MASS BALANCES AND MODELLING OVER WASTEWATER TREATMENT PLANTS

Report to the

WATER RESEARCH COMMISSION

by

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EXECUTIVE SUMMARY

INTRODUCTION

Recently research attention has been devoted to linking simulation models for activated sludge (AS) and anaerobic digestion (AD) such as Activated Sludge Model No 1 (ASM1, Henze et al., 1987) and Anaerobic Digestion Model No 1 (ADM1, Batstone et al., 2002) to develop plant wide wastewater treatment plant (WWTP) models (Jeppsson et al., 2006). In such models, the outputs of one unit operation become input to the next down stream one. However, plant wide models assembled by linking simulation models are large, complex and require significant modelling skills, experience and understanding to master and use effectively. Furthermore, such models are not compatible with design because they require all the reactor sizes and inter-connecting flows and all the starting concentrations in all the reactors to be quantitatively defined.

Steady state models are more practical for design because they are simpler, require less experience and expertise and demand less input data than the complex simulation models, and so are used more often by designers and operators. With steady state models, one can (i) estimate reasonably simply and quickly the principal system design and operating parameters, such as sludge age, unaerated (anoxic and anaerobic) mass fractions, reactor volume, recycle ratios from system performance criteria specified for the design, such as effluent and sludge quality, (ii) investigate the sensitivity of the system performance to the design and operation parameters, (iii) estimate product stream concentrations for design of down- (or up-) stream unit operations of the WWTP and (iv) very importantly, provide a basis for cross-checking simulation model output results, all with very little input data requirements compared with the simulation models. Once the overall WWTP scheme is established and the main system defining parameters of the individual unit operations estimated, complex simulation models can be applied to the individual unit operations to refine their design and evaluate their performance under cyclic flow and load conditions. Steady state models of WWTP unit operations are therefore a very useful complement to the complex simulation models and so both steady state and dynamic simulation WWTP models need to be developed.

RESEARCH OBJECTIVES

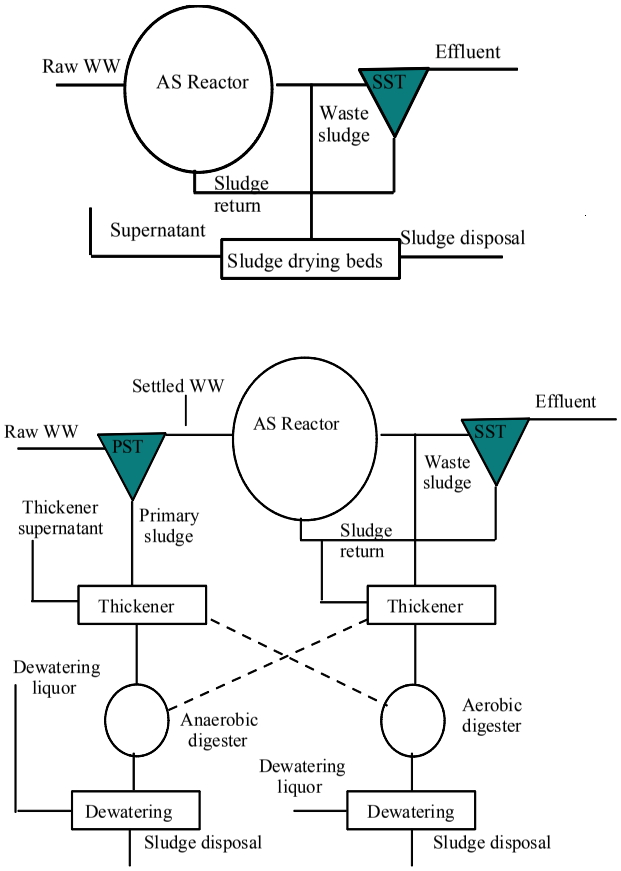
In this research project the primary focus was on developing steady state models to a point where they can be connected into a plant wide WWTP model (Fig 1). Because of the (1) common use of the total suspended solids (TSS) parameter at WWTPs, the inorganic suspended solids (ISS) needs to be incorporated into the steady state models, and (2) current interest in green house gas generation, carbon also needs to be included in the steady state models via stoichiometry of the biological processes in the various unit operations of WWTPs. To provide the required information to develop a plant wide steady state WWTP model, the main objectives of this project were:

(i) Determine experimentally the characteristics and biodegradability of primary (PS) and waste activated sludge (WAS) under anaerobic and aerobic digestion conditions.
(ii) Track the inorganic suspended solids (ISS) through the WWTP to check whether or not it is conserved.

Are existing, and to be developed, steady state models for the different wastewater treatment plant (WWTP) unit operations sufficiently accurate to be linked to make a steady state mass balance plant wide WWTP model for initial reactor and interconnection flow sizing and concentration determination for WWTP simulation models?

How does wastewater treatment plant (WWTP) layout, such as long sludge age (30d) extended aeration treating raw wastewater (upper) or short sludge age (8d) treating settled wastewater with anaerobic digestion of primary sludge and aerobic digestion of waste activated sludge (lower), affect green house gas (CO_2, CH_4) generation by the WWTP?

Are influent inorganic suspended solids (ISS) conserved through the WWTP comprising primary settling, activated sludge, aerobic and anaerobic digestion?



Are wastewater unbiodegradable particulate organics as determined in the activated sludge (AS) reactor also unbiodegradable in anaerobic digestion?

Are activated sludge unbiodegradable particulate organics (endogenous residue) generated in the activated sludge (AS) reactor also unbiodegradable in anaerobic digestion?.

Can activated sludge simulation models including biological excess P removal (BEPR, e.g. ASM2) predict the P release behaviour of BEPR waste activated sludge under aerobic digestion conditions?

Fig 1: *Research questions addressed in this research project (K5/1620) from which the specific research objectives were formulated.*

(iii) Include Carbon in the mass balance based steady state WWTP model.
(iv) Investigate kinetics of P release from biological excess P removal (BEPR) nutrient removal WAS under aerobic digestion conditions.

To meet these objectives the following was undertaken:
(i) Develop a steady state WWTP model in spreadsheet form incorporating activated sludge (AS), nitrification, denitrification, BEPR, aerobic and anaerobic digestion of PS and /or WAS, sludge dewatering and dewatering sludge liquor (N and P) recycling.
(ii) Integrate the ISS parameter into the above model by extending existing steady state models to incorporate the behavior of this parameter from own and literature data.
(iii) Develop mass balance bioprocess stoichiometry for Carbon (C), Hydrogen (H), Oxygen (O), Nitrogen (N), Chemical Oxygen Demand (COD) and Total Oxygen Demand (TOD=COD + 4.57xTotal Kjeldahl Nitrogen, TKN) for each unit operation included in a WWTP to enable incorporation of the C, H, O, N, COD and TOD parameters.
(iv) Determine experimentally the kinetics of P release from BEPR nutrient removal WAS under aerobic digestion conditions.
(v) Develop steady state (continuous flow) and batch reactor models for aerobic digestion of WAS from BEPR plants based on VSS and include also ISS and TSS concentrations and compare these models against experimental data and the ASM2 simulation model also extended to include ISS and TSS parameters.

Each of these objectives were achieved. In so doing, 11 referred journal papers and 11 international conference papers were published. Details of this research can be found in these publications, listed in Appendix A. Only the main conclusions are summarized in this report.

MAIN RESEARCH CONCLUSIONS

This project made significant advances towards developing steady state mass balances based integrated WWTP models which link primary sedimentation, nitrification denitrification (ND) activated sludge and aerobic or anaerobic digestion of primary and waste activated sludges. The most significant of these developments is the finding that particulate organics that are unbiodegradable in the activated sludge reactor, i.e. those from the influent wastewater and from the endogenous process generated in the reactor, are also unbiodegradable under anaerobic digestion conditions. Activated sludge and anaerobic digestion simulation models can therefore be linked with common compounds at the link to form plant wide WWTP models. Development of a mass balances based steady state model for the entire WWTP comprising primary settling, ND activated sludge and aerobic or anaerobic digestion of primary and waste activated sludge was completed in this project. Mass balance carbon (C), nitrogen (N), oxygen (O), hydrogen (H) and total oxygen demand (TOD) stoichiometry was also developed to complement the steady state models so that the different products exiting the WWTP via the solid, liquid and gas streams can be calculated, such N loads in recycle streams, methane production for energy recovery and green house gas (CO_2, CH_4) generation. It was found from this stoichiometry addition that for two very different WWTPs, one a raw WW extended aeration NDAS system at 30d sludge age, the other a settled wastewater short sludge age (8d) NDAS system with anoxic-aerobic digestion of WAS and anaerobic digestion of primary sludge (Fig 1), if all the methane is combusted (beneficially or flared), both WWTPs convert the same % of influent Carbon to CO_2. WWTP type therefore makes little difference to green house gas generation if the disposed sludge contains the same percentage residual biodegradable organics. From the experimental results of aerobic digestion of concentrated WAS (2% TSS) from BEPR AS systems only about 1/3rd of the P in the polyphosphate accumulating organisms (PAOs)

appeared as ortho-P in the bulk liquid due to struvite precipitation. Aerobic digestion, modified to include intermittent aeration to promote denitrification and lime addition to enhance P precipitation is a simple system to stabilize concentrated BEPR WAS yielding a dewatering liquor with low N and P for recycle back to the biological reactor.

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TABLE OF CONTENTS

MASS BALANCES AND MODELLING OVER WASTEWATER TREATMENT PLANTS

1. INTRODUCTION

Recently research attention has been devoted to linking simulation models for activated sludge (AS)[1] and anaerobic digestion (AD) such as Activated Sludge Model No 1 (ASM1, Henze et al., 1987) and Anaerobic Digestion Model No 1 (ADM1, Batstone et al., 2002) to develop plant wide wastewater treatment plant (WWTP) models (Jeppsson et al., 2006). In such models, the outputs of one unit operation become input to the next down stream one. However, the output compounds of ASM1 are not compatible with the input compounds of ADM1. Two approaches have been proposed to resolve this – (i) develop mass balances based compound transformation interfaces which map one set of compounds (outputs) onto another set of compounds (inputs) (interface approach, Vanrolleghem et al., 2005, Volcke et al., 2006, Zaher et al., 2007) and (ii) define all the compounds required in the entire WWTP and model the changes in these through each unit operation (the super-model approach, Jones and Takacs, 2004, Seco et al., 2004, Grau et al., 2007). Irrespective of the approach, such plant wide models are large, complex and require significant modelling skills, experience and understanding to master and use effectively. Furthermore, such models are not compatible with design because they require all the reactor sizes and inter-connecting flows and all the starting concentrations in all the reactor to be quantitatively defined.

