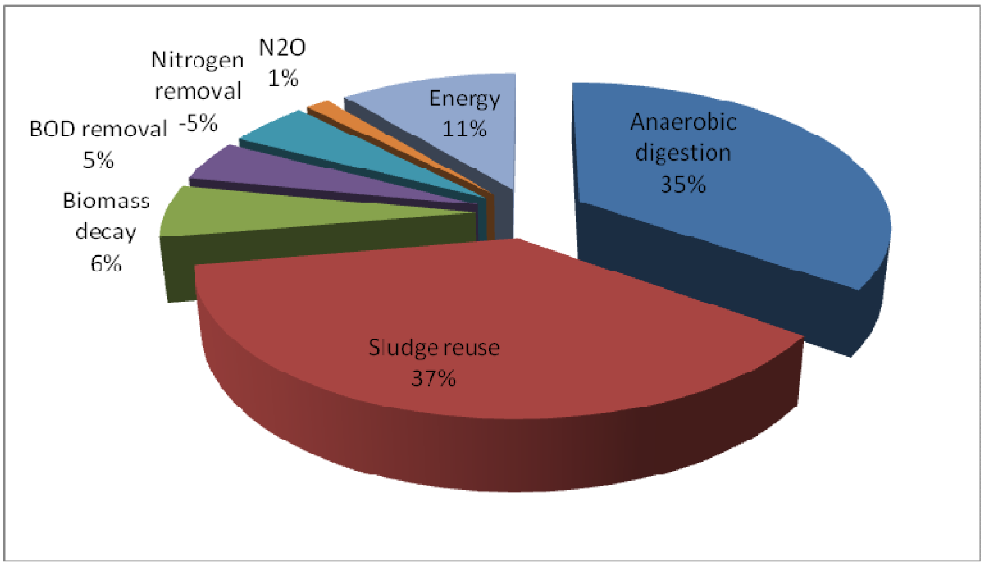

Figure 4.3. The contribution of processes in the BSM2 WWTP to the GHG emissions.

Table 4.1. Comparison of the GHG emissions of different WWTPs.

Process	Bridle Beenyup WWTP [kg CO2e/m^3]	BSM2 WWTP [kg CO2e/m^3]	Literature (Bani Shahabadi *et al.*, 2009) [kg CO2e/m^3]
Biotreatment	0.07	0.25	0.153-0.280
Sludge digestion + biotreatment	1.89	1.46	1.759
Sludge disposal	0.167	0.134	0.006
Chemicals	0.03	-	0.206
Power	0.353	0.392	0.512
Biogas used	-0.324	-0.2	-0.058

5. The ASM_2N4DN

Besides the replacements in the Bridle model already done in the BSM2 study of chapter 4, also the N_2O emissions can be replaced. This will make it possible to calculate the N_2O production more accurately and dynamically as mentioned in chapter 3. In this chapter first the ASM1 extension with two step nitrification and four step denitrification is described. Then the model is verified with two other mathematical models.

5.1 Implementation of two step nitrification and four step denitrification in the ASM1

From the literature review in chapter 3.2 it is concluded that the model described in the paper of Hiatt & Grady (2008) is the best to use as it has included the two nitrifying bacteria as components, the five components involved in denitrification and all the processes concerning nitrification and denitrification. However, the model has to be extended with the component S_{N2} to include all intermediates of the denitrification and to close the nitrogen balance. Besides the denitrification and nitrification processes the model also considers the Assimilative Nitrate Reduction to Ammonia in two steps and mixotrophic growth of nitrite oxidizing bacteria. As these processes are too detailed they are excluded. Also the processes for the biodegradation of an inhibitory compound and of a special interest compound are excluded as they will not have an effect on the nitrogen dynamics in the system The goal of including the two step nitrification and four step denitrification is to replace the conversion factors of the Bridle model and creating thereby a more realistic simulation of the production of GHGs. The replacements in the Bridle model can be seen in figure 3.1. Instead of using the concentrations of TN, total nitrogen, which is the sum of nitrate, nitrite and TKN, the concentrations of NH, NO_3^-, NO_2^-, NO, N_2O and N_2 are used separately.

The model with the two step nitrification and four step denitrification is named ASM_2N4DN. After implementing the adjustments that are mentioned above, the rate equations and the continuity was checked with the method of Hauduc *et al.*(2009). In the rate equation 3, the anoxic growth of heterotrophs, reducing nitrite to nitric oxide, an error was found. The inhibition term for oxygen in the model of Hiatt & Grady is

$\mathbf{K_{OH}} / (K_{OH3} + S_O)$ which needs to be $\mathbf{K_{OH3}} / (K_{OH3} + S_O)$.

There was another error in the equations, namely in the calculation of the free nitrous acid concentration. The temperature dependent coefficient that was used should have been calculated by

$K_A = e^{-(2300 / (273+T))}$ (Anthonisen, *et al.*, 1976) and not by $K_A = e^{-(2300(273+T))}$ as Hiatt & Grady had in their paper.

Also the value of converting the temperature from degrees Celsius to Kelvin was rounded in the paper of Hiatt & Grady. The temperature conversion is done in the calculation of K_A and K_B/K_W, the coefficients to calculate the free nitrous acid concentration (FNA) and the free ammonia (FA) concentration respectively. The conversion factor 273 was changed to 273.15 which is more accurate. The equations to calculate the concentrations of FNA and FA come from the paper of Anthonisen. Anthonisen uses the units mg NH_3/L and mg HNO_2^-/L for the concentration FA and FNA. As the unit in the Petersen matrix for the nitrogen components is in N g/m^3, the conversion of N mg/L to mg NH_3/L and mg HNO_2^-/L is not needed.

The implementation of a new component S_{N2} led to a difference in the elements of process five anoxic growth of heterotrophs, reducing nitrous oxide to nitrogen. The amount of nitrous oxide that is consumed is transformed into nitrogen gas. The stoichiometric value of S_{N2O} in process five is the amount of nitrous oxide consumed and this value is then also filled into S_{N2} with a positive sign, as the same amount of nitrogen is formed.

After the implementation of the model in WEST the continuity check was done with the balances mentioned in chapter 3.3. The balances made for the continuity check for the ASM_2N4DN can be found in the appendix. The continuity check revealed that numbers used in the matrix by Hiatt & Grady were rounded. This concerned the numbers 3.43, 1.14, 1.143 and 0.571. These numbers come from the COD balance, i_{COD/S_NO3}, i_{COD/S_NO2}, i_{COD/S_NO}, i_{COD/S_N2O} and i_{COD/S_N2}. 3.43 is the rounded value of i_{COD/S_NO2}, 1.14 is the rounded difference between i_{COD/S_NO3} and i_{COD/S_NO2}. The number 1.143 is the same as 1.14 and the number 0.571 is the difference between i_{COD/S_NO2} and i_{COD/S_NO}, the difference between i_{COD/S_NO} and i_{COD/S_N2O} and the difference between i_{COD/S_N2O} and i_{COD/S_N2}. To minimize the error in the continuity check the numbers used in WEST in the Petersen matrix have seven decimals, as the program can not use equations in the continuity check. The process rates used for the ASM_2N4DN can be seen in table 5.1. The parameter values set by Hiatt & Grady can be found in appendix C.

Table 5.1. The process rates and equations for the ASM_2N4DN

Process nr	Process name	Process rate
1	The aerobic growth heterotrophic biomass	$\mu_{max,B,H} * X_{OHO} * (S_{B,Org} / (K_S + S_{B,Org})) * (S_{O2} / (K_{O,H1} + S_{O2}))$
2	The anoxic growth of heterotrophic biomass, reducing NO_3^- to NO_2^-	$\mu_{max,B,H} * \eta_{g2} * X_{OHO} * (S_{B,Org} / (K_{S2} + S_{B,Org})) *(S_{NO3}/(K_{NO3} + S_{NO3})) *(K_{O,H2} / (K_{O,H2} + S_{O2}))$
3	The anoxic growth of heterotrophic biomass, reducing NO_2^- to NO	$\mu_{max,B,H} * \eta_{g3} * X_{OHO} * (S_{B,Org} / (K_{S3} + S_{B,Org})) *(S_{NO2}/(K_{NO2} + S_{NO2})) *(K_{O,H3} / (K_{O,H3} + S_{O2})) * (K_{I3NO}/(K_{I3NO}+S_{NO}))$
4	The anoxic growth of heterotrophic biomass, reducing NO to N_2O	$\mu_{max,B,H} * \eta_{g4} * X_{OHO} * (S_{B,Org} / (K_{S4} + S_{B,Org})) *(S_{NO}/(K_{NO} + S_{NO} + (S_{NO}^2/K_{I4NO})) *(K_{O,H4} / (K_{O,H4} + S_{O2}))$
5	The anoxic growth of heterotrophic biomass, reducing N_2O to N_2	$\mu_{max,B,H} * \eta_{g5} * X_{OHO} * (S_{B,Org} / (K_{S5} + S_{B,Org})) *(S_{N2O}/(K_{N2O} + S_{N2O})) *(K_{O,H5} / (K_{O,H5} + S_{O2})) * (K_{I5NO}/(K_{I5NO}+S_{NO}))$
6	The decay of heterotrophic biomass	$b_H * X_{OHO}$
7	The autotrophic growth of AOB	$\mu_{max,A1} * X_{ANO} * (S_{FA} / (K_{FA} + S_{FA} + (S_{FA}^2 / K_{I9FA})) * (S_{O2} / (K_{OA1} + S_{O2}) * (K_{I9FNA} / (K_{I9FNA} + S_{FNA}))$
8	The autotrophic growth of NOB	$\mu_{max,A2} * X_{NNO} * (S_{FNA} / (K_{FNA} + S_{FNA} + (S_{FNA}^2 / K_{I10FNA})) * (S_{O2} / (K_{OA2} + S_{O2}) * (K_{I10FA} / (K_{I10FA} + S_{FA}))$
9	The decay of AOB	$b_{A1} * X_{ANO}$
10	The decay of NOB	$b_{A2} * X_{NNO}$
11	The ammonification of soluble organic nitrogen	$k_a * S_{BN} * X_{OHO}$
12	The hydrolysis of particulate organics	$k_h * X_{OHO} * (XC_B / X_{OHO}) / (K_X + (XC_B / X_{OHO})) * ((S_{O2} / (K_{OH1} + S_{O2})) + \eta_h * (K_{OH1} / (K_{OH1} + S_{O2})) * (S_{NOx} / (K_{NO3} + S_{NOx})))$
13	The hydrolysis of particulate organics nitrogen	$k_h * X_{OHO} * (XC_B / X_{OHO}) / (K_X + (XC_B /X_{OHO})) * ((S_{O2} / (K_{OH1} + S_{O2})) + \eta_h * (K_{OH1} / (K_{OH1} + S_{O2})) * (S_{NOx} / (K_{NO3} + S_{NOx}))) * X_{BN} / XC_{B\,S}$
14	Aeration	$K_La\_Actual * (S_{O\,Sat} - S_{O2})$

$\mathbf{S_{NOx} = S_{NO3} + S_{NO2} + S_{NO} + S_{N2O}}$

The component and process matrix is shown in table 5.2.

Table 5.2. The component and process matrix of the ASM_2N4DN

	$S_{B,Org}$	S_{O2}	S_{NO3}	S_{NO2}	S_{NO}	S_{N2O}	S_{N2}	S_{NH}	S_{BN}	S_{ALK}	X_S	X_{OHO}	X_{ANO}	X_{NNO}	X_P	X_{BN}
1	$-1/Y_H$	$-(1-Y_H)\,/\,Y_H$						$-i_{N/XB}$		$-i_{N/XB}/14$		1				
2	$-1/(Y_H*\eta_Y)$		-A	A				$-i_{N/XB}$		$-i_{N/XB}/14$		1				
3	$-1/(Y_H*\eta_Y)$			-B	B			$-i_{N/XB}$		C		1				
4	$-1/(Y_H*\eta_Y)$				-B	B		$-i_{N/XB}$		$-i_{N/XB}/14$		1				
5	$-1/(Y_H*\eta_Y)$					-B	B	$-i_{N/XB}$		$-i_{N/XB}/14$		1				
6											$1-f_D$	-1			f_D	$i_{N/XB} - f_D - i_{N/XP}$
7		$-(3.4285714 - Y_{A1})\,/\,Y_{A1}$		$1/Y_{A1}$				$-i_{N/XB} - (1/Y_{A1})$		D			1			
8		$-(1.1428571 - Y_{A2})\,/\,Y_{A2}$	$1/Y_{A2}$	$-1/Y_{A2}$				$-i_{N/XB}$		$-i_{N/XB}/14$				1		
9											$1-f_D$		-1		f_D	$i_{N/XB} - f_D - i_{N/XP}$
10											$1-f_D$			-1	f_D	$i_{N/XB} - f_D - i_{N/XP}$
11								1	-1	1/14						
12											-1					
13									1							-1
14																

The letters A, B, C, and D represent:

$A = (1-Y_H*\eta_Y) / ((-64/14 - -48/14) * \mathbf{Y_H} * \eta_Y)$

$B = (1-Y_H*\eta_Y) / ((-48/14 - -40/14) * Y_H*\eta_Y)$

$C = -(i_{N/XB} / 14) + (1-Y_H*\eta_Y) / (14*(-48/14 - -40/14) * Y_H*\eta_Y)$

$D = (i_{N/XB} / 14) - (1 / (7 * Y_{A1}))$

5.2 Stripping N2O, NO and N2 as a process in the ASM_2N4DN

To calculate the greenhouse gas emissions the stripping of the gases has to be included in the processes of the ASM_2N4DN. During denitrification gases are produced in the form of N_2, N_2O and NO. If the gases stay in the liquid phase the model does not realistically show what happens in a WWTP, namely that gases are going into the air. More importantly, the concentrations of NO and N_2O in the liquid influence the process rates as can be seen in the figure 5.1. below.

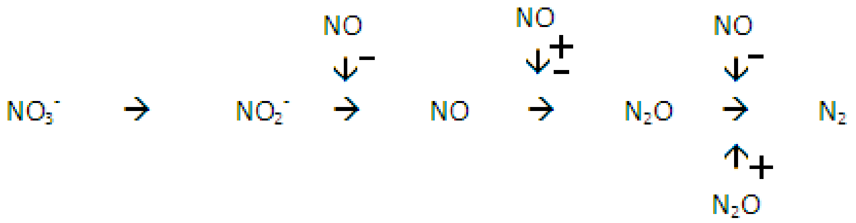

Figure 5.1. The influence of NO and N_2O on the process rates in denitrification.

Figure 5.1. indicates that the concentration of NO inhibits the process from nitrite to nitric oxide, the process from nitric oxide to nitrous oxide and the process of nitrous oxide to dinitrogen gas. The process from nitric oxide to nitrous oxide uses nitric oxide as a substrate but if the concentration is too high the process is inhibited. N_2O is not an inhibitor in any process, it is only used as a substrate in the process from nitrous oxide to dinitrogen. The higher the concentration of nitrous oxide is, the faster the process takes place. N_2 has no influence on any of the processes.

The stripping is included the same way as aeration is included. An example is given with the gas N_2 in table 5.3.

Table 5.3. The process and component matrix for stripping of N_2 gas with the rate equation included.

Component →	*i*	1	Process rate, ρ_j
j Process	↓	*S_N₂*	$[ML^{-3}T^{-1}]$
1 Stripping of N_2 gas		1	$K_La_{N2} * (S\_N_{2,sat} - S\_N_{2,liquid})$
		Dinitrogen $[M(N)L^{-3}]$	

The parameter K_La_{N2} is calculated by

$$\mathbf{K_La_{N2} = \sqrt{(D_{O2})}/\sqrt{(D_{N2})} * Kla_{O2}}$$

where

D_{O2} is the diffusion coefficient of oxygen in water at 20 °C	$[m^2/s]$
D_{N2} is the diffusion coefficient of dinitrogen in water at 20 °C	$[m^2/s]$
K_La_{O2} is the oxygen transfer coefficient	$[d^{-1}]$

The parameter $S\_N_{2,sat}$ is calculated by dividing the concentration of N_2 in the air by the Henry coefficient of N_2. The volume percentage of dinitrogen in air is 78%. Assuming ideal gas behavior, the concentration can be estimated with the ideal gas law, p*V = n*R*T. The volume of 1 mole of gas at a pressure of 1 atm. and 20 °C is $24{,}7*10^{-3}$ m^3. Of this volume 78% is dinitrogen gas, which gives a concentration of $19.3*10^{-3}$ mole N/m^3 that equals 0.266 gN/m^3. The Henry coefficient of N_2 at 20°C is 63.9 (Sander, 1999). The Henry coefficients for N_2O and NO are not needed as the concentrations of those gases in the air are very small and are therefore considered zero. The diffusion coefficients used for N_2, N_2O and NO are $1.86*10^{-9}$, $8.7\ *10^{-11}$ and $1.77\ *\ 10^{-9}$ m^2/s respectively (Reid *et al.*, 1987). After including stripping in the processes, the concentration of N_2 in the influent should not be considered irrelevant anymore. It can be assumed that the N_2 in the influent water is in equilibrium with the N_2 in the air. If the influent water does not contain N_2, the driving force will make the N_2 in the air transfer into the water as $S\_N_{2,sat}$ - $S\_N_{2,liquid}$ will be positive, indicating a transfer towards the water.

5.3 Verification of the ASM_2N4DN

The ASM_2N4DN model implementation needs to be verified. If the model gives the same results as the model of Hiatt & Grady using the same configuration and influent, the model can be considered to work properly. The model of Hiatt & Grady has no stripping included and therefore stripping was switched off during the simulations done for the verification of the ASM_2N4DN. The steady state results of three configurations using the ASMN (Hiatt, W.C., 2006) are compared with the steady state results using the ASM_2N4DN. Steady state is reached when the variables do not change in time anymore.