Steady state models are more practical for design, because they allow reactor sizes and interconnecting flows reactor concentrations at steady state to be simply determined. Steady state models of WWTP unit operations are therefore a very useful complement to the complex dynamic simulation ones because with them one can (i) estimate reasonably simply and quickly the principal system design and operating parameters, such as sludge age, unaerated (anoxic and anaerobic) mass fractions, reactor volume, recycle ratios and oxygen requirement or gas production from system performance criteria specified for the design, such as effluent and sludge quality, (ii) investigate the sensitivity of the system performance to the design and operation parameters, (iii) estimate product stream concentrations for design of down- (or up-) stream unit operations of the WWTP and (iv) very importantly, provide a basis for cross-checking simulation model output results, all with very little input data requirements compared with the simulation models. Once the overall WWTP scheme is established and the main system defining parameters of the individual unit operations estimated, complex simulation models can be applied to the individual unit operations to refine their design and evaluate their performance under cyclic flow and load conditions. Accordingly, both steady state and dynamic simulation WWTP models need to be developed. Ideally, all WWTP simulators should have a pre-processor based on mass balance steady state models that assist with WWTP layout design, reactor sizing, option exploration and comparisons, recycle ratio determination and initial concentration calculation. The WWTP layout so developed then gets read seamlessly into the simulators for simulation of the individual unit operations, be they activated sludge, aerobic and/or anaerobic digestion.

[1]Definition of all abbreviations and symbols is given in Appendix A

2. RESEARCH OBJECTIVES

In this research project the focus was on developing steady state models to a point where they can be connected into a plant wide WWTP model for municipal wastewater treatment. Steady state models are used more often by designers and operators because they are simpler, require less experience and expertise and demand less input data than the complex simulation models. Because of the (i) common use of the total suspended solids (TSS) parameter at WWTPs, the inorganic suspended solids (ISS) would be incorporated into the steady state models, and (ii) requirement to include carbon to model anaerobic digestion, carbon would also be included in the steady state models via stoichiometry of the biological processes in the other unit operations of WWTPs. Because development of steady state models and stoichiometry was deemed a higher priority than further development of simulation models at this time, this project expanded the scope and objectives of the former at the expense of further developments of the latter. To provide the required information to develop a plant wide steady state WWTP model, the objectives of this project approved by its reference committee were:

1 Determine experimentally the characteristics and biodegradability of primary (PS) and waste activated sludge (WAS) under anaerobic and aerobic digestion conditions.
2 Validate the steady state anaerobic digestion (AD) model for PS and WAS.
3 Develop a steady state WWTP model in spreadsheet form incorporating activated sludge (AS), nitrification, denitrification, biological excess P removal, aerobic and anaerobic digestion of PS and /or WAS, sludge dewatering and dewatering sludge liquor (N and P) recycling.
4 Extend steady state models for aerobic digestion of WAS to include the inorganic suspended soolids (ISS).
5 Apply the steady state AS model including inorganic suspended solids (ISS) to track ISS through the WWTP.
6 Develop mass balance based stoichiometry for organics removal, nitrification and denitrification and use it to include the Carbon parameter in the steady state WWTP model.
7 Determine experimentally the kinetics of P release from biological excess P removal nutrient removal WAS under aerobic digestion conditions.
8 Develop steady state (continuous flow) and batch reactor models for aerobic digestion of WAS from BEPR plants based on VSS and include also ISS and TSS concentrations and compare these models against experimental data and the ASM2 simulation model also extended to include ISS and TSS parameters.
9 Identify a programmer to translate the spreadsheet steady state mass balances WWTP model to a Windows based user-friendly programme.

Each of these objectives were realized and is summarized below. In accomplishing these objectives, 11 referred journal papers and 11 international conference papers were published. Details of the research can be found in these publications, which are listed in Appendix A. Only the conclusions from some of these papers are given below to summarize the research.

3. BIODEGRADABILITY OF WASTEWATER ORGANICS UNDER ANAEROBIC CONDITIONS (Objectives 1 and 2) – Wentzel et al. (2006)

From this investigation of the continuity of wastewater organic (COD) and N compounds across the link between the primary settling tank (PST) and anaerobic digestion (AD) unit operations, the following conclusions were made:

3.1 Application of the COD, carbon (C) and nitrogen (N) mass balances steady state anaerobic digestion (AD) model of Sötemann et al. (2005a) to literature data of AD of primary sludge (PS) showed that this model satisfactorily predicted AD performance (gas production and composition, effluent COD, free and saline ammonia and alkalinity concentrations) and provided a mass balance based structure to determine the unbiodegradable organic (COD) fraction of PS ($f_{PS,up}$). This fraction determined from the AD model matches very closely that calculated for PS from a mass balance around the PST for typical raw and settled wastewater characteristics.

3.2 It follows from 3.1 that (i) the PS characteristics can be calculated from mass balances around the PST so that the organic (COD) and N (and C if measured) concentrations and components, *viz.* biodegradable and unbiodegradable soluble and particulate, conform to continuity principles, and (ii) the influent unbiodegradable particulate organics determined from response of the AS system (essentially aerobic) are also unbiodegradable under anaerobic digestion conditions.

3.3 Anaerobic digestion of PS provides a basis to determine the COD/VSS, N/COD and C/VSS ratios of the influent wastewater biodegradable and unbiodegradable particulate organics. From data from several anaerobic digester studies, it was found that the COD/VSS (f_{cv}) and N/COD ($f_{ZB,N}$) ratios of influent unbiodegradable particulate organics (S_{upi}) are significantly higher than the ratios for biodegradable particulate organics (S_{bpi}). For example - the N/COD ratio of unbiodegradable particulate organics was found to be four times higher (~40 mg N/g COD) than for biodegradable particulate organics (~10 mg N/g COD). Also, the COD/VSS and N/COD ratios for unbiodegradable organics are significantly different to the ratios commonly assumed for these organics in AS models, *viz.* f_{cv} = 1.48 mg COD/mg VSS and $f_{ZB,N}$ = 67.6 mg N/g COD (f_n=0.10 mg N/mg VSS). While these differences in the ratios make little difference to the AS system as a stand alone operation, the differences are significant when tracking COD, VSS and N fluxes through a network of unit operations of a WWTP. Different N/COD ratios for the biodegradable and unbiodegradable particulate organics have been incorporated in ASM2 (Henze et al., 1995) but the experimental basis for the given values (40 and 30 mg N/g COD respectively) are not given. This aspect requires further exploration in the context of plant wide WWTP models.

3.4 An aspect only peripherally considered in this part of the project was the carbon (C) balance over the WWTP. While the C balance is not important for the AS system itself, the C content of PS and waste activated sludge (WAS) is important for anaerobic digestion. From one data set on anaerobic digestion of PS, the calculated CHON composition of the particulate biodegradable organics of the PS from the VSS and biodegradable COD removed and free and saline ammonia generated (i.e. $C_{3.5}H_7O_2N_{0.196}$) correlated closely with elemental analysis of PS from two full scale WWTPs (Sötemann et al., 2005a). The CHON stoichiometry of AD of wastewater organics will be modified

and applied to AS and aerobic digestion of WAS to include these unit operations in the C balance over the WWTP. This, and the feasibility of developing approximate CHON stoichiometric formulae for the different influent wastewater organic fractions were explored under Objective 5 (Section 7) to complete the C balance over the WWTP.

From the above, because, in the steady state AD model of Sötemann et al. (2005a), (i) the feed PS characteristics are specified in terms of commonly measured parameters like COD, VSS, Total Kjeldahl Nitrogen (TKN), Free and Saline ammonia (FSA), Total Phosphorus (TP) (and TSS, see Section 4 below) and (ii) the unbiodegradable particulate COD fraction of the PS ($f_{PS,up}$) (and VSS/TSS ratio) can be calculated from the raw and settled wastewater characteristics selected for the PST, this AD model could be readily integrated into a steady state mass balances model for the entire WWTP. This established the link between the PST and AD of PS, by ensuring common and readily measurable compounds at the interconnection between these two unit operations.

4. TRACKING THE INFLUENT INORGANIC SUSPENDED SOLIDS (Objectives 4 and 5) – Ekama et al. (2006)

From this investigation of the continuity of wastewater organic, inorganic and N compounds across the links between the primary settling tank (PST), fully aerobic or N removal activated sludge (AS) and anaerobic (AD) and aerobic (AerD) digestion unit operations, the following was concluded:

4.1 From the experimental data of Van Haandel et al. (1998a), the influent wastewater (fixed) ISS concentration is conserved through AS and waste activated sludge (WAS) aerobic digestion (AerD) systems.

4.2 From the experimental data of Izzett et al. (1992) and Moen et al. (2001), the evidence is inconclusive whether the influent wastewater (fixed) settleable ISS concentration is conserved through primary sludge (PS) AD. The ISS mass balance over the ADs were narrowly within ±10%. More data on this aspect needs to be evaluated.

4.3 The measured ISS flux at different stages through a series of WWTP unit operations is not equal to the influent ISS flux. The ordinary heterotrophic organism (OHO) biomass contributes to the fixed ISS flux by differing amounts depending on the active (OHO) fraction of the Volatile Suspended Solids (VSS) solids.

4.4 The ISS model of Ekama and Wentzel (2004), which assigns an ISS content to OHOs of 0.15 mg ISS/mg OHOVSS, correlates very well with experimental data from a WWTP comprising an aerated lagoon and four in series aerobic digesters, covering an effective sludge age range from 2 to 60 days (Van Haandel et al., 1998a). This not only provides additional validation for the ISS model, but also shows that it can be used for tracking the ISS through AerD systems down to very low active fractions.

4.5 The steady state AerD model developed for stabilization of WAS in terms of VSS and TSS was found to correlate very well with literature data. This model also can be applied to model AerD of PS and PS-WAS blends (Section 5 below). To use the model requires the equivalent influent active fraction of the PS to be calculated. This influent active fraction can be calculated from the biodegradable COD fraction of the PS determined from a mass balance around PST (Section 3 above).

4.6 The steady state model for aerobic digestion in terms of VSS and TSS yields virtually identical results as Activated Sludge Model No 1 (ASM1), modified to include the ISS model of Ekama and Wentzel (2004). The steady state model therefore can be used to design aerobic digesters as an initial step to simulating them for more detailed performance evaluation, such as anoxic (air-off) aerobic (air-on) operation.

This research has indicated that the mass balances based steady state and dynamic simulation activated sludge and aerobic digestion models, modified to include the ISS compound, provide internally consistent and externally compatible elements that can be coupled to produce an integrated steady state model for the whole WWTP.

5. BIODEGRADABILITY OF ACTIVATED SLUDGE ORGANICS UNDER ANAEROBIC CONDITIONS (Objectives 1 and 2) – Ekama et al. (2006)

From this investigation of the continuity of wastewater organic, inorganic and N compounds along the link connecting the fully aerobic or N removal activated sludge (AS) and anaerobic digestion (AD) unit operations, the following conclusions were made:

5.1 Applying the COD, carbon (C) and nitrogen (N) mass balances steady state AD model of Sötemann et al. (2005a) to literature and author generated data of waste activated sludge (WAS) AD showed that this model satisfactorily predicted AD performance (gas production and composition, effluent COD, free and saline ammonia and alkalinity concentrations) and provided a mass balance based structure to determine the unbiodegradable particulate organic (COD) fraction of WAS ($f_{AS,up}$). For the Van Haandel et al. (1998a,b) data, the $f_{AS,up}$ determined from the AD model matched very closely that calculated for the WAS feed from the steady state AS model of Marais and Ekama (1976) or WRC (1984), provided the unbiodegradable fraction of the ordinary heterotrophic organisms (OHOs) is assigned the value from the death-regeneration model (i.e. $f'_{EH} = 0.08$), not the value from the net effect endogenous respiration model ($f_{EH} = 0.20$). This was confirmed with the authors own experimental data, which included CHON composition measurement of AD influent and effluent by elemental analysis.

5.2 It follows from (1) above that the influent wastewater unbiodegradable particulate organics determined from the response of the AS system and the unbiodegradable organics that are generated in the AS system itself, i.e. endogenous residue, are both unbiodegradable under AD conditions. The residual biodegradable organics of WAS that can be anaerobically digested therefore can be calculated from the active fraction of the WAS using the widely accepted AS stoichiometric ($f_{EH} = 0.20$ or $f'_{EH} = 0.08$, $f_{cv} \approx 1.48$ mg COD/mg VSS, $Y_H = 0.45$ mg VSS/mg COD) and kinetic constants ($b_{H20} = 0.24$ /d or $b'_{H20} = 0.62$/d) included in steady state and dynamic simulation AS models. Earlier, Gossett and Belser (1982) came to the same conclusion but the b_{H20} and f_{EH} values on which this was based (0.10/d and 0.317) are not compatible with those widely accepted in steady state and dynamic simulation AS models, possibly because they did not use real municipal wastewater.

5.3 From the Van Haandel et al. (1998a,b) and author experimental results, between 138% and 78% of the influent wastewater (fixed) ISS mass flow was recovered in the AD effluent. Section 4 above showed that influent ISS was conserved through aerobic digestion of WAS, but with such wide variation, the same cannot be concluded for AD of WAS.

5.4 The COD/VSS and N/COD ratios obtained for the WAS biodegradable and unbiodegradable (endogenous) organics appear to be similar in magnitude and close to the commonly accepted ratios for activated sludge (COD/VSS = 1.48 mg COD/mg VSS and N/COD = 67.6 mg N/g COD or $f_n = 0.10$ mg N/mg VSS). The variations observed in these ratios in this investigation seems to be mostly due to experimental error. Therefore, it seems reasonable to assign these ratio values to the OHO biomass and endogenous residue, which made up most of the VSS in this investigation (>2/3rds). In contrast, this is not true for the unbiodegradable particulate organics in the influent wastewater – the COD/VSS and N/COD ratios of these organics are significantly higher

and lower respectively than these ratios of the OHO and endogenous residue VSS (see Section 3 above).

5.5 While the C balance is not important for the AS system itself, the C content of PS and WAS is important for AD. From the Van Haandel et al. (1998a,b) data set on AD of WAS, the CHON composition of the biodegradable component of the WAS was estimated from the measured VSS/COD and N/COD ratios to be $C_{5.67}H_7O_2N_{0.865}$. From COD, VSS and TSS measurements and C, H and N elemental composition analysis, the biodegradable component of the WAS in the author data set was measured to be $C_{3.691}H_{7.0}O_{1.99}N_{0.503}$ and yielded a reasonable correlation between calculated and measured AD performance. A sensitivity analysis with the AD model stoichiometry showed that the gas flow and composition are not very sensitive to biodegradable organics composition for the same COD load. The CHON stoichiometry of AD of wastewater organics were modified and applied to all the unit operations of the WWTP, aerobic and anaerobic, to include the C balance over the entire WWTP (see Section 7 below).

This research, together with that of Sötemann et al. (2005b), which showed that the steady state AD model gives very closely the same results as their dynamic simulation model, demonstrates that the mass balances based steady state and dynamic simulation AS and AD models provide internally consistent and externally compatible elements that can be coupled to produce plant wide steady state and dynamic simulation WWTP models for the whole WWTP without changing the values of the widely accepted stoichiometric and kinetic constants included in the AS models.

6. AEROBIC DIGESTION OF PRIMARY AND WASTE ACTIVATED SLUDGES (Objective 1) – Sötemann et al. (2006)

From this investigation of the continuity of wastewater organic, N and inorganic suspended solids (ISS) compounds along the links connecting the primary settling tank (PST), fully aerobic or N removal activated sludge (AS) and anaerobic and aerobic digestion unit operations, the conclusions can be summarized as follows:

6.1 Application of the COD, carbon (C) and nitrogen (N) mass balances steady state anaerobic digestion (AD) model of Sötemann et al. (2005a) to literature data of AD of primary sludge (PS) and waste activated sludge (WAS) showed that this model satisfactorily predicted AD performance for both sludge types (gas production and composition, effluent COD, free and saline ammonia and alkalinity concentrations and digester pH) and provided a mass balance based structure to determine the unbiodegradable particulate organic (COD) fraction of PS ($f_{PS'up}$) and WAS ($f_{AS'up}$). The unbiodegradable particulate COD fraction of PS ($f_{PS'up}$) determined from the AD model matched very closely that calculated for PS from a mass balance around the PST for typical raw and settled wastewater characteristics. Also, the unbiodegradable particulate COD fraction of WAS ($f_{AS'up}$) determined from the AD model matched very closely that calculated for WAS from the steady state activated sludge model of Marais and Ekama (1976) and WRC (1984), provided the unbiodegradable fraction of the ordinary heterotrophic organisms (OHOs) is assigned the value from the death-regeneration model (f'_{EH}=0.08), not the value from the net effect endogenous respiration model (f_{EH}=0.20).

6.2 It follows from (1) above that (i) the PS characteristics need to be calculated from mass balances around the PST so that the organic (COD) and N concentrations and components, *viz.* biodegradable and unbiodegradable, soluble and particulate, conform to continuity principles, (ii) the influent unbiodegradable particulate organics determined from response of the activated sludge system are also unbiodegradable under anaerobic digestion conditions, (iii) the unbiodegradable particulate organics that are generated in the activated sludge reactor, i.e. endogenous residue, also are unbiodegradable under anaerobic digester conditions and (iv) the residual biodegradable particulate organics that can be anaerobically digested can be calculated from the active fraction of the WAS using the widely accepted stoichiometric and kinetic constants in AS models such as ASM1 (Henze et al., 1987).

6.3 Anaerobic digestion of PS provides a basis to determine the COD/VSS and N/COD ratios of the influent wastewater biodegradable and unbiodegradable particulate organics. From data from several anaerobic digester studies, it was found that the COD/VSS (f_{cv}) and N/COD ($f_{ZB,N}$) ratios of influent unbiodegradable particulate organics (S_{upi}) are significantly higher than the ratios for biodegradable particulate organics (S_{bpi}). For example – the N/COD ratio of unbiodegradable particulate organics was found to be four times higher (~40 mg N/g COD) than for biodegradable particulate organics (~10 mg N/g COD). Also, the COD/VSS and N/COD ratios for unbiodegradable particulate organics are significantly different to the ratios commonly assumed for these organics in activated sludge models, *viz.* f_{cv} = 1.48 mg COD/mg VSS and $f_{ZB,N}$ = 67.6 mg N/g COD (f_n=0.10 mg N/mg VSS). While these differences in the ratios make little difference to the activated sludge system as a stand alone operation, they are significant when tracking COD, VSS and N fluxes through a network of unit operations of a WWTP. Different

N/COD ratios for biodegradable and unbiodegradable particulate organics have been incorporated in ASM2 (Henze et al., 1995), but the experimental basis for the listed values (40 and 30 mg N/g COD respectively) are not given. This aspect requires a further exploration in the context of an integrated WWTP wastewater model.

6.4 From the experimental data in several literature sources, it is reasonable to accept that the influent wastewater (fixed) ISS concentration is conserved through activated sludge and aerobic digestion systems. However, the measured ISS flux at different stages through a series of WWTP unit operations is not equal to the influent ISS flux. The OHO biomass contributes to the fixed ISS flux by differing amounts depending on the active fraction of the VSS solids. The ISS model of Ekama and Wentzel (2004), which assigns an ISS content to OHOs of 0.15 mgISS/mgOHOVSS, correlates very well with experimental data from a WWTP comprising an aerated lagoon and four in series aerobic digesters. This not only provides additional validation for the ISS model, but also shows that it can be used for tracking the ISS though activated sludge and aerobic digester systems down to very low active fractions. The data on conservation of influent ISS in PS and WAS anaerobic digestion is variable and from the data evaluated, it could not be concluded that influent ISS is conserved.