Hiatt (2006) has described three different systems in his thesis. The three different systems use the same influent that is shown in table 5.4. To work with the ASM_2N4DN model the influent had to be adjusted. Every component that is used in the model needs to be specified in the influent. The amount of components used in the influent is extended to 18 components for the ASM_2N4DN.

Table 5.4. The influent in the systems of ASMN and the adjusted influent for the systems of ASM_2N4DN

Component	ASMN influent [mg/L as COD]	ASM_2N4DN influent [mg/L as COD]
X_U	35	35
XC_B	150	150
X_{OHO}	0	0
X_{ANO}	0	0
X_{NNO}		0
X_P	0	0
S_U	15	15
$S_{B,Org}$	115	115
S_{O2}	2	2
S_{NO3}	0	0
S_{NO2}		0
S_{NO}		0
S_{N2O}		0
S_{N2}		0
S_{NH}	25	25
S_{BN}	6.5	6.5
X_{BN}	8.5	8.5
S_{ALK}	5	5

In the first subchapter the adjustments needed to make the ASM_2N4DN work are explained. The other three subchapters are about the comparison of the results of the different systems using the ASMN and using the ASM_2N4DN.

5.3.1 Parameters of the ASM_2N4DN

With the default parameters (see appendix) of Hiatt & Grady the system did not work. With the default parameters the nitrite oxidizing bacteria did not grow. However, the model of Hiatt and Grady is made for elevated nitrogen conditions, and parameters needed to be adjusted to get the nitrite oxidizing bacteria growing in normal wastewater. To make the nitrite oxidizing bacteria grow, only the parameter K_{FNA} had to be changed from $1 * 10^{-4}$ to $1 * 10^{-6}$. This was the value closest to the original at which the syjstem worked, and was therefore chosen to use with the configurations. The nitrogen level in the influent was not high enough. The low level caused a low concentration of FNA, as can be seen from the equation

$$\mathbf{S\_FNA = S_{NO2} * 1/(K_A + 10^{pH})}$$

where

S_FNA is the concentration of the Free Nitrous Acid	[mole/m^3]
S_{NO2} is the total concentration of nitrite	[mole/m^3]

K_A comes from the equation:
$K_A = e^{-(2300/(273,15+T))}$ in which T is temperature [°C]
pH is the acidity

The growth of nitrite oxidizing bacteria is inhibited by the FNA according to the following equation:

$$\rho_8 = \mu_{A2} * X_{ANO} * (S\_FNA/(K_{FNA} + S\_FNA + S\_FNA^2/K_{I10FNA}))*(S_{O2}/(K_{OA2} + S_{O2}))*(K_{I10FA}/(K_{I10FA} + S_{FA}))$$

where

ρ_8 is the growth rate of the nitrite oxidizing bacteria	[1/d]
μ_{A2} is the maximum growth rate of the nitrite oxidizing bacteria	[1/d]
X_{ANO} is the amount of biomass of nitrite oxidizing bacteria	[mg/L]
K_{FNA} is the half saturation coefficient for free nitrous acid	[mg/L]
K_{I10FNA} is the free nitrous acid inhibition coefficient for the growth rate of the nitrite oxidizing bacteria	[mg/L]
S_{O2} is the concentration of oxygen	[mg/L]
K_{OA2} is the half saturation coefficient for oxygen for nitrite oxidizing bacteria	[mg/L]
K_{I10FA} is the free ammonia inhibition coefficient for the growth rate of the nitrite oxidizing bacteria	[mg/L]

When the nitrite concentration is low the concentration of FNA is low. If that concentration is low the inhibition term (S_FNA / (K_{FNA} + S_FNA + S_FNA^2/K_{I10FNA})) is going to be low provided that K_{FNA} is larger than S_FNA. A low inhibition term will lead to a low growth rate. The maximum growth rate is best reached if all other terms, except biomass, are 1. Thus, K_{FNA} must be smaller than S_FNA in the reactor so that the inhibition term will approximately be S_FNA / S_FNA because K_{FNA} is negligible compared to S_FNA. This can be seen in figure 5.2. At the same concentration of S_FNA with a lower K_{FNA} value the growth rate is much higher. At a high concentration of S_FNA the growth rate will become zero.

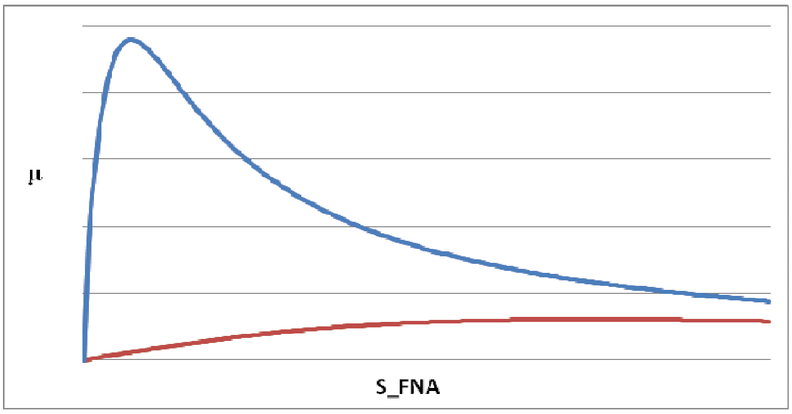

Figure 5.2. The growth rate of nitrite oxidizing bacteria as a function of the concentration of the free nitrous acid at two different K_{FNA} values.

5.3.2 Comparison between ASMN and ASM_2N4DN with the first configuration

After changing the K_{FNA} parameter the first system created by Hiatt & Grady worked properly. The first system was a configuration with one aerobic reactor and a settler. The oxygen controller was set at 2 mg/L and the volume of the tank was 1000 m^3. The configuration of the system in WEST is shown in figure 5.3. The sludge waste was set at 17 m^3/day, which makes the sludge retention time (SRT) 10 days, calculated by:

$$\mathbf{SRT = (V_{reactor} * X_{TSS,\ reactor})/(\ Q_{ef} * X_{TSS,ef} + Q_{wastage} * X_{TSS,wastage})}$$

where

SRT is the sludge retention time	[days]
$V_{reactor}$ is the volume of the reactor	[m^3]
$X_{TSS,reactor}$ is the amount of total suspended solids in the reactor	[g/m^3]
Q_{ef} is the flow of the effluent from the settler	[m^3/d]
$X_{TSS,ef}$ is the amount of total suspended solids in the effluent of the settler	[g/m^3]
$Q_{wastage}$ is the flow of the waste sludge	[m^3/d]
$X_{TSS,\ wastage}$ is the amount of total suspended solids in the waste sludge	[g/m^3]

For the calculation the amount of total suspended solids in the flow of the effluent is minimum which makes the term $\mathbf{Q_{ef} * X_{TSS,ef}}$ negligible.

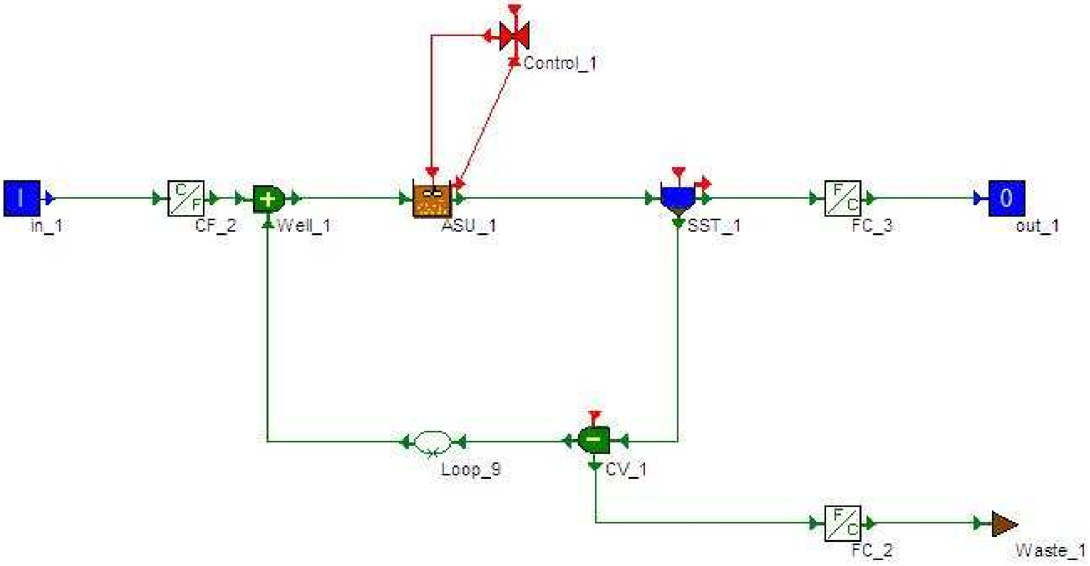

Figure 5.3. System 1 of Hiatt & Grady with one aerobic reactor

The results of Hiatt & Grady are presented in table 5.5. The different nitrogen oxides were summed in their results. The difference between the ASMN and the ASM_2N4DN is calculated by summing up S_{NO3}, S_{NO2}, S_{NO}, and S_{N2O} and then subtracting that from S_{NO} of the ASMN model.

Also as mentioned before the ASMN did not distinguish two nitrifying bacteria. The difference between the nitrifiers in ASMN and the nitrifiers in the ASM_2N4DN is calculated by subtracting the X_{ANO} and X_{NNO} from the concentration of nitrifiers in ASMN, X_{ANO}. The ASMN has not calculated the concentration of S_{N2} and is therefore not taken into account in the comparison. The last column shows the percentage difference of the ASM_2N4DN result with the ASMN result.

Table 5.5. Comparison of the result concentrations in the reactor of Hiatt & Grady's first system with ASM_2N4DN

	ASMN	ASM_2N4DN	Difference	Difference percentage with ASMN result
X_U	**350**	341.08	8.9	2.5
XC_B	**36.2**	35.64	0.6	1.5
X_{OHO}	**567**	548.87	18.1	3.2
X_{ANO}	**46.5**	29.26	9.7	20.8
X_{NNO}		7.57		
X_P	**188**	177.35	10.7	5.7
$S_{B,Org}$	**1.9**	1.81	0.1	4.7
S_{NO3}	**30.9**	22.27	0.9	2.9
S_{NO2}		7.09		
S_{NO}		0.04		
S_{N2O}		0.62		
S_{N2}	**-**	2.27	-	-
S_{NH}	**0.6**	0.93	-0.3	-55.0
S_{BN}	**0.4**	0.24	0.2	40.0
X_{BN}	**2.7**	2.68	0.0	0.7
S_{ALK}	**1.1**	1.18	-0.1	-7.3

The differences between the concentrations obtained with ASMN and concentrations obtained with the ASM_2N4DN are mainly between the autotrophic biomass, ammonia and ammonium and soluble biodegradable organic nitrogen. There is less autotrophic biomass in the ASM_2N4DN, probably due to not including the mixotrophic growth of the nitrite oxidizing bacteria in the ASM_2N4DN although this is included in the ASMN. The mixotrophic growth rate in ASMN is the autotrophic growth rate of the nitrite oxidizing bacteria multiplied with a mixotrophic growth factor and a Monod term, $(S_U/(S_U + K_{S1}))$. The mixotrophic growth factor used by Hiatt & Grady is 6. Thus the extra growth due to mixotrophic growth is relevant as can be seen at the percentage difference of 20%. When there is less autotrophic biomass, there will be less ammonia converted and thus the concentration of ammonia and ammonium is higher in the ASM_2N4DN. Looking at the results overall the differences between the ASM_2N4DN and the ASMN are small or can be explained. From this it can be concluded that the ASM_2N4DN works similar as ASMN.

5.3.3 Comparison between ASMN and ASM_2N4DN with the second configuration

After the first system worked properly the second system was implemented. Compared to the first system this system has an extra tank, which is also aerobic with an oxygen controller set at an oxygen level of 2 mg/L. The volume of both tanks is 500 m^3, thus together again a volume of 1000 m^3. This system also operates at a sludge waste flow of 17 m^3/day to keep the SRT at 10 days. The configuration of the system is shown in figure 5.4.

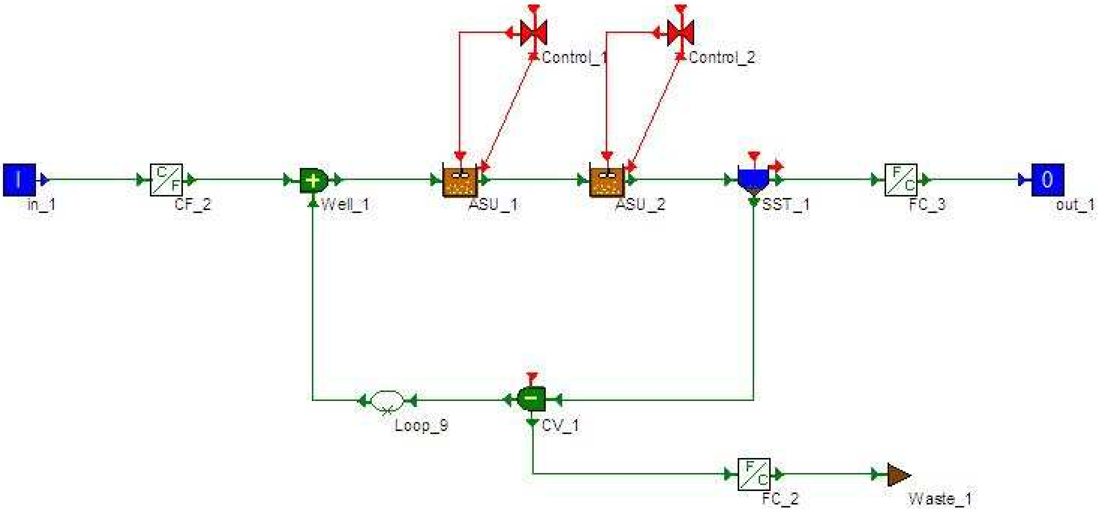

Figure 5.4. System 2 of Hiatt & Grady with two aerobic reactors

The tables with the comparison of all components in the two aerobic tanks can be found in the appendix B. Again the main differences in the aerobic reactors are between the autotrophic biomass, ammonia and ammonium and soluble biodegradable organic nitrogen. The second aerobic reactor has the same main differences. The explanations for these differences are given in the previous subchapter. Again the same conclusion can be drawn from this, that is that the ASM_2N4DN works similar as ASMN, or the differences can be explained.

5.3.4 Comparison between ASMN and ASM_2N4DN with the third configuration

The third system of Hiatt & Grady has again two tanks, but the first tank operates at an oxygen level of 0,05 mg/L and the second one at an oxygen level of 2 mg/L. Both tanks have the same volume, namely 500 m^3. Also for this system the sludge waste flow was set at 17 m^3/day. New in this configuration is the nitrate loop of 3000 m^3/day. A nitrate loop is needed to convert the NH in the influent to N_2. In the first anoxic tank the heterotrophs convert NO_3^- to N_2. In the second tank, the aerobic tank, the nitrifiers convert the NH to NO_3^-. This nitrate needs to be brought to the anoxic tank to be completely converted to N_2. In the other configurations the NH was only converted to NO_3^- as can be seen by the low S_{NH} concentration. The amount of N_2 was low too. There were no anoxic circumstances and thus, the heterotrophic anoxic growth was very small. Due to the denitrification the concentration of FNA was lower in this system. This led to a slow growth of the nitrite oxidizing bacteria. With a value of 1 * 10^{-6} for the parameter K_{FNA} the nitrite oxidizing bacteria were flushed out. Hence for this system the parameter K_{FNA} was changed to 1 * 10^{-8}. The configuration used in WEST is shown in figure 5.5.

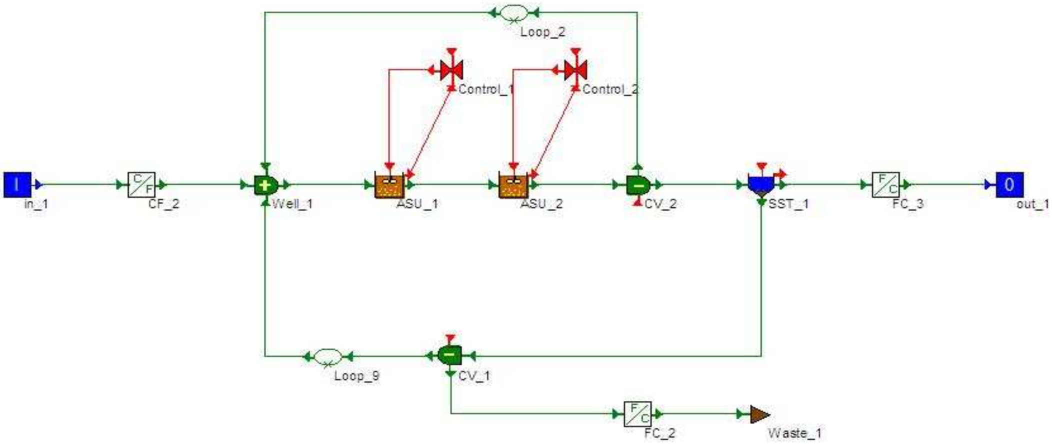

Figure 5.5. System 3 of Hiatt & Grady with an anoxic and aerobic tank and an internal recycle

In the thesis of Hiatt (2006) the results of the anoxic tank and the aerobic tank are believed to be mixed up. The aerobic tank has to have more nitrate than the anoxic tank as in the anoxic tank the bacteria use nitrate as a electron donor instead of oxygen and therefore the nitrate level should be lower. The ammonia should be higher in the anoxic tank than in the aerobic tank, because the ammonia oxidizing bacteria need oxygen and therefore are only active in the aerobic tanks. Thus only there the ammonia is converted to nitrite and the ammonia concentration should be lower. The tables with the comparison can be found in appendix B.