6.5 The COD/VSS and N/COD ratios obtained for the WAS biodegradable and unbiodegradable organics appear to be similar in magnitude and close to the commonly accepted ratios for activated sludge (COD/VSS = 1.48 mg COD/mg VSS and N/COD = 67.6 mg N/g COD or f_n = 0.10 mg N/mg VSS) and the variations observed in these ratios in this investigation seems to be mostly due to experimental error. Therefore, it seems reasonable to assign these ratio values to the OHO biomass and endogenous residue.

6.6 An aspect only peripherally considered in this part of the research project is the carbon (C) balance over the WWTP. While the C balance is not important for the activated sludge system itself, the C content of PS and WAS is important for anaerobic digestion. From one data set on anaerobic digestion of WAS, the CHON stoichiometric composition of the biodegradable organics of the WAS was determined from chemical and elemental analysis to be $C_{3.691}H_{7.0}O_{1.99}N_{0.503}$, which yielded a reasonable correlation between calculated and measured AD performance. Although this WAS stoichiometry seems to differ quite widely from $C_{4.80}H_{7.0}O_{2.0}N_{0.77}$, it makes relatively little difference to the digester effluent and gas streams per COD load. The CHON stoichiometry of AD of wastewater organics can be modified and applied to nitrification denitrification activated sludge to include this system in the C balance over the WWTP. This, and the feasibility of developing approximate CHON stoichiometric formulae for the different influent wastewater organic fractions will be explored in further research to try to complete the C balance over the WWTP.

6.7 The steady state aerobic digester model developed for stabilization of WAS was found to correlate very well with literature data. This model can also be applied to model aerobic digestion of PS and PS-WAS blends. To use the model requires the equivalent influent active fraction of the PS to be calculated. This influent active fraction can be calculated from the biodegradable COD fraction of the PS determined from a mass balance around PST (see 6.1 above).

6.8 The steady state activated sludge and aerobic digestion models were applied to two WWTP schemes treating the same raw wastewater – one comprising PST, short sludge age activated sludge and aerobic digestion of PS-WAS blend, the other a long sludge age extended aeration activated sludge system. The models were found to yield COD, N and influent ISS mass balances within 0.1% and gave almost identical results for the two WWTP schemes for the same final residual biodegradable COD fraction.

6.9 For both WWTP schemes, the steady state models gave virtually identical results to ASM1 and therefore can be used to check simulation model outputs. An Activated Sludge Model No 1 (ASM1, Henze et al., 1987) Aquasim (Reichert, 1998) dynamic simulation model was set up for the raw and settled WW treatment plants above, including thickening and aerobic digestion of PS and WAS. For both systems, the simulation model gives virtually identical results for all the AS and aerobic digestion effluent COD, TKN, FSA, TP, OP, VSS, ISS and TSS concentrations from both systems. There is therefore close correlation between the far more complex dynamic simulation WWTP model in which ASM1 is used to model the AS and aerobic digester systems and the much simpler steady state model programmed into the spreadsheet described here.

This research has indicated that the mass balances based steady state activated sludge, aerobic digestion and anaerobic digestion models, modified to include the ISS component, provide internally consistent and externally compatible elements that can be coupled to produce an integrated steady state model for the whole WWTP. Not considered in this research project were phosphorus, phosphorus accumulating organisms (PAOs) and biological excess P removal (BEPR) plants. The PAOs introduce several complex issues which require further investigation, e.g. in the BEPR system, the ordinary heterotrophic organisms (OHO) and PAOs have different endogenous respiration/die off rates, the former high (b_{H20} = 0.24 /d at 20°C) and the latter low (b_{G20} = 0.04 /d at 20°C). These b rates influence the rates at which the nutrients N and P bound in the cell mass are released in aerobic and anaerobic digestion. The release rates of N and P from the solid cell bound phase to the dissolved phase under aerobic and anaerobic digestion conditions needs to be investigated to include P and BEPR systems into plant wide WWTP models.

7. USING STOICHIOMETRY TO BUILD A PLANT WIDE STEADY STATE WWTP MODEL (Objectives 3 and 6) – Brink et al. (2007)

7.1 Stoichiometry of WWTP bioprocesses

In this part of the research project the steady state kinetic models of AS organics degradation, nitrification, denitrification and anaerobic (AD) and aerobic (AerD) digestion are extended and linked with compound transformation stoichiometry to form a mass balances based WWTP model to complement the simulation WWTP models. By assigning a stoichiometric composition (X, Y, Z and A in $C_XH_YO_ZN_A$) to the five main influent wastewater organic components, these, and the products generated from them via the biological processes, are tracked through the WWTP. This approach is feasible because the research in Section 5 above showed that the unbiodegradable particulate organics, as defined by aerobic (AS) conditions are also unbiodegradable under anaerobic (AD) conditions. This applies to both the influent wastewater and endogenously generated unbiodegradable particulate organics. This greatly simplifies the plant wide steady state model development because it allows calculation of the unbiodegradable particulate fraction of (i) the primary sludge (PS) from the wastewater characteristics of the raw and settled wastewater and component mass balances around the primary settling tank (PST) and (ii) of the waste activated sludge (WAS) from the ordinary heterotrophic organism (OHO) active fraction.

Sötemann et al. (2005a) developed a mass balance based steady state model for AD of sewage sludge. This model comprises three sequential sub-models: (i) A COD mass balance based kinetic model which links the biodegradable organics (COD only) concentration removed, methane production and AD biomass generation to the digester sludge age, (ii) a C, H, O, N and COD mass balance based stoichiometry model which transforms the biodegradable COD removed and its C, H, O and N composition (reactant) to live AD biomass, gaseous CO_2, ammonia and dissolved CO_2 ($HCO_3^- \approx$ alkalinity) (products) and links to the kinetics part via the COD mass balance and (iii) an inorganic carbon weak acid/base chemistry part from which the digester pH is calculated from the partial pressure of CO_2 and alkalinity generated. Steady state COD and N mass balance based kinetic models already exist for the activated sludge system and aerobic digestion, both including nitrification and denitrification. In this part of the project, similar stoichiometric C, H, O, N and COD (e^-) mass balance models as was developed for anaerobic digestion, were developed for activated sludge and aerobic digestion of waste activated sludge (WAS), both with nitrification and denitrification. The COD based kinetic and CHON and COD based stoichiometric models are similar in that each considers masses of products formed from masses of reactants, but are different in that the kinetic model considers only the COD of the products and reactants and the rate of the bioprocess (which establishes the degree of reactant removal), whereas the stoichiometric model includes the CHON and COD of the reactants and products and obtains the change in reactant COD concentration from the kinetic model.

7.2 Using the Stoichiometry in a Plant Wide WWTP Example

The two example WWTPs comprise (i) raw wastewater (WW) treatment in a long sludge age (30d) AS system (extended aeration) (Fig 2) and (ii) primary settling tanks (PST) and anaerobic digestion (AD) of primary sludge (PS), activated sludge (AS) treatment of settled WW at a short sludge age (8d), flotation thickening of the waste activated sludge (WAS) and aerobic (AerD) or anaerobic (AD) digestion to stabilize the WAS to the same final residual biodegradable COD as the extended aeration WWTP (Fig 3). The raw and settled WW concentrations and characteristics are identical to those used in Section 5 above (see Sötemann et al., 2006 for

details). The only difference is that the influent VSS (and hence TSS) concentrations in the raw and settled WWs were increased and Total Organic Carbon (TOC) concentrations added to obtain similar CHON compositions for the particulate organics compared with those measured in PS AD (Wentzel et al., 2006). Also TOC concentrations for soluble organics were added to obtain approximate measured COD/TOC ratios for these organics. The raw WW average dry weather flow (ADWF) is 15.0 Mℓ/d and the PST underflow is 0.5% of this ADWF. The person equivalent of the WWTP at 0.10 kg COD/person/d is 112 000. The seasonal minimum and maximum WW temperatures are 14 and 22°C.

The steady state kinetics AD model of Sötemann et al. (2005a) was applied to the design and performance determination of the PS and WAS AD and the WRC (1984) nitrification-denitrification (ND) AS steady state models for the AS reactors and aerobic digester. A maximum specific growth rate at 20°C (μ_{A20}) of 0.60/d and a primary anoxic mass fraction of 0.40 were accepted for the modified Ludzack-Ettinger (MLE) ND AS systems. Where required, mainly for the effluent ammonia and nitrate concentrations, the kinetic model outputs provided the mass changes in ammonia and nitrate over the systems for the stoichiometric model. The WAS was thickened to 7% TSS before anoxic-aerobic digestion or AD. Complete ND of the WAS released N was accepted for the aerobic digester.

From the WW concentrations and characteristics, the CHON composition of the five influent organic compounds were calculated from mass balances around the PST, *viz*. influent VFA (assumed to be acetic acid), fermentable readily biodegradable soluble organics (F-RBO), unbiodegradable soluble organics (USO), biodegradable particulate organics (BPO) and unbiodegradable particulate organics (UPO).

7.3 Description of the spreadsheet steady state WWTP model

The steady state kinetic AS, AD and AerD models and the stoichiometry of the bioprocesses taking place in the different unit operations were programmed into a spreadsheet. The stoichiometry was applied to each organic (VFA, F-RBO, BPO, USO UPO, OHO biomass and endogenous residue) and inorganic (ISS, FSA, nitrate) compounds entering a unit operation and added to obtain the overall behaviour in that unit operation reactor. The stoichiometric and kinetic model predictions for reactor outputs (products) such as VSS, oxygen demand or methane gas production matched within 1%. The COD balance over the WWTPs is >100% (~101%) due to the inclusion of the autotrophic nitrifier (ANO) biomass in the mass balances – the ANOs synthesize biomass from CO_2, H_2O and NH_3, which have zero COD. However, the C, H, O, N and TOD (which includes the electron donating capacity of the TKN) balances were 100.0% over each unit operation and over the WWTPs as a whole, which validated that the kinetic and stoichiometric models were developed and programmed correctly. *The spreadsheet is completely general and can accommodate any realistic influent wastewater characteristics and unit operation design conditions.* Because the TOC concentrations of the different influent organics are not well defined or measured at this stage, these have to be estimated from reasonable assumptions. In this investigation, the COD/VSS, TKN/VSS and TOC/VSS ratios of the five organics groups, from which the CHON composition can be calculated, were estimated from some measured results (Wentzel et al., 2006). As examples, the spreadsheet output for the 8d sludge age ND system treating the settled wastewater at 14°C and for the PS AD are given in Tables 1 and 2. Compound mass balances over these two unit operations and their exit routes via the solid, liquid and gas streams are also shown.

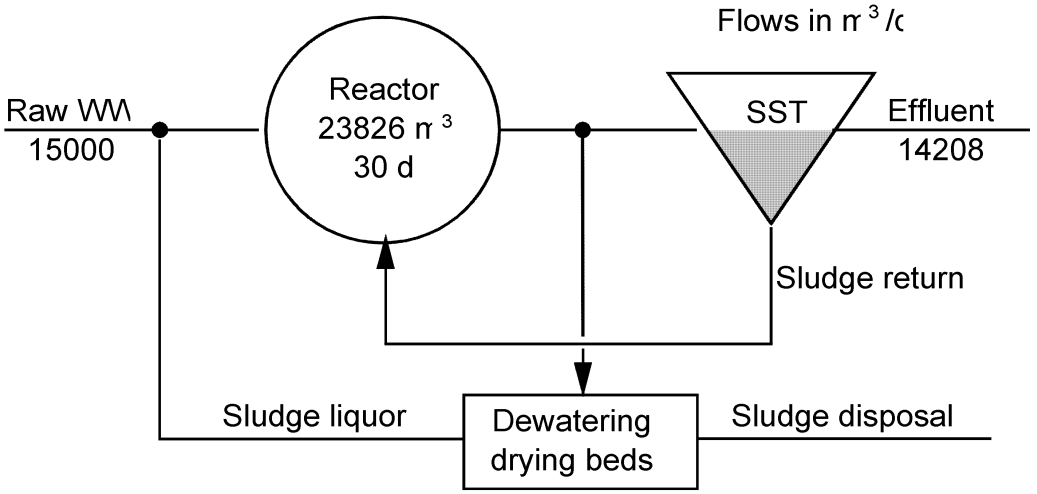


Fig 2: *Extended aeration raw wastewater long sludge age ND AS system (all flows in m^3/d).*

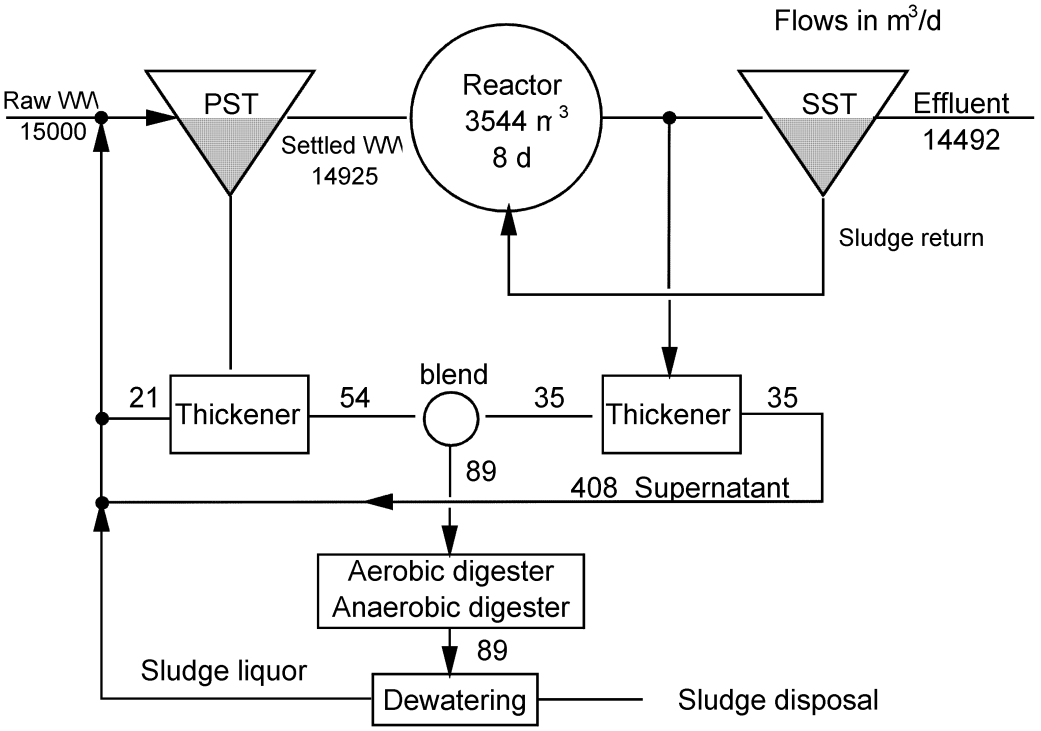


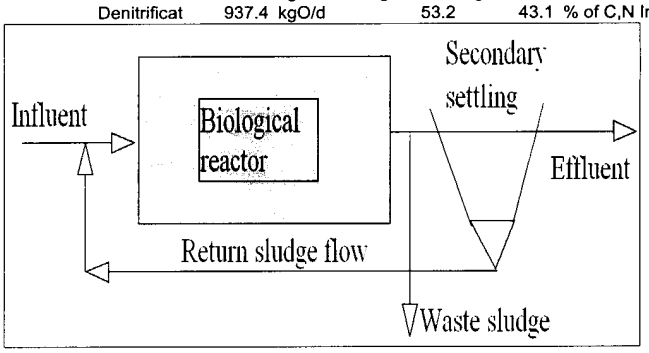
Fig 3: *Settled wastewater short sludge age ND AS system with AD of primary sludge and aerobic or anaerobic digestion of WAS (all flows in m^3/d).*

Table 1 (Part 1): *Spreadsheet output for 8d sludge age nitrification denitrification activated sludge treating settled wastewater at 14°C - stoichiometric model calculations.*