In the anoxic tank the main difference between the ASMN and the ASM_2N4DN is the concentration of soluble biodegradable organic nitrogen and the concentration of nitric oxide. In the aerobic tank the differences are between the ammonia concentration and the concentration of soluble biodegradable organic nitrogen. The complete comparison of the two different tanks can be consulted in the appendix.

After comparing the models for the three systems, the ASM_2N4DN is confirmed to work similar as the ASMN and thus to describe the nitrification and denitrification properly. An extra check to verify the model is done in the next section with the comparison of the ASM_2N4DN with the ASM1.

5.3.5 Verification of ASM_2N4DN with ASM1

After verifying ASM_2N4DN by comparing the model with ASMN it is concluded that the model works similar as the ASMN. In this chapter the model is compared with a widely accepted model for nitrogen removal WWTPs, namely ASM1. Hiatt & Grady also compared their ASMN with the ASM1 in the platform Matlab. During this verification the nitrification inhibition and the mass transfer equations for nitric oxide and nitrous oxide were disabled. Hiatt & Grady concluded that the only significant difference between ASM1 and ASMN was the concentration of autotrophic biomass. This was higher in the ASMN due to the included mixotrophic growth. The ASM_2N4DN is going to be compared with the ASM1 while the nitrification inhibition and the mass transfer equations for nitric oxide and nitrous oxide are enabled. This because the goal of this study is to replace the ASM1 with the ASM_2N4DN to be able to calculate the nitrous oxide production.

The configuration that is used for this comparison is the third system created by Hiatt & Grady which is shown in figure 5.5. The ASM1 model is used with the default parameters of that model. Some default parameters of ASM1 were copied to the ASM_2N4DN to make the comparison better, namely the parameters for the aerobic growth of heterotrophic biomass, the maximum heterotrophic growth, μ_{max}, the heterotrophic yield, Y_H, and the decay coefficient b_H. This was done because of the large differences between those parameters. The ASM1 has different components than ASM_2N4DN as mentioned in chapter 3.2. The autotrophic biomass is not split up in X_{ANO} and X_{NNO} and the concentrations of nitrate and nitrite are summed up in the component S_{NO}. In the ASM_2N4DN the component S_{NO} stands for the concentration of nitric oxide. The components S_{NO3} and S_{NO2} are the concentrations of nitrate and nitrite respectively. The difference between the autotrophic biomass of both models is calculated by summing the two autotrophic bacteria in the ASM_2N4DN and subtracting that from the ASM1. The concentrations of S_{NO3} and S_{NO2} of ASM_2N4DN are subtracted from the concentration of S_{NO} from the ASM1. These differences are stated in the fourth column of table 5.6.

Table 5.6. Comparison of the concentrations of the components in the aerobic tank using ASM_2N4DN with the concentrations of the corresponding components of ASM1.

	ASM1	ASM_2N4DN	Difference	Difference percentage with ASM1 result
X_U	**341**	341.0	0.0	0.00
XC_B	**27.6**	65.9	-38.3	-138.77
X_{OHO}	**683.9**	630.4	53.5	7.82
X_{ANO}	**63.8**	47.9	-0.8	-1.25
X_{NNO}		16.7		
X_P	**211.6**	195.4	16.2	7.66
$S_{B,Org}$	**5.8**	4.5	1.3	22.41
S_{NO3}	**1**	1.9	-1.7	-170.00
S_{NO2}	**-**	0.8		
S_{NO}	**-**	0.0	-	-
S_{N2O}	**-**	0.3	-	-
S_{N2}	**-**	21.6	-	-
S_{NH}	**5.3**	5.8	-0.5	-9.43
S_{BN}	**0.9**	0.9	0.0	0.00
X_{BN}	**2**	4.8	-2.8	-140.00
S_{ALK}	**3.5**	3.4	0.1	2.86

The table shows a difference between the concentrations of the heterotrophic biomass and the XC_B. The ASM1 results indicate that the slowly biodegradable substrate is used more than in the ASM_2N4DN leading to a slightly increased production of heterotrophic biomass. This is probably due to a different k_H parameter. There is also a difference between the nitrate and nitrite and the particulate biodegradable organic nitrogen. As there is less substrate consumed in the ASM_2N4DN than in the ASM1 there is less nitrate and nitrite converted. This leads to higher concentrations of nitrate, nitrite and particulate biodegradable organic nitrogen in ASM_2N4DN than in ASM1.

For the anoxic tank the differences are similar as for the aerobic tank as can be seen in table 5.7.

Table 5.7. Comparison of the concentrations of the components in the anoxic tank using ASM_2N4DN with the concentrations of the corresponding components of ASM1.

	ASM1	ASM_2N4DN	Difference	Difference percentage with ASM1 result
X_U	**341**	341.0	0.0	0.00
XC_B	**6.8**	43.2	-36.4	-535.29
X_{OHO}	**687.5**	635.2	52.3	7.61
X_{ANO}	**65.1**	48.9	-0.9	-1.38
X_{NNO}	**-**	17.1		
X_P	**214.3**	197.8	16.5	7.70
$S_{B,Org}$	**2.6**	2.7	-0.1	-3.85
S_{NO3}	**6.2**	8.5	-2.4	-38.23
S_{NO2}		0.1		
S_{NO}	**-**	0.0	-	-
S_{N2O}	**-**	0.1	-	-
S_{N2}	**-**	21.9	-	-
S_{NH}	**0.6**	0.8	-0.2	-33.33
S_{BN}	**0.8**	0.9	-0.1	-12.50
X_{BN}	**0.5**	3.4	-2.9	-580.00
S_{ALK}	**2.8**	2.7	0.1	3.57

Looking at the percentage differences in both tables the differences on the slowly biodegradable substrate and particulate biodegradable organic nitrogen is large. Except for these two differences the performance of the ASM_2N4DN is similar to that of the ASM1. After the verification with the ASMN model also the verification with ASM1 seems to be good and therefore the model ASM_2N4DN can be used to realistically predict the performance of a WWTP. Although this is a more complex model, with more parameters that need to be estimated, it realistically predicts the production of the GHG N_2O, which is needed to estimate the overall GHG production of a WWTP.

6. Effect of different conditions on the production of GHG

After establishing that the ASM_2N4DN realistically predicts a WWTP performance, the effect of different conditions on the production of GHG can be investigated. First, the configuration of BSM1 (Copp, 2000) is extended with oxygen controllers in the three aerated tanks and the effect of oxygen level on the production of N_2O and the GHGs within the WTTP boundaries is examined. Then the configuration is extended with two extra controllers, a cascade ammonia controller manipulating the oxygen set point and secondly a nitrate controller manipulating the internal recirculation. First, the effect of the ammonia set point on the production of N_2O and the GHG will be analyzed. Next, the effect of nitrate set point on the production of N_2O and other GHG's will be examined. In all simulations the default parameters of the ASMN model were used for the kinetic processes. Only the parameter K_{FNA}, the inhibition constant of Free Nitrous Acid on the anoxic growth of nitrite oxidizing bacteria, was decreased to $1 * 10^{-10}$, to ensure that the NOB could grow in the reactors.

For this study the stripping of the gases was used in the model. The gases are mainly formed in the anoxic tanks and stripping could also occur there. The rates of stripping are based on the K_La and therefore a value for the mass transfer efficiency of the anoxic tanks should be given. The K_La for anoxic tanks is not 0, because gas bubbles are formed, there is an interface to the air there is stirring affecting the K_La. According to Siegrist & Gujer (1994) the K_La for an anoxic tank should be between 0.5 and 3 d^{-1}. The K_La_{O2} used for the anoxic tanks is 2 d^{-1}.

The simulation was run with a steady input for 100 days, which puts the system in steady state. After that the values of the state variables were copied to the initial values and the input was changed to a dynamic input for dry weather. This simulation was run for 14 days. Again the values of the state variables were copied to the initial values and the simulation was run for 14 days with the dynamic dry weather input. The results of the last seven days of the second simulation with dry weather input was saved in a text file which was used for evaluation. The evaluation program automatically calculated for example the average concentration of oxygen in the effluent and the energy needed. It also calculated the amount of N_2O produced. The results were also run in a Matlab file to calculate the GHGs (appendix E).

6.1 The selected controllers for the WEST configuration

The controllers used in the WEST configuration are all PI anti windup controllers. For the dissolved oxygen controller the measured variable (y_s) is the concentration of the dissolved oxygen and the manipulated variable (u) is the airflow expressed as K_La. The 'K_L' is the transfer coefficient and the 'a' is the interface area where the transfer can take place. The K_La is dependent on the temperature and the substance that is transferred. Each aerobic tank has a dissolved oxygen controller, thus three different controllers are implemented as can be seen in figure 6.10.

The name PI stands for proportional integral and works according to the following equation (Knoop & Moreno Perez, 1993):

$$\mathbf{u(t) = K_p * \mathit{e}(t) + K_I\ {}_0\!\int^t \mathit{e}(t') \, dt'}$$

where

u is the input
K_p is the proportional gain
K_I is the integral gain
e is the error, the difference between the measured value and the set point

The error is indicated in figure 6.1. with the arrow. The integral of the error is indicated by the shaded surface.

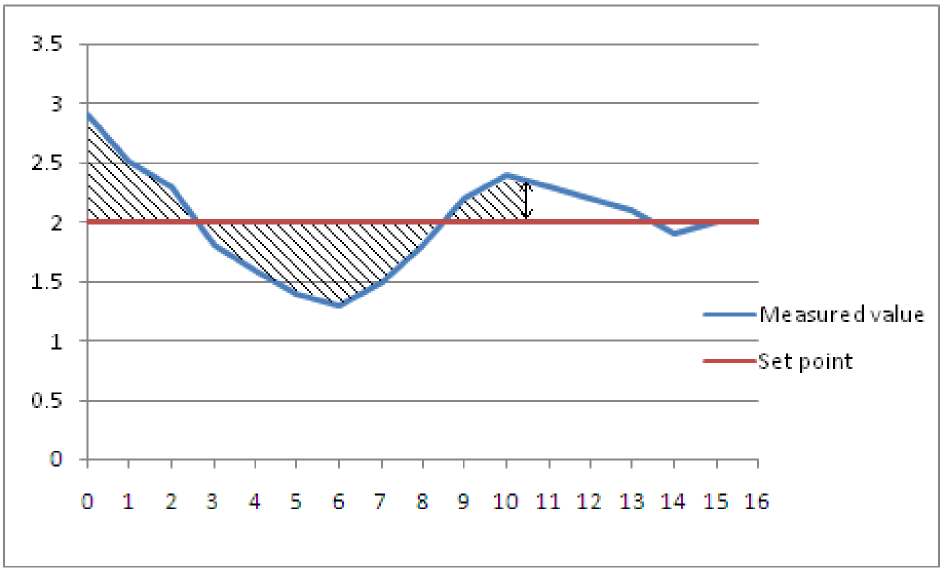

Figure 6.1. The error between measured value and the set point indicated with an arrow and the integral of the error indicated by the shaded surface.

The larger K_p is the larger the control input difference with the error will be. If the K_p is chosen too large this can sometimes result in unstable control as the action becomes larger and larger. If the K_p is too small, the controller can be less responsive and it will take quite some time before the error is small again. K_I is multiplied with the integral of the error. This way the controller output will be affected by the magnitude of the error as well as the duration of the error.

The anti windup is to prevent a large overshoot and long settling time caused by limitations imposed on the control action (Hanus *et al.*,1987) (Vrančić *et al.*, 2001). For example the nitrate controller is regulated by recycling water from the last aerobic tank to the anoxic tanks. There are limitations for the recycle as it can not be negative, the water will not go from the anoxic tanks to the aerobic tanks, and no more water can be recycled. If the controller is set for a higher set point than can be reached with the recycle loop, the difference between the set point and the actual concentration will be large and remain large. As a result the integral of the error will become larger and larger. When the concentration of nitrate in the recycle is increased, the set point can be reached again and the error will decrease. However, the integral of the error will still be large as the time the error occurred was long. This will make the controller react slower. The anti windup gives an extra term to the equation of the controller to prevent that the integral of error during limitations becomes too large and affects the controller (WEST model guide):

$$u(t) = u_0 + K_p * (e(t) + K_p/\tau_i \, {}_0\int^t e(t')\, dt') + 1/\tau_t$$

where

u_0 is the initial input
τ_i is the integral time constant
τ_t is the tracking time constant
Notice the extra term $+ 1/\tau_t$.

With the Cohen-Coon method the controller parameters K_p and τ_i can be calculated. For this method, first the dead time, θ, and time constant T should be estimated. This can be done by making a graph of the output versus the time, as can be seen in figure 6.2.

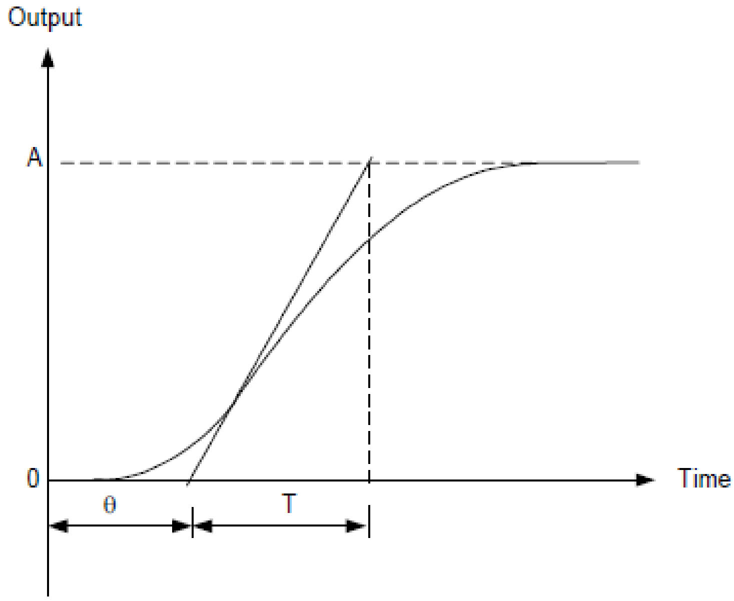

Figure 6.2 The step response of the output as a function of time to establish the dead time and the time constant (http://www.remotelab.ntnu.no/refrig/pdf/controller_tuning.pdf).

A straight line should be drawn in the graph from the point where the curve stops curving upwards and starts curving downwards. The straight line should have the same gradient as the graph at that point. The dead time can then be found at the intersection of the straight line with the initial value of the output. The straight line reaches the steady state output at time $\vartheta + T$. The parameter K is A/B in which B is the step size in the input.

With the formula in table 6.1 the K_p and T_i can be calculated for the PI controller.

Table 6.1. Standard equations of the Cohen-Coon method to calculate the controller parameter http://www.remotelab.ntnu.no/refrig/pdf/controller_tuning.pdf).

	Kp	**Ti**	**Td**
P	T/(Kθ) (1 + θ/(3T))	-	-
PI	T/(Kθ) (0.9 + θ/(12T))	θ (30+3 θ/T)/(9+20 θ/T)	-
PID	T/(Kθ) (4/3 + θ/(4T))	θ (32+6 θ /T)/(13+8 θ/T)	θ (4/(11+2 θ/T)

θ is the dead time
T is the time constant
K is the sum of the step change in the output divided by the change in the input

The larger the dead time is, the smaller the controller parameter K_p should be. At a small dead time, a change in the dead time will lead to a large difference in the K_p as can be seen in figure 6.3. For small dead times the difference in Ti is also larger. If the dead time is small the Ti is also small and becomes larger with a larger dead time.