	WINTER	Temperature oC		14	DesMan										PrintSetTn		
		DENITRIFICATION		ANOXIC	AEROBIC	ANOXIC	AEROBIC	ANOXIC	AEROBIC	AEROBIC	AEROBIC	AEROBIC	NIT-DENIT				
	SETTLED	Wastewater		SETTLED	SETTLED	SETTLED	SETTLED	SETTLED	SETTLED	SETTLED	SETTLED	SETTLED	SETTLED		System	Portrait	
		Type		Organics	Organics	Organics	Organics	Organics	Organics	Organics	Organics	Nitrification	Total		Masses		
		Substrate		Acetate	Acetate	F-RBCOD	F-RBCOD	SBCOD	SBCOD	USCOD	UPCOD	Ammonia			Balances		
1	WASTEW	COD	mgCOD/l	36.0	0.0	58.7	51.5	0.0	233.4	52.5	18.0	0.00	450.13		6718.1	kgCOD/d	
		N	mgN/l	0.00	0.00	0.923	0.811	0.000	1.332	1.80	1.22	44.97	51.05		761.9	kgN/d	
		TOD	mgTOD/l	36.00	0.00	62.92	55.25	0.00	239.48	60.72	23.57	205.56	683.49		10201.1	kgTOD/d	
		fZ,BN	mgN/gCO	0.0	0.0	15.7	15.7	0.0	5.7	34.3	67.6	0					
		COD/VSS	fcv	1.0667	1.0667	1.4200	1.4200	1.4892	1.4892	1.4200	1.4800						
		C/VSS	fc	0.4000	0.4000	0.4702	0.4702	0.4833	0.4833	0.4869	0.5151						
		N/VSS	fn	0.0000	0.0000	0.0223	0.0223	0.0000	0.0085	0.0487	0.1000						
		Concs	mgC/l	13.500	0.000	19.435	17.066	0.000	75.734	18.000	6.266	0.000	150.00		2238.8	kgC/d	
			mgH/l	2.250	0.000	3.270	2.872	0.000	12.596	2.750	0.896	12.848	37.48		559.4	kgH/d	
			mgO/l	18.000	0.000	17.707	15.549	0.000	67.055	14.420	3.787	0.000	136.52		2037.5	kgO/d	
			mgN/l	0.000	0.000	0.923	0.811	0.000	1.332	1.799	1.217	44.967	51.05		761.9	kgN/d	
			e- mmol/l	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	3.212	3.21				
		DenitPot	mgNO3-N	8.36		25.59		101.84									
		mg/l	mg/l	36.0	0.0	58.7	51.5	0.0	233.4	52.5	18.0	35.59					
2	SUBSTRATE		umol/l	562.5	0.0	467.2	410.2	0.0	1799.5	392.8	128.0	2542.1					
	12	Carbon	X	2.000	2.000	3.467	3.467	3.537	3.507	3.818	4.081	0.000					
	1	Hydrogen	Y	4.000	4.000	7.000	7.000	7.000	7.000	7.000	7.000	4.000					
	16	Oxygen	Z	2.000	2.000	2.369	2.369	2.399	2.329	2.294	1.849	0.000					
	14	Nitrogen	A	0.000	0.000	0.141	0.141	0.000	0.053	0.327	0.679	1.000					
		Charge	e-	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	1.000					
		MolMass	g/mol	60.0	60.0	88.5	88.5	87.8	87.1	94.1	95.1	18.0					
		EDC/mol	Ds	8.000	8.000	15.706	15.706	16.350	16.212	16.704	17.586	64.000			98.7	%SSMod	
3	OXYGEN	umol/l	O2	0.00	0.00	0.00	1068.26	0.00	4837.21	0.00	0.00	4914.46	10819.93		5167.6	kgO/d	
															102.8	%SSMod	
4	BIOMASS	umol/l		86.17	0.00	140.50	123.37	0.00	558.64	0.00	127.98	29.49	1066.15		1512.6	kgVSS/d	
		Carbon	K	4.081	4.081	4.081	4.081	4.081	4.081	0.000	4.081	4.081	4.081		779.2	kgC/d	
		Hydrogen	L	7.000	7.000	7.000	7.000	7.000	7.000	0.000	7.000	7.000	7.000		111.4	kgH/d	
		Oxygen	M	1.849	1.849	1.849	1.849	1.849	1.849	0.000	1.849	1.849	1.849		470.8	kgO/d	
		Nitrogen	N	0.679	0.679	0.679	0.679	0.679	0.679	0.000	0.679	0.679	0.679		151.3	kgN/d	
		COD/VSS	fcv	1.480	1.480	1.480	1.480	1.480	1.480	0.000	1.480	1.480	1.480		2238.7	kgCOD/d	
		C/VSS	fc	0.515	0.515	0.515	0.515	0.515	0.515	0.000	0.515	0.515	0.515		111.4	kgC/d	
		N/VSS	fn	0.100	0.100	0.100	0.100	0.100	0.100	0.000	0.100	0.100	0.100		151.3	kgOrgN-N/	
		EDC/mol	Db	17.586	17.586	17.586	17.586	17.586	17.586	0.000	17.586	17.586	17.586		288.0	kgISS/d	
		MolMass	g/mol	95.1	95.1	95.1	95.1	95.1	95.1	0.0	95.1	95.1	95.1				
		Yield	Yz	0.666	0.666	0.666	0.666	0.666	0.666	0.000	1.000	0.148					
		EndResp	bH	0.202	0.202	0.202	0.202	0.202	0.202	0.000	0.000	0.034					
		EndRes	f	0.20	0.20	0.20	0.20	0.20	0.20	0.000	0.000	0.000					
		SludgeAg	Rs	8	8	8	8	8	8	0.000	8	8					
		FracSludg	E	0.3368	0.3368	0.3368	0.3368	0.3368	0.3368	1.0000	1.0000	0.1166					
5	CO2	umol/l	CO2	234.98	0.00	102.45	944.56	0.00	4315.76	0.00	0.00	-120.33	6649.58		1190.94	kgCO2/d	
6	AMMONIA	umol/l	NH4+	-58.51	0.00	-29.44	-25.85	0.00	-284.19	0.00	0.00	0.00	0.00		0.00	kgN/d	
7	BICARB	umol/l	HCO3-	538.40	0.00	943.80	-25.85	0.00	-284.19	0.00	0.00	0.00	0.00		0.00	kgAlk/d	
8	WATER	umol/l	H2O	671.22	0.00	730.31	1068.59	0.00	5053.31	0.00	0.00	2448.88	11144.48		2993.96	kgWater/d	
9	Nitrate	umol/l	NO3-	-596.91	0.00	-973.24	0.00	0.00	0.00	0.00	0.00	2522.06	951.90		198.90	kN03-N/d	
10	Protons	umol/l	H+	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5064.14	3891.97		2904.39	kgAcidity/d	
11	Nitrogen	umol/l	N2	298.46	0.00	486.62	0.00	0.00	0.00	0.00	0.00	0.00	785.08		328.08	kgN/d	
	RESIDUAL REACTANTS			(dissolved	(dissolved										14.925	Ml/d	
	COD	mgCOD/l	COD	0.00	0.00	0.00	0.00	0.00	0.00	52.50	0.00	0.00	52.50		783.5	kgCOD/d	
	Ammonia	mgN/l		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.81	3.81		56.8	kgFSA-N/c	
	OrganicN	mgN/l		0.00	0.00	0.00	0.00	0.00	0.00	1.80	0.00	0.00	1.80		26.8	kgOrgN-N/	
	TKN	mgN/l		0.00	0.00	0.00	0.00	0.00	0.00	1.80	0.00	3.81	5.60		83.7	kgTKN-N/c	
	TOD	mgO/l		0.00	0.00	0.00	0.00	0.00	0.00	60.72	0.00	17.40	78.12		1165.9	kgTOD/d	
	Nitrate	mgN/l		0.00	0.00	0.00	0.00	13.33	0.00	0.00	0.00	0.00	13.33		198.9	kgNO3-N/c	
	CARBON	mgC/l	C	0.00	0.00	0.00	0.00	0.00	0.00	18.00	0.00	0.00	18.00		268.7	kgC/d	
	HYDROGI	mgH/l	H	0.00	0.00	0.00	0.00	0.00	0.00	2.75	0.00	1.09	3.84		57.3	kgH/d	
	OXYGEN	mgO/l	O	0.00	0.00	0.00	0.00	45.69	0.00	14.42	0.00	0.00	60.11		897.2	kgO/d	
	NITROGE	mgN/l	N	0.00	0.00	0.00	0.00	13.33	0.00	1.80	0.00	3.81	18.93		282.6	kgN/d	
	BALANCES		COD	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	N/A	N/A				
			TOD	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00				
			C	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00				
			H	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00				
			O	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00				
			N	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00				
			Charge	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00				

Table 1 (Part 2): *Spreadsheet output for 8d sludge age nitrification denitrification activated sludge treating settled wastewater at 14°C - mass balance calculations.*

							GAS OUT	GAS OUT			
DesMan			OXYGEN	Carbonace	2820.5	kgO/d	CO2	N2			
SETTLED WW			DEMAND	Nitrificatior	2347.1	kgO/d	1190.9	328.1			
WINTER	Temp oC	14		Total	5167.6	kgO/d	kgCO2-C/d	kgN2-N/d			
Sludge Age (d)		8		Denitrificat	937.4	kgO/d	53.2	43.1	% of C,N In		
	Influent								Effluent		
	Ml/d	14.925							Ml/d	14.485	97.1 %
	kgCOD/d	6718.1							kgCOD/d	760.4	11.3 %
	kgTOD/d	10201.1							kgTOD/d	1131.5	11.1 %
	kgC/d	2238.8							kgC/d	260.7	11.6 %
	kgH/d	559.4							kgH/d	112.0	20.0 %
	kgO/d	2037.5							kgO/d	870.7	42.7 %
	kgN/d	761.9							kgN/d	274.2	36.0 %
	kgFSA-N/(	671.1							kgFSA-N/d	55.1	8.2 %
	kgOrgN-N	90.8							kgOrgN-N/	26.1	28.7 %
	kgTKN-N/(	761.9							kgTKN-N/d	81.2	10.7 %
	kgNO3-N/	0.0							kgNO3-N/c	193.0	
	kgVSS/d	2662.5							kgVSS/d	0.0	0.0 %
	kgISS/d	141.9							kgISS/d	0.0	0.0 %
	kgTSS/d	2804.4							kgTSS/d	0.0	0.0 %
Mass Balances									Water l/d	2994	
COD	100.9 %	Biomass of autotrophs									
TOD	100.0 %										
Carbon	100.0 %										
Hydrogen	100.0 %										
Oxygen	100.0 %										
Nitrogen	100.0 %										



Waste Flov	Dissolved	Particulate	Total		
Ml/d	0.440	0.440	0.440	2.9	%
kgCOD/d	23.1	2238.7	2261.8	33.7	%
kgTOD/d	34.3	2930.2	2964.6	29.1	%
kgC/d	7.9	779.2	787.1	35.2	%
kgH/d	3.4	111.4	114.8	20.5	%
kgO/d	26.4	470.8	497.3	24.4	%
kgN/d	8.3	151.3	159.6	20.9	%
kgFSA-N/d	1.7	0.0	1.7	0.2	%
kgOrgN-N/	0.8	151.3	152.1	16.9	%
kgTKN-N/d	2.5	151.3	153.7	17.1	%
kgNO3-N/c	5.9	0.0	5.9	0.7	%
kgVSS/d	0.0	1512.6	1512.6		
kgISS/d	0.0	288.0	288.0	203.0	%
kgTSS/d	0.0	1800.7	1800.7	64.2	%

Table 2 (Part 1): *Spreadsheet output for anaerobic digestion of primary sludge - kinetic and stoichiometric model calculations.*

DesMan ANAEROBIC DIGESTION OF PRIMARY SLUDGE — PrintAD — Page 1 of 2 Portrait

				ANAEROBIC PRIMARY SLUDGE			ANAEROBIC PRIMARY SLUDGE		ANAEROBIC PRIMARY SLUDGE		System Masses Balances	
		Type		Organics		Organics	Organics	Organics	Organics	Total		
		Substrate		Undiss HAc	Diss Ac-	F-RBCOD	SBCOD	USCOD	UPCOD	+ Infl. FSA!		
1	PS	COD	mgCOD/l	18.0	18.0	110.2	41298.7	52.5	18915.1	60412.58	4530.9	kgCOD/d
		N	mgN/l	0.00	0.00	1.734	506.006	1.80	1278.05	1832.56	137.4	kgN/d
		TOD	mgTOD/l	18.00	18.00	118.17	43611.88	60.72	24757.65	68789.97	5159.2	kgTOD/d
		fZ,BN	mgN/gCOD	0.0	0.0	15.7	12.3	34.3	67.6			
		COD/VSS		1.0667	1.0847	1.4200	1.7195	1.4200	1.4800			
		C/VSS		0.4000	0.4068	0.4702	0.5454	0.4869	0.5151			
		N/VSS		0.0000	0.0000	0.0223	0.0211	0.0487	0.1000			
		Concs	mgC/l	6.750	6.750	36.500	13098.766	18.000	6583.234	19750.00	1481.3	kgC/d
			mgH/l	1.125	0.844	6.142	1960.965	2.750	941.111	2912.94	218.5	kgH/d
			mgO/l	9.000	9.000	33.256	8451.616	14.420	3978.102	12495.39	937.2	kgO/d
			mgN/l	0.000	0.000	1.734	506.006	1.799	1278.050	1832.56	137.4	kgN/d
			e- mmol/l	0.000	-0.281	0.000	0.000	0.000	0.000	-0.28		
2	KINETICS	Flow		0.075	0.075	0.075	0.075	0.075	0.075	-		Ml/d
Rad	10	Unbio fraction		0.000	0.000	0.000	0.000	1.000	1.000			-
Km	3.34	Retention Time		10	10	10	10	10	10			day
Ks	3.76	Influent COD Sti		0.0180	0.0180	0.1102	41.2987	0.0525	18.9151	60.41		gCOD/l
Yad	0.113	Influent bio COD Sbpi		0.0180	0.0180	0.1102	41.2987	0.0000	0.0000	41.44		gCOD/l
bAD	0.041	Influent unbio COD Supi		0.0000	0.0000	0.0000	0.0000	0.0525	18.9151	18.97		gCOD/l
fAD	0.000	Residual bio COD Sbp		0.0000	0.0000	0.0000	0.1466	0.0000	0.0000	0.15		gCOD/l
		Bio COD removed		0.0180	0.0180	0.1102	41.1522	0.0000	0.0000	41.30		gCOD/l
		Acidogen Biomas Zad		0.0015	0.0015	0.0091	3.4101	0.0000	0.0000	3.42		gCOD/l
		Unbio COD conc Sup		0.0000	0.0000	0.0000	0.0000	0.0525	18.9151	18.97		gCOD/l
		Total Effluent COD Ste		0.0015	0.0015	0.0091	3.5566	0.0525	18.9151	22.54		gCOD/l
		Hydrolysis rate rh		0.0019	0.0019	0.0114	4.2550	0.0000	0.0000	4.27		gCOD/(ld)
		CH4 production conc Sr		0.0165	0.0165	0.1011	37.7421	0.0000	0.0000	37.88		gCOD/l
		CH4 volume Qm		0.0063	0.0063	0.0197	6.2598	0.0000	0.0000	6.29		l CH4/(l infl.d)
		Total COD out Ste+Sm		0.0180	0.0180	0.1102	41.2987	0.0525	18.9151	60.41		gCOD/l
		COD Balance		100.00	100.00	100.00	100.00	100.00	100.00	100.00		%
		Fraction to sludge S		0.0829	0.0829	0.0829	0.0829	0.0000	0.0000	0.0829		-
		Fraction to methane		0.9171	0.9171	0.9171	0.9171	0.0000	0.0000	0.9171		-
		umol COD removed		281.3	281.3	877.4	279143.8	0.0	0.0	280583.63		mol/l
	STOICHIOMETRY											
	COD	mg/l	mg/l	18.0	18.0	110.2	41152.2	52.5	18915.1			
3	SUBSTRATE		umol/l	281.3	281.3	877.4	279143.8	392.8	134444.4			
12	Carbon	X		2.000	2.000	3.467	3.897	3.818	4.081			
1	Hydrogen	Y		4.000	3.000	7.000	7.000	7.000	7.000			
16	Oxygen	Z		2.000	2.000	2.369	1.886	2.294	1.849			
14	Nitrogen	A		0.000	0.000	0.141	0.129	0.327	0.679			
	Charge	e-		0.000	-1.000	0.000	0.000	0.000	0.000			
	MolMass	g/mol		60.0	59.0	88.5	85.7	94.1	95.1			
	EDC/mol	Ds		8.000	8.000	15.706	18.428	16.704	17.586			
4	WATER	umol/l	H20	0.00	281.25	515.37	336163.05	0.00	0.00	336959.67	454.9	kgH2O/d
5	BIOMASS	umol/l		0.00	0.00	64.93	24237.91	0.00	134444.44	158747.28	1131.8	kgVSS/d
	Carbon	K		0.000	0.000	4.081	4.081	0.000	4.081	4.081	583.0	kgC/d
	Hydrogen	L		0.000	0.000	7.000	7.000	0.000	7.000	7.000	83.3	kgH/d
	Oxygen	M		0.000	0.000	1.849	1.849	0.000	1.849	1.849	352.3	kgO/d
	Nitrogen	N		0.000	0.000	0.679	0.679	0.000	0.679	0.679	113.2	kgOrg-N/d
	COD/VSS	fcv		0.000	0.000	1.480	1.480	0.000	1.480	1.480	1675.1	kgCOD/d
	C/VSS	fc		0.000	0.000	0.515	0.515	0.000	0.515	0.515	2192.5	kgTOD/d
	N/VSS	fn		0.000	0.000	0.100	0.100	0.000	0.100	0.100		
	EDC/mol	Db		0.000	0.000	17.586	17.586	0.000	17.586	17.586		
	MolMass	g/mol		0.0	0.0	95.1	95.1	0.0	95.1	95.1		
	Yield	Yz		0	0	0.113	0.113	0.000	1.000			
	EndResp	bH		0.000	0.000	0.041	0.041	0.000	0.000			
	EndRes	f		0.00	0.00	0.00	0.00	0.000	0.000			
	SludgeAge	Rs		0	0	10	10	0.000	10			
	FracSludge	E		0.0000	0.0000	0.0829	0.0829	1.0000	1.0000			
6	CO2	umol/l	CO2	281.25	0.00	1117.21	379509.58	0.00	0.00	380908.04	342.82	kgCO2-C/d
7	AMMONIA	umol/l	NH4+	0.00	0.00	79.79	19557.21	0.00	0.00	19637.01	20.62	kgFSA-N/d
8	BICARB	umol/l	HCO3-	0.00	281.25	79.79	19557.21	0.00	0.00	19918.26	74.69	kgAlkCaCO3/
9	WATER	umol/l	H2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	kgWater/d
10	METHANE	umol/l	CH4	281.25	281.25	1579.74	589720.23	0.00	0.00	591862.47	532.68	kgCH4-C/d
11	METHANE	umol/l	CH4								2840.94	kgCH4-COD/

End Page 1

Table 2 (Part 2): *Spreadsheet output for anaerobic digestion of primary sludge - mass balnce calculations.*

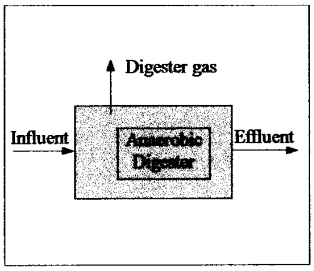
Page 2 of 2

RESIDUAL REACTANTS			(Particulate and dissolved constituents left over from stoichiometry only - not totals!)								
COD	mgCOD/l	COD	0.00	0.00	0.00	146.56	52.50	0.00	199.05	14.93	kgCOD/d
Ammonia	mgN/l		0.00	0.00	0.00	0.00	0.00	0.00	44.97	3.37	kgFSA-N/d
OrganicN	mgN/l		0.00	0.00	0.00	1.80	1.80	0.00	3.59	0.27	kgOrgN-N/d
TKN	mgN/l		0.00	0.00	0.00	1.80	1.80	0.00	48.56	3.64	kgTKN-N/d
TOD	mgO/l		0.00	0.00	0.00	154.77	60.72	0.00	421.05	31.58	kgTOD/d
Nitrate	mgN/l		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	kgNO3-N/d
CARBON	mgC/l	C	0.00	0.00	0.00	46.48	18.00	0.00	64.48	4.84	kgC/d
HYDROGI	mgH/l	H	0.00	0.00	0.00	6.96	2.75	0.00	9.71	0.73	kgH/d
OXYGEN	mgO/l	O	0.00	0.00	0.00	29.99	14.42	0.00	44.41	3.33	kgO/d
NITROGE	mgN/l	N	0.00	0.00	0.00	1.80	1.80	0.00	48.56	3.64	kgN/d

BALANCES								
	COD	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	TOD	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	C	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	H	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	O	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	N	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	Charge	100.00	100.00	100.00	100.00	100.00	100.00	100.00

	Methane	532.7	kgCH4-C/d	CO2	342.8 kgCO2-C/d
	Methane	994.3	Nm3/d	CO2	639.9 Nm3/d
	Methane	2840.9	kgCOD/d	Gas pCO2	39.2 %
DesMan	Methane	62.7	% Influent COD		
Sludge Age (d)		10	AD Volume	750.0	m3

Influent	Mass - kg	Concs - mg/l
Ml/d	0.075	0.075
COD	4530.9	60412.6
TOD	5159.2	68790.0
C	1481.3	19750.0
H	218.5	2912.9
O	937.2	12495.4
TKN-N	137.4	1832.6
FSA-N	3.4	44.967
OrgN-N	134.1	1787.6
VSS	2759.8	36797.9
ISS	574.7	7663.2
TSS	3334.6	44461.0
Water use	454.9	6065.3



Mass Balances	
COD	100.0 %
TOD	100.0 %
Carbon	100.0 %
Hydrogen	100.0 %
Oxygen	100.0 %
Nitrogen	100.0 %

Effluent	Particulate Mass - kg	Particulate Conc - mg/l	Dissolved Mass - kg	Dissolved Conc - mg/l	Total Mass - kg
Ml/d	0.075	0.075	0.075	0.075	0.075
COD	1675.1	22334.3	14.93	199.1	1690.0
TOD	2192.5	29233.0	125.84	1677.8	2318.3
C	583.0	7773.3	22.76	303.5	605.8
H	83.3	1111.2	8.11	108.2	91.5
O	352.3	4697.2	75.04	1000.5	427.3
TKN-N	113.2	1509.1	24.26	323.5	137.4
FSA-N	0.0	0.0	23.99	319.9	24.0
OrgN-N	113.2	1509.1	0.27	3.6	113.5
VSS	1131.8	15090.8	0.0	0.0	1131.8
ISS	574.7	7663.2	0.0	0.0	574.7
TSS	1706.5	22753.9	0.0	0.0	1706.5