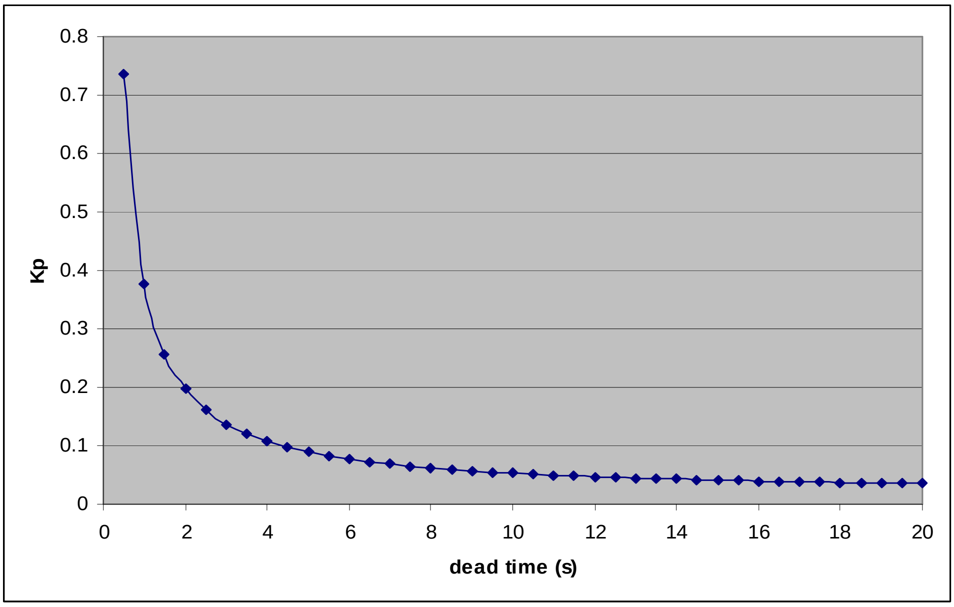

Figure 6.3 The controller parameter Kp as a function of dead time according to the Cohen-Coon method

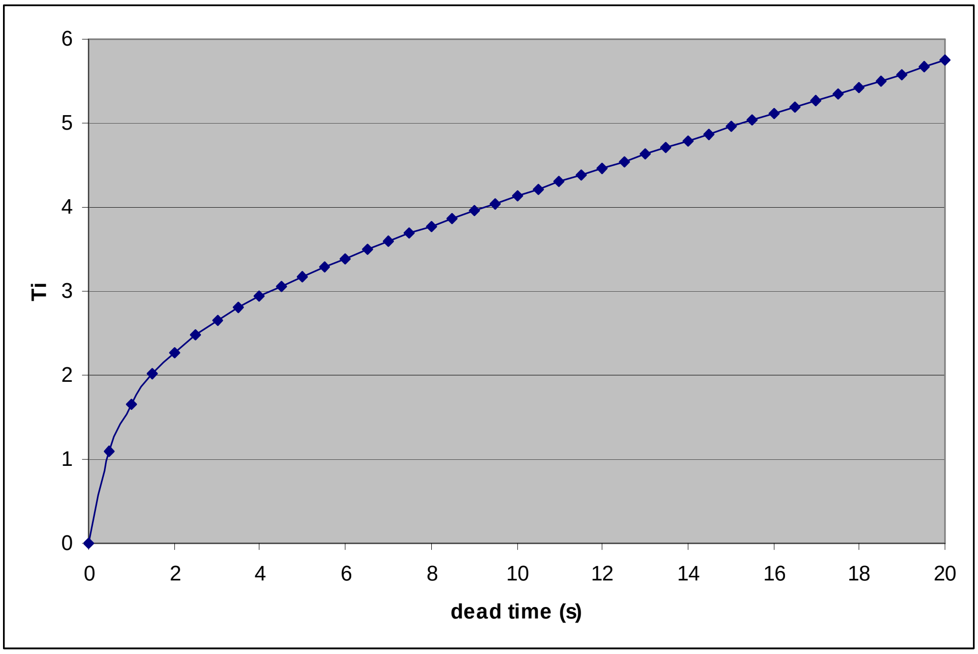

Figure 6.4 The controller parameter Ti as a function of dead time according to the Cohen-Coon method

The dynamics that are simulated with the different controllers implemented can be seen in the figures 6.5 to 6.10. The total configuration of the system with the controllers is shown in figure 6.11. The ammonia controller was set at 2 mg/L for the last tank and the nitrate controller was set at 1 mg/L for the last anoxic tank. To prevent a high oxygen concentration in the anoxic tanks a data limiter was implemented between the oxygen controller of the last aerobic tank and the ammonia controller. The maximum limit is set at a level of 2 mg/L of oxygen. Thus, the set point of the oxygen concentration in the last aerobic tank cannot exceed 2 mg/L. The days displayed are the days 3 to 5 from the dynamic dry weather input. In the simulation program WEST the controller parameters K_p and T_i are Kp, and Ti respectively. For the anti windup there is also the control parameter Tt For the DO controller the parameters were Kp 25 and Ti and Tt both 0.1. For the ammonia controller the Kp value was set at 10000 and the Ti and Tt value at 0.01. For the last controller of nitrate the Kp value was -2 and the Tt and Ti value 0.01.

Simulating the performance of a WWTP dynamically is important, as the design should take the extremes into account, meaning the peaks in the graphs. Also calculating with averages can give a different output than calculating with dynamics and then taken the average value of those outputs.

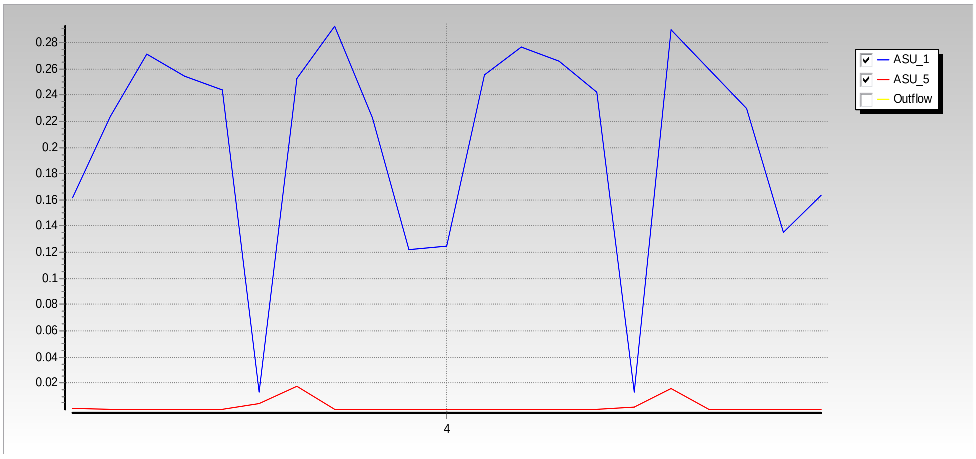

Figure 6.5. The dynamic simulated N_2O concentration [mg/L] in the first tank, ASU_1 and the last tank, ASU_5 as a function of time.

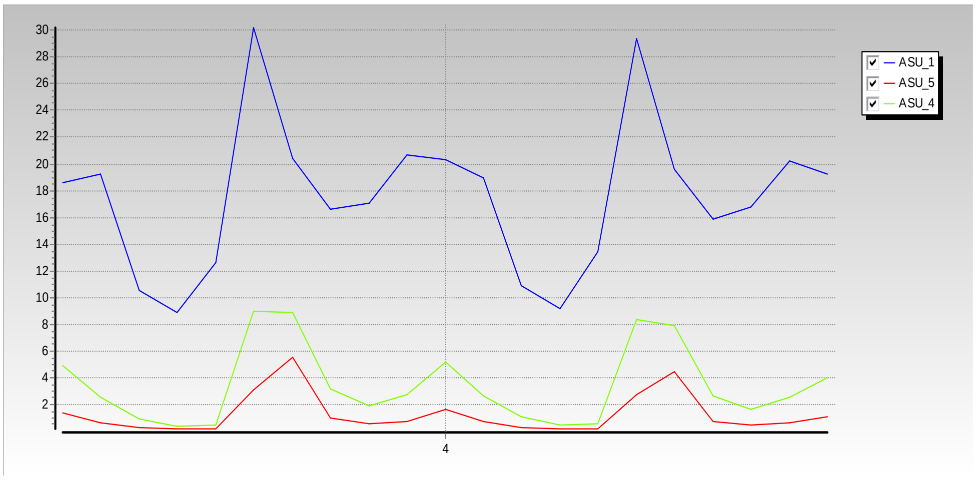

Figure 6.6. The dynamic simulated NH concentration [mg/L] in the first, ASU_1, fourth, ASU_4 and last tank, ASU_5 as a function of time

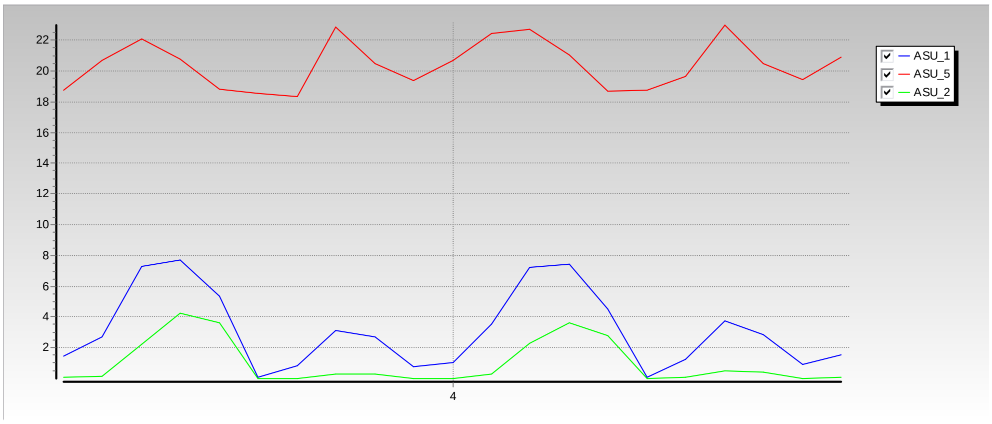

Figure 6.7. The dynamic simulated NO_3 concentration [mg/L] in the first, ASU_1, second, ASU_2 and last tank, ASU_5 as a function of time

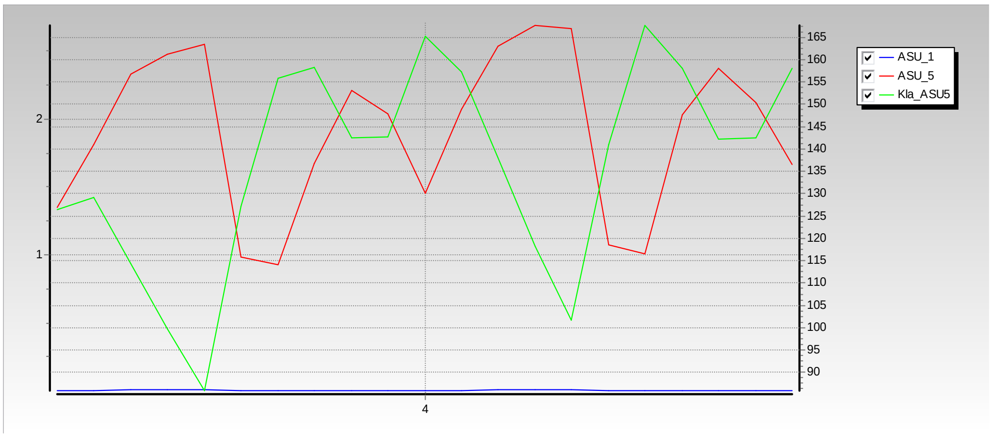

Figure 6.8. The dynamic simulated oxygen concentration [mg/L] in the first, ASU_1, and last tank, ASU_5 and the K_La in the last tank as a function of time.

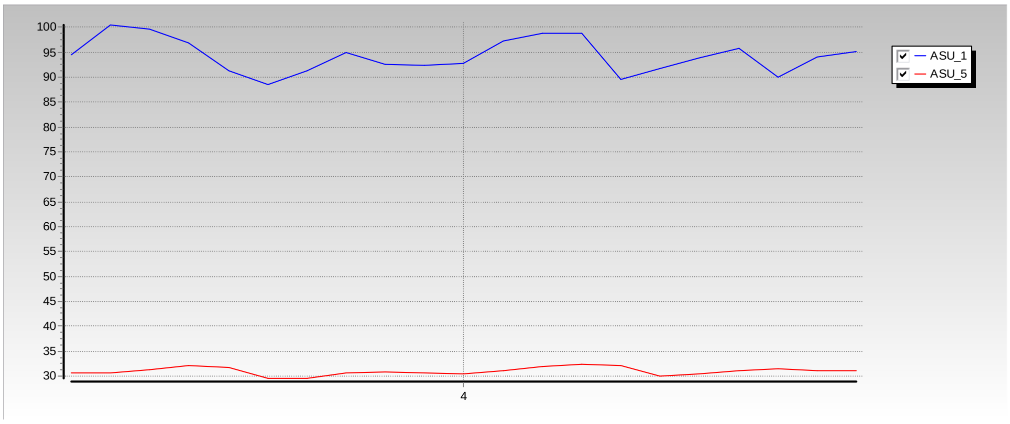

Figure 6.9. The dynamic simulated AOB concentration [mg/L] in the first, ASU_1, and last tank, ASU_5 as a function of time

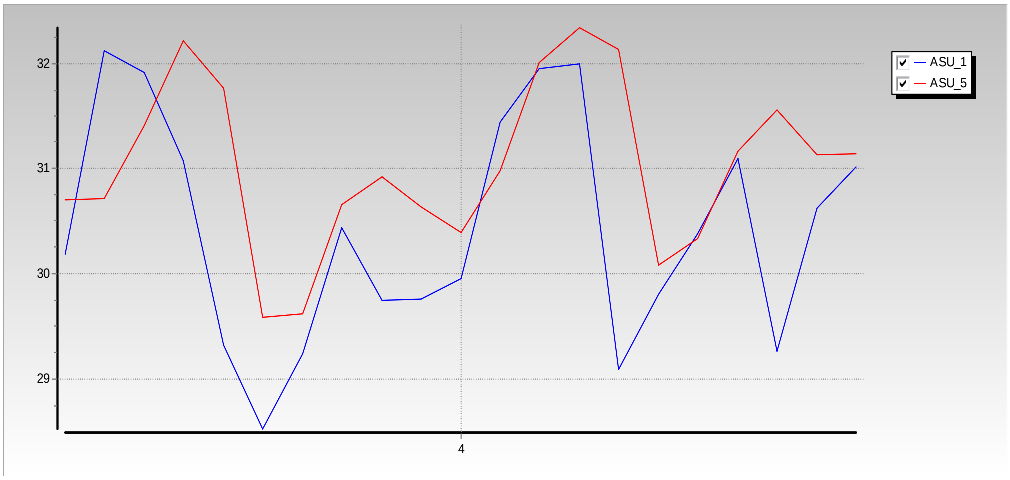

Figure 6.10. The dynamic simulated NOB concentration [mg/L] in the first, ASU_1, and last tank, ASU_5 as a function of time

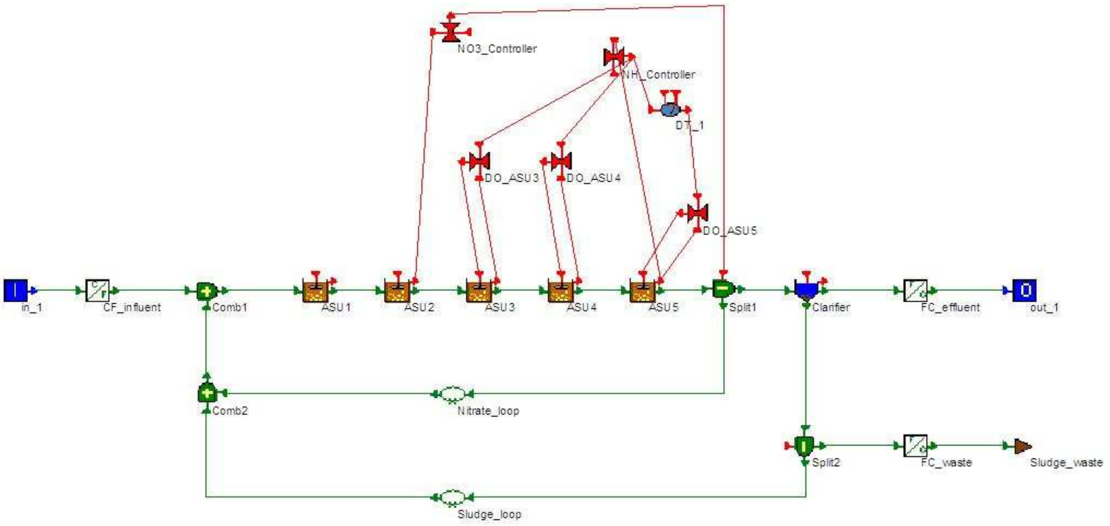

Figure 6.11 The Benchmark Simulation Model 1 with three oxygen controllers, an ammonia cascade controller with data treatment and a nitrate controller.

6.2 Effect of controlled dissolved oxygen concentration in the aerobic tanks on the production of N2O

In this subchapter the effect of the oxygen level in the three aerobic reactors is studied. The WEST configuration can be seen in figure 6.12. The controllers were tuned manually and had a Kp value of 25 and Ti and Tt of 0.1. These values were copied from another WWTP, the Neptune, and were manually changed to see if it worked properly, by looking at the graphs of the controlled variables and the time it took to return to the set point.

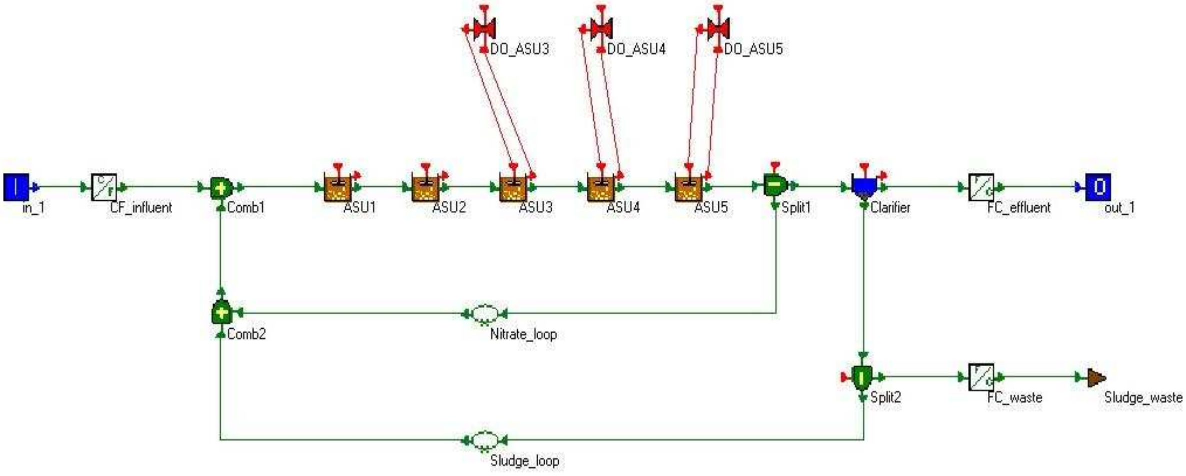

Figure 6.12. The Benchmark Simulation Model 1 configuration with three oxygen controllers.

The desired dissolved oxygen concentration was changed in the range of 1 to 3.25 mg/L to see the effect on the N_2O production. The total N_2O production was calculated by multiplying the volumetric stripping rates with the volume of the tank, for each tank and summing that up.

Then, the average over seven days was taken to compare the effect of dissolved oxygen concentrations. The concentration of N_2O in the effluent is very low and therefore negligible compared to the stripping of N_2O. For this reason it was not taken into account in the average production of N_2O. The results of the different oxygen set points can be seen in the figures 6.13 to 6.20.

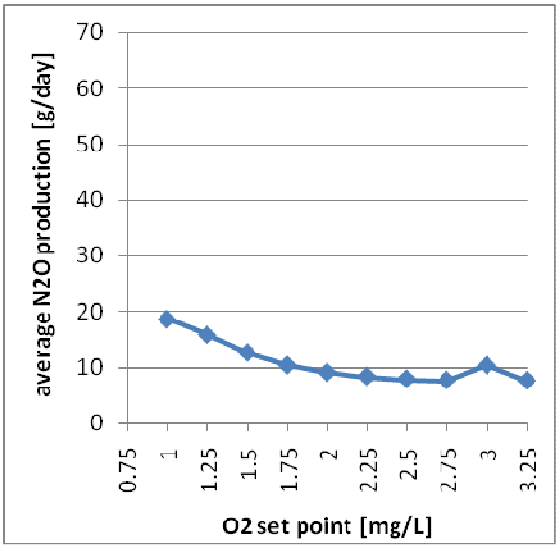

Figure 6.13. Average N_2O produced per day as function of the oxygen set point in the three aerobic tanks.

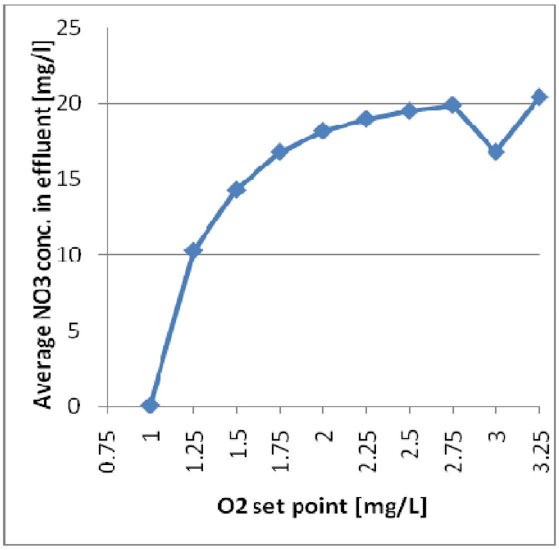

Figure 6.14. Average NO_3^- concentration in the effluent as function of the oxygen set point in the three aerobic tanks.

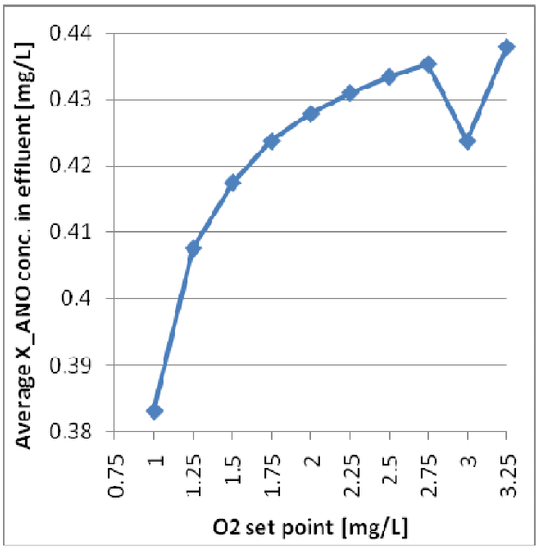

Figure 6.15. Average AOB concentration in the effluent as function of the oxygen set point in the three aerobic tanks.

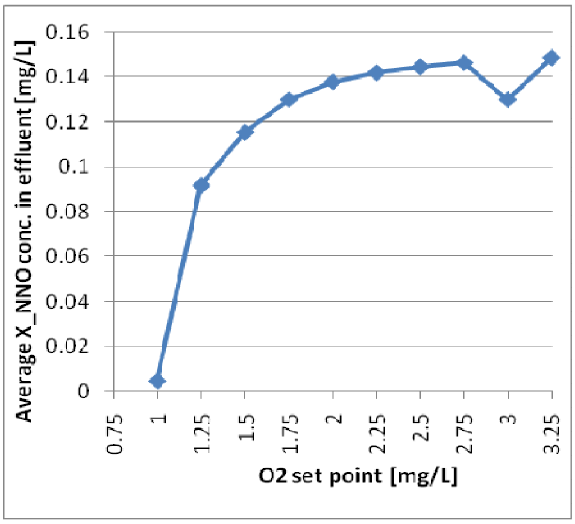

Figure 6.16. Average NOB concentration in the effluent as function of the oxygen set point in the three aerobic tanks.

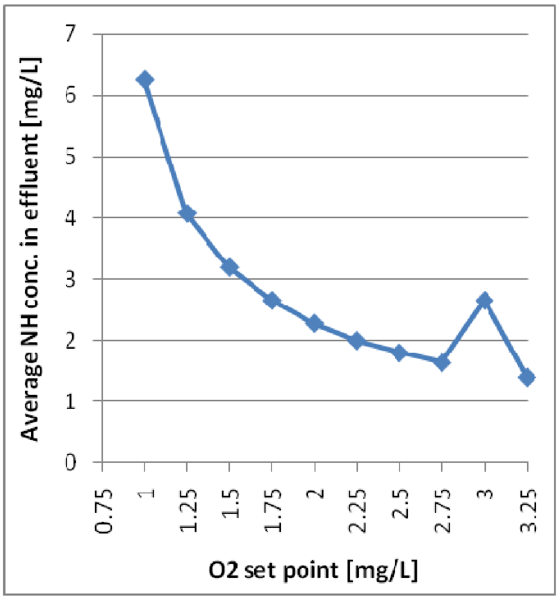

Figure 6.17. Average concentration of ammonia in the effluent as function of the oxygen set point in the three aerobic tanks.

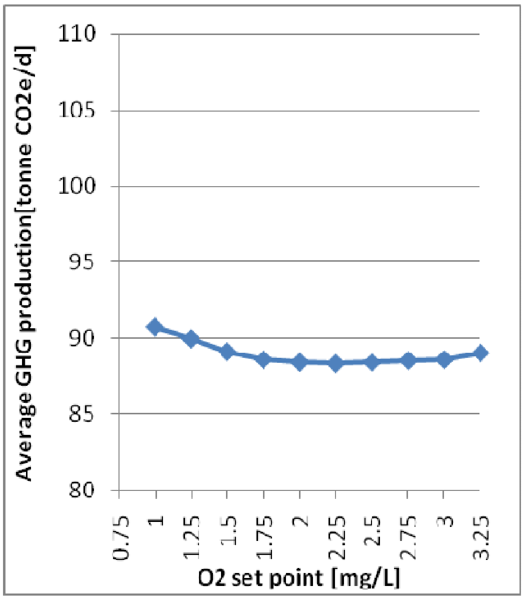

Figure 6.19. Average GHG production as function of the oxygen set point in the three aerobic tanks.

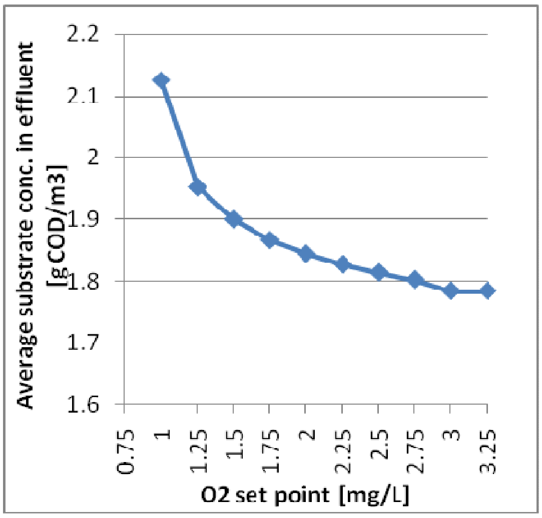

Figure 6.18. Average substrate concentration in the effluent as a function of the oxygen set point in the three aerobic tanks.

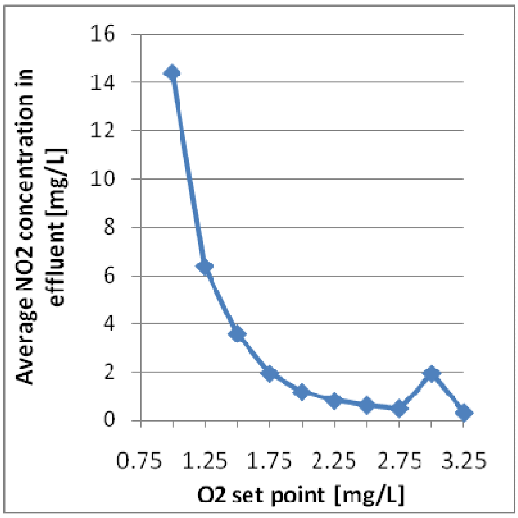

Figure 6.20. Average substrate concentration in the effluent as a function of the oxygen set point in the three aerobic tanks.

The higher the oxygen concentration in the tank is the lower the production of N_2O is. This is due to a higher oxygen concentration in the anoxic tanks. This leads to less anoxic conditions and thus the denitrifying bacteria are not able to perform the denitrification. As can be seen in figure 6.14 the concentration of nitrate increases, which is due to more conversion of ammonia to nitrate performed by the nitrifying bacteria. The concentration of ammonia decreases with an increase in oxygen as is shown in figure 6.17, which is a result of the higher conversion of ammonia. At an oxygen concentration of 1 mg/l and lower, there was no net growth of the nitrite oxidizing bacteria. The bacteria are washed out of the system. This was also found in literature Zeng *et al.* (2009). The nitrite oxidizing bacteria are more sensitive to a lack of oxygen. Figure 6.19 shows that the total GHG production also decreases as the production of N_2O decreases. At an oxygen concentration of 2.25 this total production starts to increase again due to a higher power use. The higher the desired oxygen concentration is, the higher the aeration intensity needs to be and the more power is used.

At the oxygen concentration set point of 3 mg/L there was an numerical error with the simulation. The integration constants were too large which made the calculations go into negative values. WEST gave the error that the variable N_2O became negative, which is not possible. Therefore at that point an unexpected decrease or increase in the figures is shown.

6.3 Effect of controlled ammonia concentration in the last aerobic tank on the production of N2O

After the oxygen controllers were evaluated also the nitrate and ammonia controllers were included. The configuration can be seen in figure 6.11. First the ammonia controller was studied. This PI controller works in a cascade manner, i.e. the controller uses the input to regulate the set point of another controller (Shaw, 2006) (Minxia & Atherton, 1994). The NH controller measures the ammonia concentration in the last aerobic tank and then modifies the set point of the three oxygen controllers to keep the ammonia concentration at the set point. The data limiter had a maximum of 2 mg/L for the dissolved oxygen. The K_p value was set at 10000 and the T_i and T_t value at 0.01. The ammonia concentration set point was changed from 0 till 4.5 mg/L. The nitrate set point was kept on a level of 1 mg/L.

From the results generated in figures 6.21 to 6.27, the following conclusions can be drawn. The highest production of N_2O is obtained at a set point between 3 and 4 mg/L of ammonia in the last aerobic tank. The amount of N_2O produced decreases when the ammonia set point increased further because the nitrifying bacteria are washed out. This is due to the induced low dissolved oxygen in the aerobic zone and limits the growth of X_{NNO}. Therefore the second step of nitrification will not take place, which leads to a lower concentration of NO_3^-. When there is less NO_3^-, there is also less denitrification and thus less N_2O produced. This can be seen in the figures with the average oxygen concentration, the average X_{NNO} concentration and the average NO_3^- concentration. At an ammonia set point of 3 mg/L the oxygen concentration is lower than 1 mg/L and the X_{NNO} concentration decreases rapidly with increasing ammonia set point which leads to a rapid decrease in the concentration of nitrate. Even though the N_2O emissions increase with a higher ammonia concentration the total GHG production decreases at the ammonia set point between 0.5 and 1.5 mg/L. This is due to the lower oxygen concentration which leads to a lower aeration intensity and thus less power usage. This shows that the total GHG production is more sensitive to aeration power than to N_2O production at low ammonia concentration.

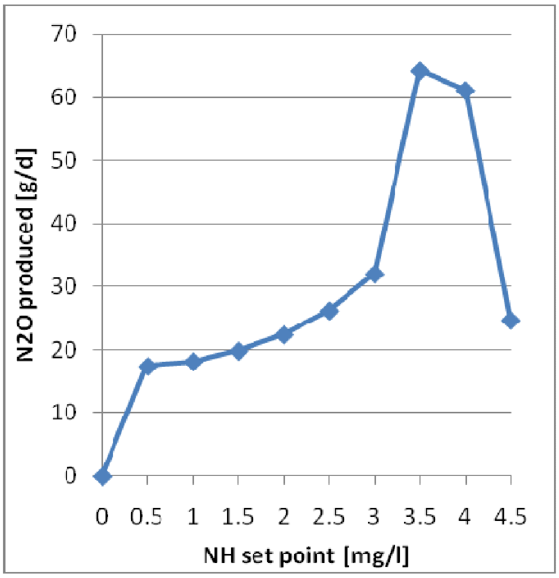

Figure 6.21. Average N_2O produced per day as function of the NH set point in the last aerobic tank.

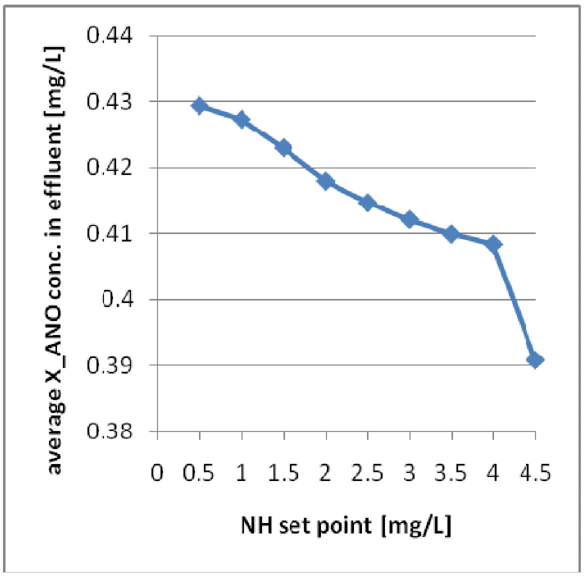

Figure 6.23 Average AOB concentration in the effluent as function of the NH set point in the last anoxic tank.

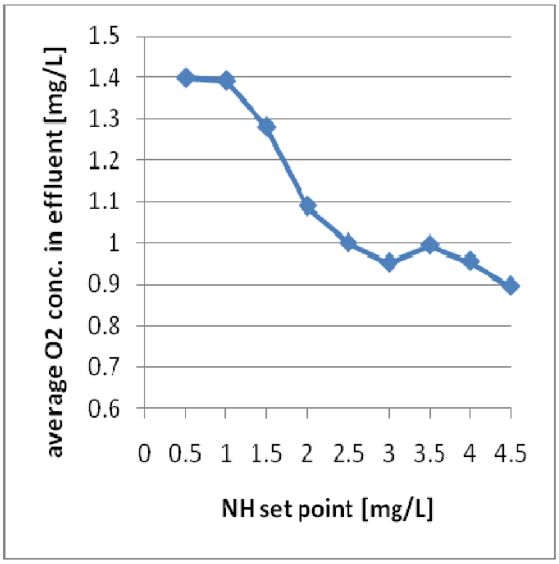

Figure 6.22. Average oxygen concentration in the effluent as a function of the NH set point in the last anoxic tank.

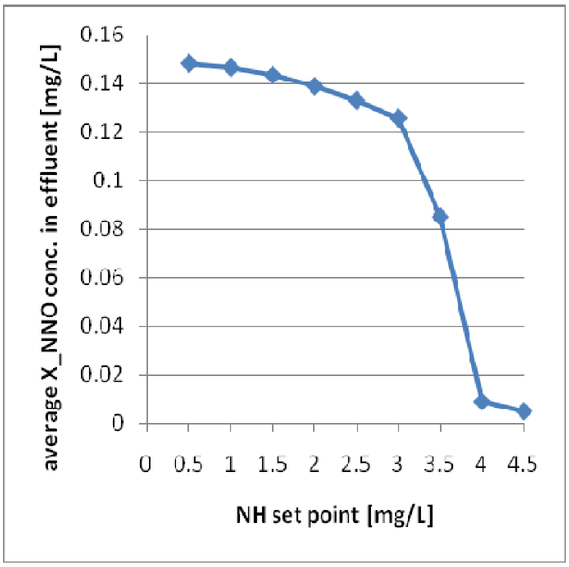

Figure 6.24. Average NOB concentration in the effluent as function of the NH set point in the last anoxic tank.

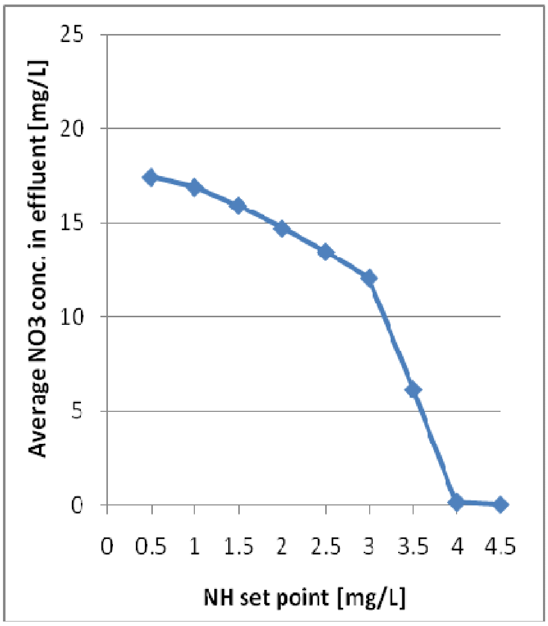

Figure 6.25. Average NO_3^- *concentration in the effluent as function of the NH set point in the last aerobic tank.*

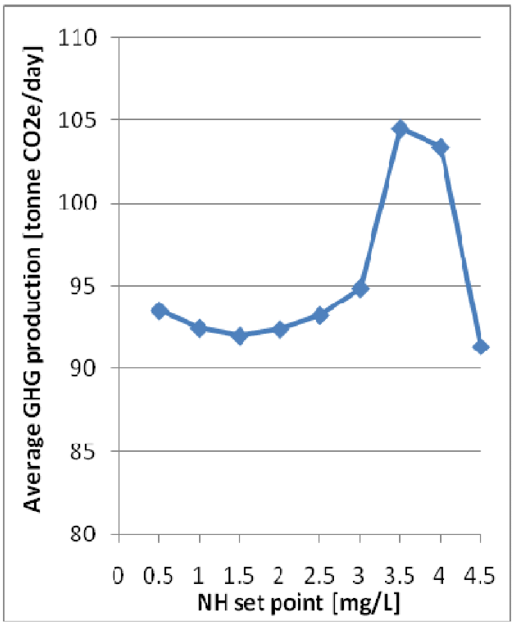

Figure 6.27. Average total GHG production as function of the NH set point in the last aerobic tank.

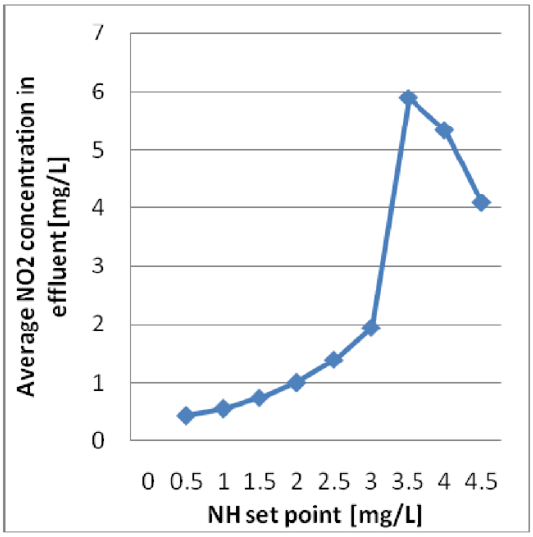

Figure 6.26. Average NO_2^- *concentration in the effluent as function of the NH set point in the last aerobic tank.*

6.4 Effect of nitrate concentration in the last aerobic tank on the production of N2O

After examining the effect of ammonia concentration, the effect of controlled nitrate concentrations in the last anoxic tank will also be analyzed. The implemented nitrate controller is also an anti windup PI controller. The controller measures the NO_3^- concentration in the second tank, which is the last anoxic tank. It then adjusts the internal recycle to keep the NO_3^- concentration in the second tank at the desired concentration. The nitrate set point was changed from 0.5 to 4 while the ammonia set point was maintained at 2 mg/L. Looking at the figures 6.21 to 6.27 this is a good ammonia set point as there are less GHGs produced. The K_p value was -2 and the T_t and T_i value 0.01 as was stated before. The same simulation procedure was applied, 100 days steady input to reach steady state, two times 14 days dynamic input. Only the last seven days are used for the evaluation. The results of the different nitrate set points can be seen in the figures 6.28 to 6.34.

Figure 6.28 shows that the production of N_2O increases as the NO_3^- set point increases. To increase the NO_3^- concentration, it is necessary to increase the recycle of nitrate coming from the aerobic zone. It is important to highlight that with the recirculation also oxygen is transported from the aerobic tanks to the anoxic tanks. With a higher oxygen input the processes of denitrification are increasingly inhibited as can be deduced from the process kinetics in table 5.2. When denitrification is not performed completely, it results in a higher N_2O production. The WWTP is not as sensitive to the nitrate concentration as to the oxygen and ammonia concentration. This can be seen in the figures as the graphs do not change with a different NO_3^- concentration. This is also the case for the total GHG production that was more or less constant for different NO_3^- concentrations as can be seen in figure 6.34.

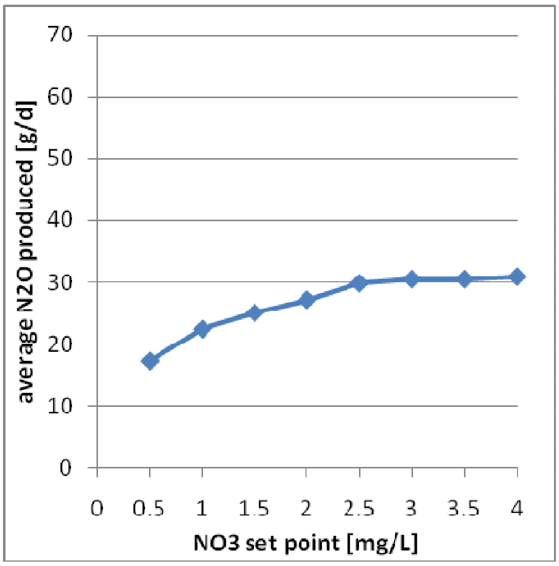

Figure 6.28. Average N_2O produced per day as function of the NO_3^- set point in the last aerobic tank.

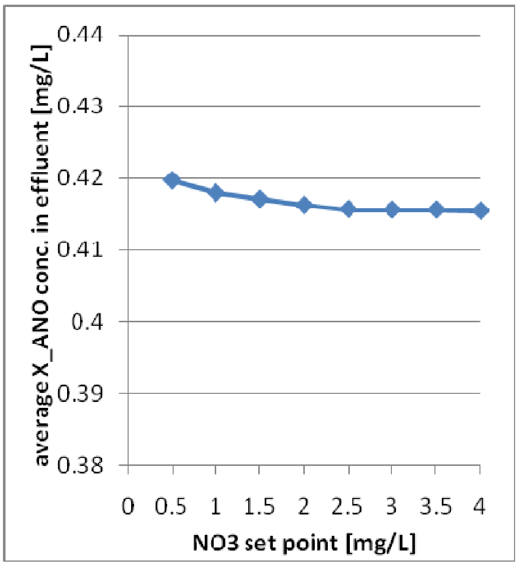

Figure 6.30. Average AOB concentration in the effluent as function of the NO_3^- set point in the last aerobic tank.

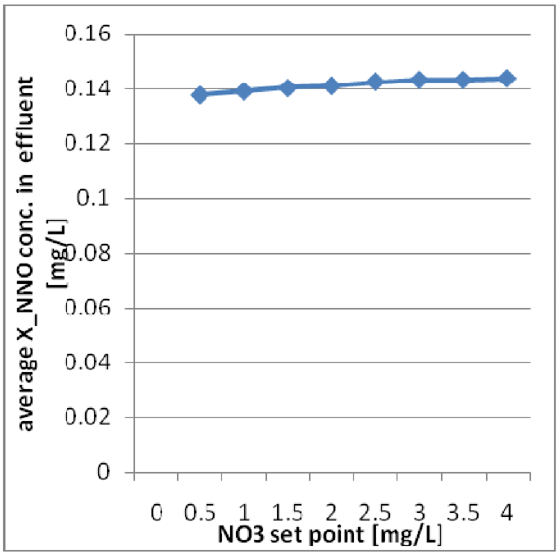

Figure 6.29. Average NOB concentration in the effluent as funtion of the NO_3^- set point in the last aerobic tank.

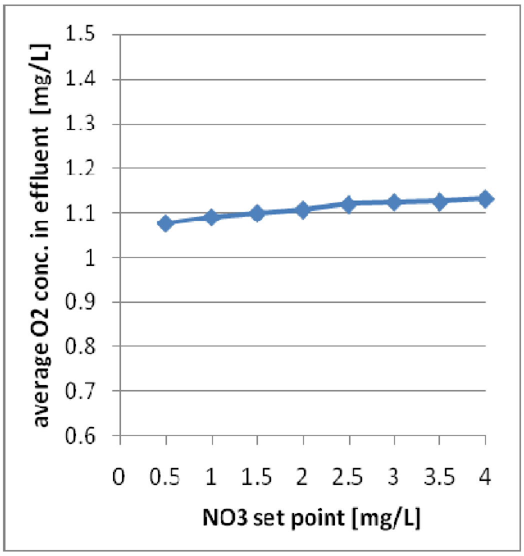

Figure 6.31. Average oxygen concentration in the effluent as function of the NO_3^- set point in the last aerobic tank.

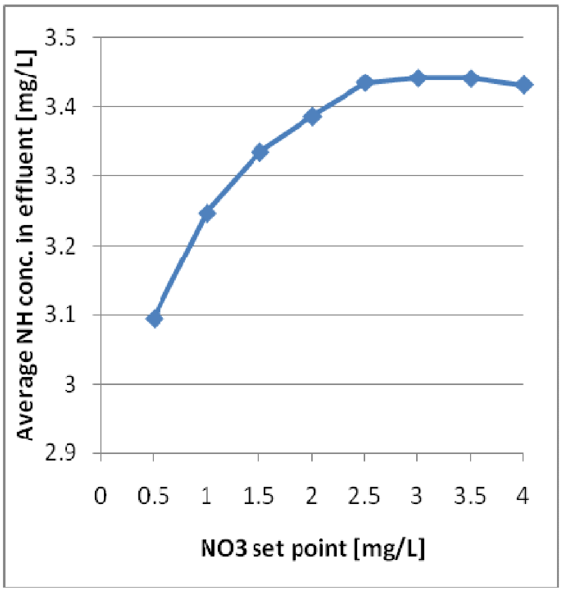

Figure 6.32. Average ammonia concentration in the effluent as function of the NO_3^- set point in the last aerobic tank.

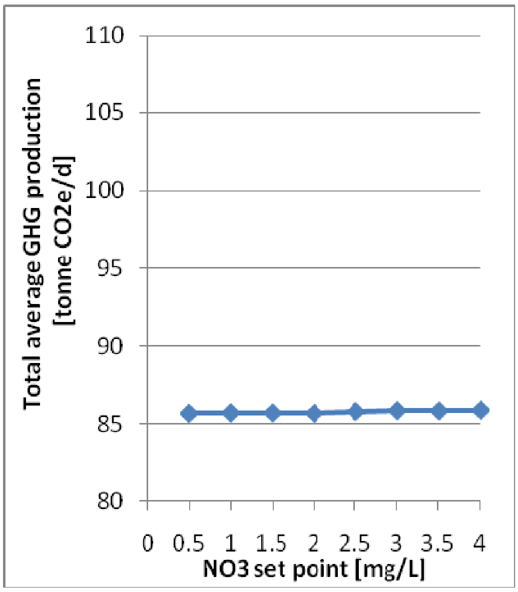

Figure 6.34. Average total GHG production as function of the NO_3^- set point in the last aerobic tank.

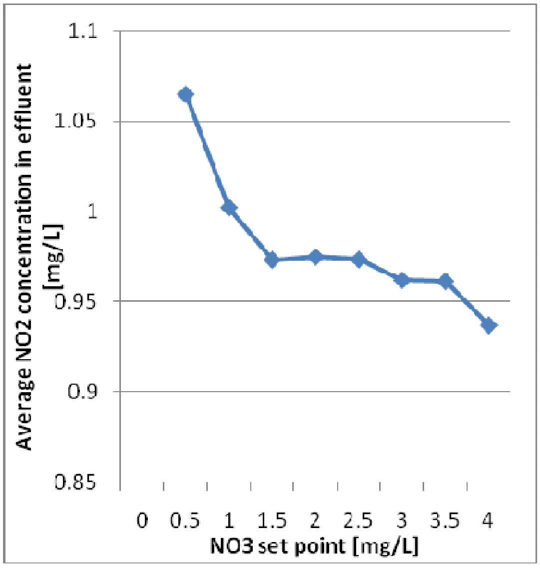

Figure 6.33. Average NO_2^- concentration in the effluent as function of the NO_3^- set point in the last aerobic tank.

Comparing the effects of oxygen, ammonia and nitrate it can be seen in the graphs that the system is more sensitive to ammonia. The N_2O production changes the most with different ammonia concentrations. For oxygen the changes in the different variables above an oxygen concentration of 1.75 are not large anymore. When looking at the average GHG production the oxygen concentration and nitrate concentration have almost no influence.

7. Conclusion and future work

The objective of this study was to quantify the GHGs for wastewater treatment plants using a model based approach. The model created by Bridle was adjusted with outputs of the BSM2 plant, which replaced the estimations of sludge production, biogas production and power usage. The GHGs can be realistically estimated with the created model as the results obtained are in the range of the results obtained by Bani Shahabadi *et al.* (2009) and Keller & Hartley (2003). The most GHGs are produced during anaerobic digestion and sludge reuse.

By extending the ASM1 into the ASM_2N4DN using the equations proposed by Hiatt & Grady (2008) the N_2O emissions can be modeled dynamically and in more detail. This gives a more realistic view of the N_2O production during the treatment of wastewater than the generation rate of Bridle. In the model of Hiatt & Grady some errors were found, the component S_{N2} was left out of the matrix, the equation rate for the anoxic growth of heterotrophs, reducing nitrite to nitric oxide had the wrong oxygen inhibition term and the stoichiometric matrix had rounded numbers in it. Also the equation to calculate the substrate FNA was probably mistyped.

The model was verified by using the continuity check, by comparing the results with the three different configurations used in the thesis of Hiatt (2006) and by comparing the results with the standard nitrogen removal plant modeled by ASM1. The default values for the parameters proposed by Hiatt & Grady (2008) worked expect for the value of K_{FNA} which needed to be decreased to $1 * 10^{-6}$. By including more processes into the ASM1 also more parameters are involved. More parameters mean more uncertainties as these parameters are estimated. However as the objective of this study was to estimate the GHGs of a WWTP, and therefore also the production of N_2O, it is important to include these extra processes.

The set point of the oxygen concentration had a small effect on the N_2O production in the BSM1 plant but a larger effect on the total GHG emissions as the power for aeration increases at a higher oxygen demand and aeration is a large part of the total GHGs. The higher the concentration of oxygen is, the higher the N_2O production and the total GHG production are. The effluent ammonia set point had the largest effect on the production of N_2O. For the BSM 1 plant the ammonia concentration should not exceed 4 mg/L as the NOB will be washed out and the WWTP will not work properly anymore. Until a concentration of 1.5 mg/L the N_2O production increases even though the total GHG production decreases, which is due to less oxygen demand and thus less aeration. Changing the set point of the nitrate concentration in the last anoxic tank has little effect on the N_2O and total GHG production. To minimize the average GHG production the ammonia concentration in the last tank should be around 1.5 mg/L. Overall it can be concluded that the system is more sensitive to the concentration of ammonia than the concentration of oxygen and nitrate.

Further work that can be done is replacing more parts of the empirical model of Bridle Consulting by dynamical models. This can be made possible by including CO_2 as a component and the processes in which it is produced and consumed in the ASM_2N4DN. Also, the implementation of a variable K_La in the anoxic tanks will lead to a better description of the stripping of the gases. This can be based on a model of the bubble formation of the gases. It is also possible to improve the model by making the variables temperature dependent. Besides extending the model it is also important to improve the model by checking the parameters set by Hiatt & Grady.

Further work can also focus on the effects of other conditions on the production of GHGs, such as the sludge retention time, hydraulic retention time and temperature. Besides improving the model, it is also wise to investigate the other two processes in which N_2O can be formed, namely nitrification and the chemical reactions.

With the results of this research the main contributors to the GHG emissions of a WWTP are known. Therefore to decrease the GHG emissions of a WWTP the most impact will probably be made by changing the processes of anaerobic digestion and reuse of sludge as these are the main contributors. Thus to decrease the GHG emissions of a WWTP improvements in those processes is needed.

List of symbols

b	specific decay rate,
b_{LA1}	decay coefficient, AOB,
b_{LA2}	decay coefficient, NOB**,**
$b_{L,H}$	decay coefficient, heterotrophs,
BOD	biological oxygen demand,
D_{O2}	diffusion coefficient of oxygen in water at 20 °C**,**
D_{N2}	diffusion coefficient of dinitrogen in water at 20 °C,
e	error, the difference between the measured value and the set point,
FA	free ammonia,
FNA	free nitrous acid,
f_D	fraction active biomass contributing to biomass debris,
HRT	hydraulic retention time,
$i_{N/XB}$	mass of nitrogen per mass of COD in active biomass,
$i_{N/XD}$	mass of nitrogen per mass of COD in biomass debris,
k_a	ammonification rate coefficient,
K_{FA}	half-saturation coefficient for free ammonia,
K_{FNA}	half saturation coefficient for free nitrous acid,
k_h	hydrolysis coefficient,
K_I	integral gain,
K_{I3NO}	nitric oxide inhibition coefficient, R3,
K_{I4NO}	nitric oxide inhibition coefficient, R4,
K_{I5NO}	nitric oxide inhibition coefficient, R5,
$K_{I,9FA}$	free ammonia inhibition coefficient, R9,
$K_{I,9FNA}$	free nitrous acid inhibition coefficient, R9,
$K_{I,10FA}$	free ammonia inhibition coefficient, R10,
$K_{I,10FNA}$	free nitrous acid inhibition coefficient, R10,
K_La_{O2}	oxygen transfer coefficient,
K_{N1}	half-saturation coefficient for NH3, heterotrophs,
K_{NO3}	half-saturation coefficient for nitrate-nitrogen, heterotrophs,
K_{NO2}	half-saturation coefficient for nitrite-nitrogen, heterotrophs,
K_{NO}	half-saturation coefficient for nitric oxide-nitrogen, heterotrophs,
K_{N2O}	half-saturation coefficient for nitrous oxide-nitrogen, heterotrophs,
$K_{O,A1}$	half-saturation coefficient for O_2, AOB,

$K_{O,A2}$	half-saturation coefficient for O_2, NOB,
$K_{O,H1}$	half-saturation coefficient for oxygen, heterotrophs, R1,
$K_{O,H2}$	half-saturation coefficient for oxygen, heterotrophs, R2,
$K_{O,H3}$	half-saturation coefficient for oxygen, heterotrophs, R3,
$K_{O,H4}$	half-saturation coefficient for oxygen, heterotrophs, R4,
$K_{O,H5}$	half-saturation coefficient for oxygen, heterotrophs, R5,
K_p	proportional gain,
K_S	half saturation constant,
K_{S1}	half-saturation coefficient for substrate, R1,
K_{S2}	half-saturation coefficient for substrate, R2,
K_{S3}	half-saturation coefficient for substrate, R3,
K_{S4}	half-saturation coefficient for substrate, R4,
K_{S5}	half-saturation coefficient for substrate, R5,
K_{S11}	half-saturation coefficient for substrate, R11,
K_X	half-saturation coefficient for hydrolysis of slowly biodegradable substrate,
MLVSS	mixed liquor volatile suspended solids,
η_y	anoxic yield factor,
η_g	anoxic growth factor, R1,
η_{g2}	anoxic growth factor, R2,
η_{g3}	anoxic growth factor, R3,
η_{g4}	anoxic growth factor, R4,
η_{g5}	anoxic growth factor, R5,
η_h	anoxic hydrolysis fractor,
pH	acidity,
Q_{ef}	flow of the effluent from the settler,
$Q_{wastage}$	flow of the waste sludge,
S_{ALK}	alkalinity,
S_{BN}	soluble biodegradable organic nitrogen,
$S_{B,Org}$	readily biodegradable substrate,
S_FNA	concentration of the Free Nitrous Acid,
S_{NHx}	$NH_4^+ + NH_3$ nitrogen,
S_{NO3}[1]	nitrate and nitrite nitrogen,
S_{NO3}	nitrate,
S_{NO2}	nitrite,
S_{NO}	nitric oxide,

S_{N2O}	nitrous oxide,
S_{N2}	dinitrogen,
S_{O2}	oxygen (negative COD),
S_U	soluble inert organic matter,
SRT	sludge retention time,
TKN	total Kjeldahl nitrogen, which is the ammonia and ammonium together,
TN	total nitrogen which is nitrate, nitrite with the TKN,
TSS	total suspended solids,
u	input,
u_0	initial input,
μ_{max}	maximum specific growth rate,
$\mu_{max, B,H}$	maximum specific growth rate, heterotrophs,
$\mu_{max, B,A1}$	maximum specific growth rate of ammonia oxidizing bacteria, AOB,
$\mu_{max, B,A2}$	maximum specific growth rate of the nitrite oxidizing bacteria, NOB,
VS	volatile solids,
$V_{reactor}$	volume of the reactor,
X_{ANO}^{1}	active autotrophic biomass,
X_{ANO}	ammonia nitrifying organisms,
X_{BN}	particulate biodegradable organic nitrogen,
XC_B	slowly biodegradable substrate,
X_{NNO}	nitrite nitrifying organisms,
X_{OHO}	active heterotrophic biomass,
X_P	particulate products arising from biomass decay,
$X_{TSS,ef}$	amount of total suspended solids in the effluent of the settler,
$X_{TSS,reactor}$	amount of total suspended solids in the reactor,
$X_{TSS, wastage}$	amount of total suspended solids in the waste sludge,
X_U	particulate inert organic matter,
Y	true growth yield,
Y_{A1}	autotrophic yield, AOB,
Y_{A2}	autotrophic yield, NOB,
Y_H	heterotrophic yield,

Appendixes

A. Tables used for the continuity check

Table 1. COD balance of components used in the ASM2N_4DN for the continuity check

Component	COD
S_U	1
S_B,Org	1
X_U	1
XC_B	1
X_OHO	1
X_ANO	1
X_NNO	1
X_P	1
S_O2	-1
S_NO3	-64/14
S_NO2	-48/14
S_NO	-40/14
S_N2O	-32/14
S_N2	-24/14

Table 2. Nitrogen balance of components used in the ASM2N_4DN

Component	N
X_OHO	0.086
X_ANO	0.086
X_NNO	0.086
X_P	0.06
S_NO3	1
S_NO2	1
S_NO	1
S_N2O	1
S_N2	1
S_NH	1
S_BN	1
X_BN	1
S_N2	1

Table 3. Charge balance of components used in the ASM2N_4DN for the continuity check

Component	Charge
S_NO3	-0.071
S_NO2	-0.071
S_NH	0.071
S_ALK	-1

B. Verification tables of the ASM_2N4DN

Table 1. Comparison of the result concentrations in the first reactor of Hiatt & Gradys second system with the ASM_2N4DN model.

	ASMN	ASM_2N4DN	Difference	Difference percentage with ASMN result
X_U	**350**	341.0	9.0	2.6
XC_B	**50.3**	50.1	0.2	0.4
X_{OHO}	**583**	570.2	12.8	2.2
X_{ANO}	**48.5**	30.2	10.1	20.8
X_{NNO}		8.2		
X_P	**185**	172.5	12.5	6.8
$S_{B,Org}$	**2.7**	2.6	0.1	3.7
S_{NO3}	**25.8**	15.6	-0.3	-1.3
S_{NO2}		10.0		
S_{NO}		0.0		
S_{N2O}		0.5		
S_{N2}	**-**	1.7	-	-
S_{NH}	**1.4**	2.2	-0.8	-57.1
S_{BN}	**0.5**	0.3	0.2	40.0
X_{BN}	**3.6**	3.6	0.0	0.0
S_{ALK}	**1.5**	1.5	0.0	0.0

Table 2. Comparison of the result concentrations in the second reactor of Hiatt & Gradys second system with the ASM_2N4DN model.

	ASMN	ASM_2N4DN	Difference	Difference percentage with ASMN result
X_U	**350**	341.0	9.0	2.57
XC_B	**24.6**	24.4	0.2	0.81
X_{OHO}	**555**	545.1	9.9	1.78
X_{ANO}	**47.6**	29.9	9.6	20.17
X_{NNO}		8.1		
X_P	**193**	180.2	12.8	6.63
$S_{B,Org}$	**1.1**	1.0	0.1	9.09
S_{NO3}	**31.5**	24.8	0.8	2.44
S_{NO2}		5.3		
S_{NO}		0.0		
S_{N2O}		0.6		
S_{N2}	**-**	2.3	-	-
S_{NH}	**0.2**	0.3	-0.1	-50.00
S_{BN}	**0.3**	0.2	0.1	33.33
X_{BN}	**2.0**	2.0	0.0	0.00
S_{ALK}	**1.0**	1.1	-0.1	-10.00

Table 3. Comparison of the result concentrations in the anoxic reactor of Hiatt & Gradys third system with ASM_2N4DN model.

	ASMN	ASM_2N4DN	Difference	Difference percentage with ASMN result
X_{U}	**350.0**	341	9.0	2.6
XC_{B}	**65.3**	65.3	0.0	0.0
X_{OHO}	**551.0**	518.4	32.6	5.9
X_{ANO}	**36.6**	27.3	0.1	0.3
X_{NNO}		9.2		
X_{P}	**183.0**	166.1	16.9	9.2
$S_{B,Org}$	**2.6**	2.9	-0.3	-11.5
S_{NO3}	**2.0**	0.7	0.4	18.5
S_{NO2}		0.5		
S_{NO}		0.23		
S_{N2O}		0.2		
S_{N2}	**-**	22.9	-	-
S_{NH}	**7.4**	8.2	-0.8	-10.8
S_{BN}	**0.4**	0.3	0.1	25.0
X_{BN}	**4.7**	4.7	0.0	0.0
S_{ALK}	**3.6**	3.7	-0.1	-2.8

Table 4. Comparison of the result concentrations in the aerobic reactor of Hiatt & Gradys third system with ASM_2N4DN model

	ASMN	ASM_2N4DN	Difference	Difference percentage with ASMN result
X_U	**350.0**	341.0	9.0	2.6
XC_B	**43.9**	42.2	1.7	3.9
X_{OHO}	**544.0**	521.8	22.2	4.1
X_{ANO}	**41.1**	28.1	3.5	8.5
X_{NNO}		9.5		
X_P	**181.0**	168.2	12.8	7.1
$S_{B,Org}$	**1.7**	1.6	0.1	5.9
S_{NO3}	**8.6**	7.5	0.9	10.6
S_{NO2}		0.1		
S_{NO}		0.0		
S_{N2O}		0.1		
S_{N2}	**-**	23.1		
S_{NH}	**1.7**	2.6	-0.9	-52.9
S_{BN}	**0.4**	0.2	0.2	50.0
X_{BN}	**3.4**	3.2	0.2	5.9
S_{ALK}	**2.9**	2.9	0.0	0.0

C. Parameter values used in ASM_2N4DN

Table 1. Parameters defined by Hiatt & Grady that are used in the ASMN model

Parameter	Value	Parameter	Value
$\mu_{max\ B,H}$	6.25	K_{I5NO}	0.075
$b_{L,H}$	0.408	$\mu_{max\ BA1}$	0.78
Y_H	0.6	$\mu_{max\ BA2}$	0.78
η_y	0.9	b_{LA1}	0.096
η_g	0.8	b_{LA2}	0.096
η_{g2}	0.28	Y_{A1}	0.18
η_{g3}	0.16	Y_{A2}	0.06
η_{g4}	0.35	K_{FA}	0.0075
η_{g5}	0.35	K_{FNA}	0.0001
K_{S1}	20	K_{S11}	20
K_{S2}	20	K_{OA1}	0.6
K_{S3}	20	K_{OA2}	1.2
K_{S4}	20	K_{I9FA}	1
K_{S5}	40	K_{I9FNA}	0.1
$K_{O,H1}$	0.1	K_{I10FA}	0.2
$K_{O,H2}$	0.1	K_{I10FNA}	0.04
$K_{O,H3}$	0.1	f_D	0.08
$K_{O,H4}$	0.1	$i_{N/XB}$	0.086
$K_{O,H5}$	0.1	$i_{N/XD}$	0.06
K_{NO3}	0.2	η_h	0.06
K_{NO2}	0.2	k_a	3.8592
K_{NO}	0.05	K_X	0.15
K_{N2O}	0.05	K_{N1}	0.1
K_{I3NO}	0.5	k_h	2.208
K_{I4NO}	0.3	K_X	0.15

D. GHG calculation for BSM2 done in Matlab

```
%CO2calculation calculates the CO2 emissions of wastewater treatment
%plants
% [CO2emission]= CO2calculation(a,b,c,d)
% load workspace_ol    % BSM2 file.

%CO2 digester

% parameters
    GWPCH4 = 23;        % global warming product of methane (kg CO2/kg
CH4)
    GWPN2O = 296;       % global warming product of nitrous oxide (kg
CO2/kg CH4)
    MWCO2 = 44;         % molar weight of CO2 (g/mol)
    MWCH4 = 16;         % molar weight of CH4 (g/mol)
    CH4content = 65;    % volume percentage of CH4 in biogas (%)
    MV= 22.41;          % volume of 1 mol of gas (m3)

    %     input
Q_CO2out= Carbondioxidevec;     %%% (kgCO2.m-3)
Q_CH4out= Methanevec;         %%% (kgCH4.m-3)
Q_gasout= digesteroutpart(:,51);%%% (m3.day-1 of gas)

%     output
% CH4gasconc = (100*CH4content*MWCH4/MV)/(CH4content*MWCH4/MV + (100-
CH4content)*MWCO2/MV);  % massconc
% Q_CH4out = Q_gasout * CH4gasconc /100; %(kg/d)

%     CO2-emissions produced directly by anaerobic digester (kg/d)
    CO2ademissions = (Q_CO2out.*Q_gasout)+(Q_gasout.*Q_CH4out*GWPCH4);

% Sludge reuse CO2 emissions

    %     parameter
    C_to_CO2 = 0.80;            % carbon mineralisation (fraction of
sludge C to CO2)
    MWC = 12;                   % Molar weight of carbon (g/mol)
    fractoagri = 0.38;          % fraction of sludge that is reused at
agricultural site
    fractocomp = 0.45;          % fraction of sludge that is reused at
compost site
    fractoforest = 0.17;        % fraction of sludge that is reused at
forestry
    CO2truck = 1;               %kg CO2/km
    distanceagri = 150;         % km
    distancecomp = 20;          % km
    distanceforest = 144;       % km
    Vtruck = 40;                % Volume truck m3
    cakesolids = 19.6;          % percentage of cake solids in sludge

    %     input
Q_sludgeout= (sludgepart(:,14).*sludgepart(:,15))/1000; %% kg TSS.day-1
```

```
COD_dewatering = (dewateringoutpart(:,1)+ dewateringoutpart(:,2)+
dewateringoutpart(:,3)+ dewateringoutpart(:,4)+ dewateringoutpart(:,5)+
dewateringoutpart(:,6)+ dewateringoutpart(:,7))/1000; % gCOD/m3 sludge


    %     output
    Carboninsludge =
(COD_dewatering/(60/160)).*dewateringoutpart(:,15); % kgC/day %%%%
C5H7O2N + 5 O2 ? 5 CO2 + NH3 + 2 H2O (5*32)/(5*12)
    CO2agrisludge = MWCO2/MWC*Carboninsludge.*fractoagri*C_to_CO2;
    CO2compsludge = MWCO2/MWC*Carboninsludge.*fractocomp*C_to_CO2;
    CO2forestsludge = MWCO2/MWC*Carboninsludge.*fractoforest*C_to_CO2;
    truckagri =
Q_sludgeout*fractoagri*CO2truck*distanceagri*2/(Vtruck*cakesolids/100*1
000);
    truckcomp =
Q_sludgeout*fractocomp*CO2truck*distancecomp*2/(Vtruck*cakesolids/100*1
000);
    truckforest =
Q_sludgeout*fractoforest*CO2truck*distanceforest*2/(Vtruck*cakesolids/1
00*1000);

    totalCO2reuse=
CO2agrisludge+CO2compsludge+CO2forestsludge+truckagri+truckcomp+truckfo
rest;

% Biotreatment CO2 emissions

%             parameter
            CO2y = 1.947;   %CO2 yield from end decay (kg CO2/kg
biomass respired)
%                           C5H7O2N + 5O2 -> 5CO2 + 2H2O + NH3
%                           113:5*44 = 1:1.947 (moneith et al)
            decaycoef=0.05; % endogenous decay coefficient (1/d)

%             input
Q_influent = inpart(:,15);%% influent flow
MLVSS =
(reac1part(:,14)*VOL1+reac2part(:,14)*VOL2+reac3part(:,14)*VOL3+reac4pa
rt(:,14)*VOL4+reac5part(:,14)*VOL5)./1000; % in VSS kg
HRT= inpart (:,15)./(VOL1+VOL2+VOL3+VOL4+VOL5);%%% HRT (days)

%              output
          biomassdecayed= MLVSS*decaycoef;    % amount of biomass
decayed in the five bioreactors (kg/d)
            CO2bdemissions = biomassdecayed*CO2y;              % CO2
emissions of the biotreatment (kgCO2/d) %%%%

%          BOD oxidation all 5 reactors
%     parameter
    CO2_BOD = 1.1;      % CO2 from BOD oxidation (kg CO2/kg O2 for BOD
oxidised)
                        % stoichiometry 2 C10H19O3N + 25 O2 -> 20 CO2
+16 H2O +2 NH3
```

```
                        % 25*32 : 20*44 (Moneith et al.) Only oxygen in
the last three reactors
    BOD5_BODu = 0.67;   % fraction (Black&Veatch)
    Yh = 0.84;          % Cell yield coefficient (kgVS/kgBOD)
(Black&Veatch)
    BODrem = 36;       % BOD removal fraction in the primary clarifier
    SRT  = 13;
    %     input

Q_BOD5in = (BOD5in.*inpart(:,15))./1000; %%%kg.day
Q_BOD5out =(BOD5e.*effluentpart(:,15))./1000; %%%kg.day

    % output

obsY                = Yh/(1+decaycoef*SRT);                          %
observed yield [kgvss/kgBOD]
BODox               = (100-BODrem) *Q_BOD5in/100 - Q_BOD5out;   % BOD
oxidised (kg/d)
netbiomassproduced  = BODox*obsY;                                   %
netbiomassproduced (kg VSS/d)
oxygenBOD           = BODox/BOD5_BODu-1.42*netbiomassproduced;     %
oxygen used in the bod oxidation
CO2oxemissions      = oxygenBOD*CO2_BOD;                          % The
CO2 emissions from the BOD oxidation in the 5 reactors. %%% 34944x1



    %         Nitrogen removal all 5 reactors
%     CO2 credit from ammonia removal

%     parameter
    CO2cons=4.49; % CO2 consumed by nitrifiers (kg CO2/kg N nitrified)
(EPA nitrogen removal manual)
%                 20CO2 +14NH4 -> 10 NO3 + 4C5H7O2N + 24 H +2 H20 ...
%                 880:196 -> 4.49:1

%     input
Q_TKNin = (SNKjin.*inpart(:,15))./1000; %%%kg.day
Q_TKNout = (SNKje.*effluentpart(:,15))./1000; %%%kg.day

% output
    Nbiomass = netbiomassproduced*0.12;     % MWbiomass 113 MW N 14
14/113 = 0.12 (kg N/d)
    NH3ox=(Q_TKNin-Q_TKNout)-Nbiomass;      % amount of NH3 oxidised
(kg NH3/d)
    CO2cred=NH3ox*CO2cons;

    %     N2O formed
%     parameter
    N2Ogen = 0.004; % N2O generation rate (kgN2O/kg N feed) data from
Lee Walker
%                    different for different wwtp,

%     input
Q_TKNin = (SNKjin.*inpart(:,15))./1000; %%%kg.day
```

```
Q_TNout = ((SNKje + SNOe).*effluentpart(:,15))./1000; %%%total nitrogen
kg.day

%     output
    N2O =(Q_TKNin-Q_TNout)*N2Ogen;  %amount of N2O generated(kgN2O/m3)
    CO2_N2O=N2O*GWPN2O;             %(kgCO2/m3)

% Chemical use
%   parameters
%     lime_CO2 = 1640 % imbedded CO2 in lime (kgCO2/tonne lime)
%     caustic_CO2 = 1130 % imbedded CO2 in caustic (kgCO2/tonne
caustic)
%     hypo_CO2 = 801 %imbedded CO2 in hypochlorite (kgCO2/tonne hypo
(12,5%))
%     poly_CO2 = 1800 % imbedded CO2 in polymer (kgCO2/tonne polymer)
%     chlo_CO2 = 112 % imbedded CO2 in chlorine (kgCO2/tonne chlorine)
%     input
%     limeadded  = amount of lime added in the wwtp (kg lime/kg
drysolids)
%     causticadded = amount of caustic added in the wwtp (kg caustic/d)
%     hypoadded = amount of hypochlorite added in the wwtp (kg
hypochlorite/d)
%     polyadded = amount of polymer added in the wwtp (kg polymer/dry
t)
%     chloadded = amount of chlorine added in the wwtp (kg chlorine/d)
%     sludgetodigester =Inflow...
%     CO2_lime=limeadded/1000*sludgetodigester*lime_CO2
%     CO2_caustic=caustic_CO2*causticadded/1000
%     CO2_hypo=hypo_CO2*hypoadded/1000
%     CO2_poly=polyadded*digestedsludgemass*poly_CO2/1000000
%     CO2_chlo=chlo_CO2*chloadded/1000
%     CO2chem = CO2_lime+CO2_caustic+CO2_hypo+CO2_poly+CO2_chlo

% Parasitic power draw
 %     parameter
    CO2_kwh = 0.94; % CO2 from power plant (kg CO2/kWh)
    ox_resp = 1.416; % oxygen for respiration (kg O2/kgVSS)
                    % C5H7O2N : 5O2 113:160 1:1.416
    ox_nit = 4.32; % oxygen for nitrification (kg O2/kg N nitrified)
    ox_dn = 2.28; % oxygen credit for denitrification (kg O2/kg N
removed)

%     input
En_aer = airenergyvec; %%aeration
En_pump = pumpenergyvec;%% pumping
En_heat = Heatpower.*24;%% digester

%     output
        airCO2= En_aer*CO2_kwh;
        pumpCO2=En_pump*CO2_kwh;
        heatCO2=En_heat*CO2_kwh;
        CO2_power = airCO2+pumpCO2+heatCO2; %%% 34944x1
CO2emission=(CO2ademissions+CO2agrisludge+CO2bdemissions+CO2oxemissions
+CO2cred+CO2_N2O+CO2_power);
```

E. GHG calculations for BSM1 done in Matlab

```
%CO2calculation calculates the CO2 emissions of wastewater treatment
%plants


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%% Transformation variables for Neptune %%%%%%%%%%%%%%

Q_influent      = in_Q;%% influent flow
MLVSS           = ( ASU1_TSS*ASU1_V + ASU2_TSS*ASU2_V + ASU3_TSS*ASU3_V
+ ASU4_TSS*ASU4_V + ASU5_TSS*ASU5_V)./1000; % in VSS kg
TSSproducedperd = waste_sludge_kg_perday;
TCODsav         = waste_COD;

Total_V         = ASU1_V + ASU2_V + ASU3_V+ ASU4_V + ASU5_V;
Q_effluent      = eff_Q;

TKN_inf = in_TKN;
TKN_eff = eff_TKN;
NOx_eff = eff_S_NOx;

BOD5_inf = in_BOD5;
BOD5_eff    = eff_BOD5;

BSM_aeration = aer_energy_alter; %%aeration
BSM_pumping = pump_energy;%% pumping

timevector = t;
totalt = lag;
%Remember to change scenarios if the influent file
%changes!!!!!!!!!!!!!!!!!
scenario    =   1;
if scenario==1
sludgeprim=10784 * 0.75;   %kg sludge/day %%% (kgTSS.m-3) %6461
KgCOD·m-3 produced in the 1ari settler %0.75 is the conversion TSS/COD
end

%%%%%%%CO2 digester%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%%%%%%%% PARAMETERS
    GWPCH4      = 27;        % global warming product of methane (kg
CO2/kg CH4)
    GWPN2O      = 289;       % global warming product of nitrous oxide
(kg CO2/kg CH4)
    MWCO2       = 44;          % molar weight of CO2 (g/mol)
    MWCH4       = 16;          % molar weight of CH4 (g/mol)
    CH4content  = 65;    % volume percentage of CH4 in biogas (%)
    MV          = 22.41;           % volume of 1 mol of gas (m3)
    VSdest      = 0.60;          % fraction of VS that is destroyed in
digester (-)
    VSprimsludge = 88;  %%% percentage primary sludge that is VSS of TS
```

```
    VSsecsludge = 84;      % percentage of secondary sludge that is VS

    %%%%%%%% INPUT

sludgesec       =   TSSproducedperd; %kg sludge/day

%%%%%%%% OUTPUT
Sludgetotal     =   sludgeprim+sludgesec;       %kg sludge/day
VSdestroyed     =   Sludgetotal*VSdest;         %kg sludge/day
Sludgedigested  =   Sludgetotal-VSdestroyed;    %kg sludge/day
sludgetotalVS   =
(sludgeprim*VSprimsludge+sludgesec*VSsecsludge)/Sludgetotal;
VStotal         =   Sludgetotal*sludgetotalVS/100;
SludgedigestedVS =  100*(VStotal-VSdestroyed)/Sludgedigested;
Biogas          =   Sludgetotal-Sludgedigested; %kg biogas/day
concCH4         =
(CH4content*100*MWCH4/MV)/(CH4content*MWCH4/MV+(100-
CH4content)*MWCO2/MV); %masspercentage CH4 in biogas
Q_CH4gasout     =   concCH4/100*Biogas;         %kgCH4/day
Q_CO2gasout     =   Biogas-Q_CH4gasout;         %kgCO2/day
CO2ademissions  =   (Q_CO2gasout)+(Q_CH4gasout.*GWPCH4);   %CO2-
emissions produced directly by anaerobic digester (kg/d)



%%%Sludge reuse CO2 emissions%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%%%%%%%% PARAMETERS
    C_to_CO2 = 0.80;            % carbon mineralisation (fraction of
sludge C to CO2)
    MWC = 12;                   % Molar weight of carbon (g/mol)
    fractoagri = 0.38;          % fraction of sludge that is reused at
agricultural site
    fractocomp = 0.45;          % fraction of sludge that is reused at
compost site
    fractoforest = 0.17;        % fraction of sludge that is reused at
forestry
    CO2truck = 1;               %kg CO2/km
    distanceagri = 150;         % km
    distancecomp = 20;          % km
    distanceforest = 144;       % km
    Vtruck = 40;                % Volume truck m3
    cakesolids = 19.6;          % percentage of cake solids in sludge
    densitysludge = 1000;       % density of sludge [kg/m3]


%%%%%%%% INPUT
Q_sludgeout     = TSSproducedperd;
%(sludgepart(:,14).*sludgepart(:,15))/1000; %%% kg TSS.day-1
COD_dewatering  = TCODsav; % (dewateringoutpart(:,1)+
dewateringoutpart(:,2)+ dewateringoutpart(:,3)+ dewateringoutpart(:,4)+
dewateringoutpart(:,5)+ dewateringoutpart(:,6)+
dewateringoutpart(:,7))/1000; % gCOD/m3 sludge
HRT             = Q_influent./(Total_V);%%% HRT (days)
```

```
MLVSS;%           =
(reac1part(:,17)*VOL1+reac2part(:,17)*VOL2+reac3part(:,17)*VOL3+reac4pa
rt(:,17)*VOL4+reac5part(:,17)*VOL5 + reac6part(:,17)*VOL6 +
reac7part(:,17)*VOL7)./1000; % in VSS kg

%%%%%%%% OUTPUT
    Carboninsludge = 0.3962*Sludgedigested+9.4548; % kgC/day
    CO2agrisludge = MWCO2/MWC*Carboninsludge.*fractoagri*C_to_CO2;
    CO2compsludge = MWCO2/MWC*Carboninsludge.*fractocomp*C_to_CO2;
    CO2forestsludge = MWCO2/MWC*Carboninsludge.*fractoforest*C_to_CO2;
    truckagri =
Q_sludgeout*fractoagri*CO2truck*distanceagri*2/(Vtruck*cakesolids/100*d
ensitysludge);
    truckcomp =
Q_sludgeout*fractocomp*CO2truck*distancecomp*2/(Vtruck*cakesolids/100*d
ensitysludge);
    truckforest =
Q_sludgeout*fractoforest*CO2truck*distanceforest*2/(Vtruck*cakesolids/1
00*densitysludge);

    totalCO2reuse=
CO2agrisludge+CO2compsludge+CO2forestsludge+truckagri+truckcomp+truckfo
rest;



%%%Biotreatment CO2 emissions%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%%%% Biomass decayed all reactors%%%%

%%%%%%%% PARAMETERS
        CO2y    = 1.947;   %CO2 yield from end decay (kg CO2/kg biomass
respired)
%                           C5H7O2N + 5O2 -> 5CO2 + 2H2O + NH3
%                           113:5*44 = 1:1.947 (moneith et al)
        decaycoef = 0.05; % endogenous decay coefficient (1/d)

%%%%%%%% INPUT
Q_influent; %      = inpart(:,20);%% influent flow
MLVSS; %=
(reac1part(:,14)*VOL1+reac2part(:,14)*VOL2+reac3part(:,14)*VOL3+reac4pa
rt(:,14)*VOL4+reac5part(:,14)*VOL5)./1000; % in VSS kg
HRT; %= inpart (:,15)./(VOL1+VOL2+VOL3+VOL4+VOL5);%%% HRT (days)

%%%%%%%% OUTPUT

biomassdecayed  = Q_influent.*HRT.*MLVSS/(Total_V)*decaycoef;    %
amount of biomass decayed in the five bioreactors (kg/d)
CO2bdemissions  = biomassdecayed*CO2y;                 % CO2 emissions of
the biotreatment (kgCO2/d) %%%%34944x1

%%%%%% BOD oxidation all reactors%%%%%%%%
```

```
%%%%%%%% PARAMETERS
    CO2_BOD     = 1.1;      % CO2 from BOD oxidation (kg CO2/kg O2 for
BOD oxidised)
                        % stoichiometry 2 C10H19O3N + 25 O2 -> 20 CO2
+16 H2O +2 NH3
                        % 25*32 : 20*44 (Moneith et al.) Only oxygen in
the last
                        % three reactors
    BOD5_BODu   = 0.67;   %fraction (Black&Veatch)
    Yh          = 0.84;          % Cell yield coefficient (kgVS/kgBOD)
(Black&Veatch)
    SRT         = 13;
%%%%%%%% INPUT
Q_BOD5in        = (BOD5_inf.* Q_influent)./1000; %%%kg.day
Q_BOD5out       = (BOD5_inf.* Q_effluent)./1000; %%%kg.day

%%%%%%%% OUTPUT
obsY                = Yh/(1+decaycoef*SRT);                         %
observed yield [kgvss/kgBOD]
BODox       = (Q_BOD5in - Q_BOD5out);                        % BOD
oxidised (kg/d)
netbiomassproduced=BODox*obsY;                           %
netbiomassproduced (kg VSS/d)
oxygenBOD   =  BODox/BOD5_BODu-1.42*netbiomassproduced;   % oxygen used
in the bod oxidation
CO2oxemissions  =   oxygenBOD*CO2_BOD;                        % The CO2
emissions from the BOD oxidation in the 5 reactors. %%% 34944x1



%%%%%%Nitrogen removal all reactors%%%%%%%%
%     CO2 credit from ammonia removal

%%%%%%%% PARAMETERS
    CO2cons=4.49; % CO2 consumed by nitrifiers (kg CO2/kg N nitrified)
(EPA nitrogen removal manual)
%                 20CO2 +14NH4 -> 10 NO3 + 4C5H7O2N + 24 H +2 H20 ...
%                 880:196 -> 4.49:1

%%%%%%%% INPUT
Q_TKNin     = (TKN_inf.* Q_influent)./1000; %%%kg.day
Q_TKNout    = (TKN_eff.* Q_effluent)./1000; %%%kg.day
Q_TNout     = ((TKN_eff + NOx_eff).* Q_effluent)./1000; %%%total
nitrogen kg.day

%%%%%%%% OUTPUT
Nbiomass    = netbiomassproduced*0.12;     % MWbiomass 113 MW N 14
14/113 = 0.12 (kg N/d)
NH3ox       =(Q_TKNin-Q_TKNout)-Nbiomass;      % amount of NH3 oxidised
(kg NH3/d)
CO2cred     = -NH3ox*CO2cons;              % CO2 is consumed as carbon
source during nitrification

%%%%%%N2O formed%%%%%%%%%%%%%%%%%%%%%%

%%%%%%%% PARAMETERS
```

```
    N2Ogen  = 0.023; % N2O generation rate (kgN2O/kg N feed) data from
Lee Walker
%                    different for different wwtp,

%%%%%%%% INPUT
Q_TKNin; %= (SNKjin.*inpart(:,15))./1000; %%%kg.day


%%%%%%%% OUTPUT
N2O     =   (Q_TKNin-Q_TNout)*N2Ogen;  %amount of N2O
generated(kgN2O/m3)
CO2_N2O =   N2O*GWPN2O;             %(kgCO2/m3)

%%%Chemical use%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%   parameters
%     lime_CO2 = 1640 % imbedded CO2 in lime (kgCO2/tonne lime)
%     caustic_CO2 = 1130 % imbedded CO2 in caustic (kgCO2/tonne
caustic)
%     hypo_CO2 = 801 %imbedded CO2 in hypochlorite (kgCO2/tonne hypo
(12,5%))
%     poly_CO2 = 1800 % imbedded CO2 in polymer (kgCO2/tonne polymer)
%     chlo_CO2 = 112 % imbedded CO2 in chlorine (kgCO2/tonne chlorine)
%     input
%     limeadded  = amount of lime added in the wwtp (kg lime/kg
drysolids)
%     causticadded = amount of caustic added in the wwtp (kg caustic/d)
%     hypoadded = amount of hypochlorite added in the wwtp (kg
hypochlorite/d)
%     polyadded = amount of polymer added in the wwtp (kg polymer/dry
t)
%     chloadded = amount of chlorine added in the wwtp (kg chlorine/d)
%     sludgetodigester =Inflow...
%     CO2_lime=limeadded/1000*sludgetodigester*lime_CO2
%     CO2_caustic=caustic_CO2*causticadded/1000
%     CO2_hypo=hypo_CO2*hypoadded/1000
%     CO2_poly=polyadded*digestedsludgemass*poly_CO2/1000000
%     CO2_chlo=chlo_CO2*chloadded/1000
%     CO2chem = CO2_lime+CO2_caustic+CO2_hypo+CO2_poly+CO2_chlo

%%Parasitic power draw%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%%%%%%%% PARAMETERS

    CO2_kwh = 0.94; % CO2 from power plant (kg CO2/kWh)

%%%%%%%% INPUT

En_aer = BSM_aeration; %%aeration
En_pump = BSM_pumping;%% pumping
%En_heat = Heatpower.*24;%% digester

%%%%%%%% OUTPUT
        airCO2= En_aer*CO2_kwh;
```

```
        pumpCO2=En_pump*CO2_kwh;
%        heatCO2=En_heat*CO2_kwh;
        CO2_power = airCO2+pumpCO2;%+heatCO2; %%% 34944x1


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

%carbon footprint (Bridl model)
evaluationmatrix3(1,1)=(CO2ademissions); %Kg/d
evaluationmatrix3(1,2)=sum(totalCO2reuse.*tint)/totalt; %Kg/d
evaluationmatrix3(1,3)=sum(CO2bdemissions.*tint)/totalt; %Kg/d
evaluationmatrix3(1,4)=sum(CO2oxemissions.*tint)/totalt; %Kg/d
evaluationmatrix3(1,5)=sum(CO2cred.*tint)/totalt; %Kg/d
evaluationmatrix3(1,6)=sum(CO2_N2O.*tint)/totalt; %Kg/d
evaluationmatrix3(1,7)=sum(CO2_power.*tint)/totalt; %Kg/d

CO2emission = evaluationmatrix3(1,1) + evaluationmatrix3(1,2) +
evaluationmatrix3(1,3) + evaluationmatrix3(1,4) +
evaluationmatrix3(1,5) + evaluationmatrix3(1,6) +
evaluationmatrix3(1,7); %Kg/d

evaluationmatrix3(1,8)=CO2emission %Kg/d


%CO2emission=(CO2ademissions+CO2totalreuse+CO2bdemissions+CO2oxemission
s+CO2cred+CO2_N2O+CO2_power);
```

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