End Page 2

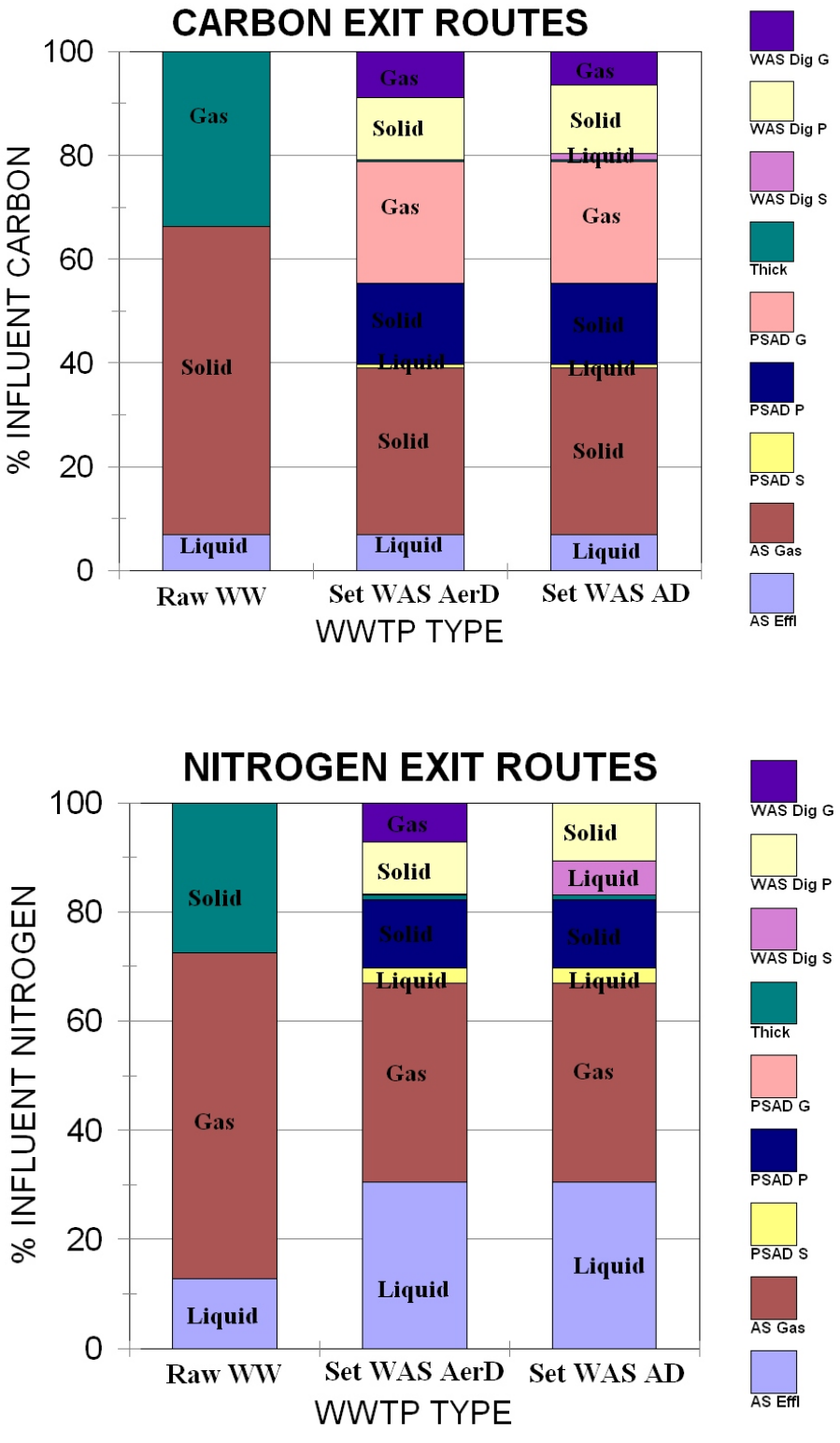
7.4 Evaluation of WWTP output streams

For the particular wastewater characteristics and example WWTPs:

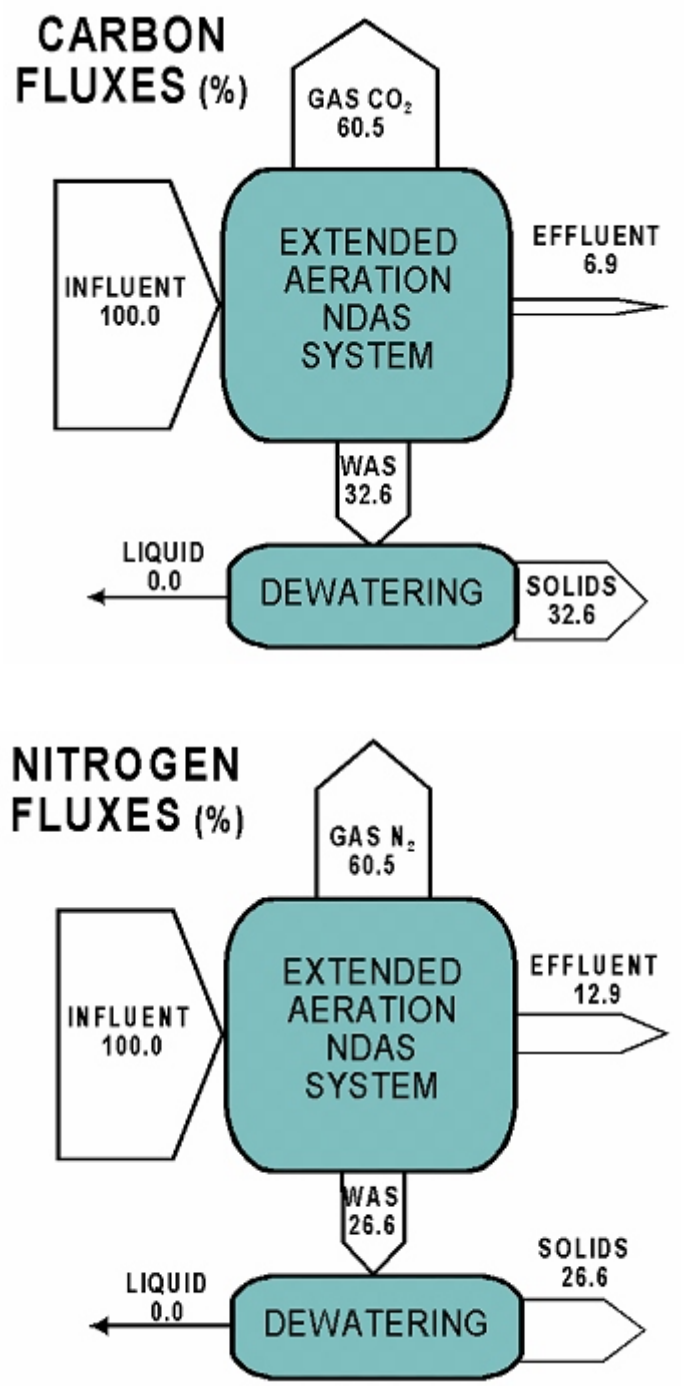
7.4.1 For the raw WW extended aeration nitrification-denitrification activated sludge (NDAS) system at 14°C (Fig 4), of the influent C and N, 6.9% and 12.8% exits via the effluent, 59.4% and 59.7% as gas (CO_2 and N_2) and 33.7% and 27.5% in the waste sludge stream, of which 0.4% and 0.7% are in the soluble form, so that supernatant from sludge thickening/drying beds can be recycled to the influent.

7.4.2 For the settled wastewater short sludge age (8d) NDAS system at 14°C (Fig 5), of the influent C and N, 7.0% and 30.5% exits via the effluent and 32.0% and 36.5% as gas (CO_2 and N_2). Of the influent C mass load, 0.6%, 15.7% and 23.5% (of which 61% is methane) and of the influent N mass load, 2.7%, 12.6% and 0.0% exits primary sludge anaerobic digestion (PSAD) in soluble, particulate and gaseous forms respectively. Of the influent C and N mass loads, 0.2% and 0.9% exits as waste activated sludge (WAS) flotation thickener supernatant, which can be discharged to the final NDAS reactor because its quality is similar to that of the effluent. With anoxic-aerobic digestion of WAS, 0.0%, 12.0% and 9.0% of the influent C mass load exits in soluble, particulate and gaseous forms and 0.0%, 9.7% and 7.2% of the influent N mass load exits in soluble, particulate and gaseous forms. With anaerobic digestion (AD) of WAS, 1.3% (mostly as dissolved CO_2), 13.2% and 6.5% of the influent C mass load exits in soluble, particulate and gaseous forms and 6.2%, 10.6% and 0.0% of the influent N mass load exits in soluble, particulate and gaseous forms. Clearly, AD of WAS increases the N content of the dewatering liquor sharply due the much higher (4 times) N content of AS compared with PS. Therefore to keep the final (AS) effluent N low, N removal from PS and WAS AD dewatering liquor is important before return to the influent. Alternatively, anoxic-aerobic digestion of WAS could be considered, in which case treatment of PSAD dewatering liquor would not be required.

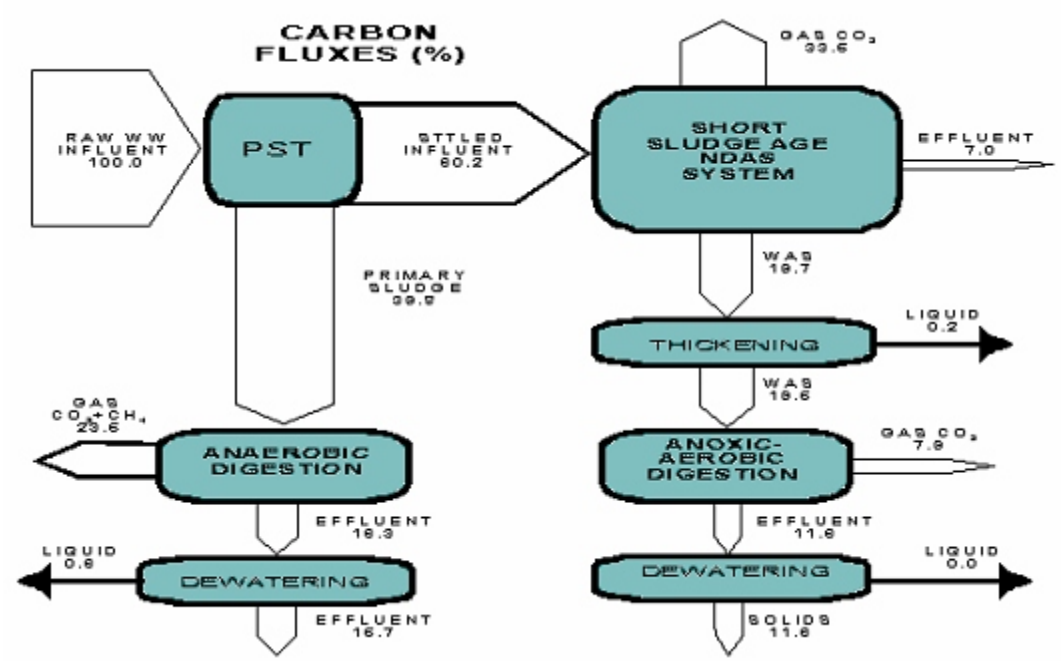
7.4.3 For the raw WW extended aeration NDAS system at 14°C, of the influent O and H mass loads, 6.9% and 16.4% exits via the effluent in dissolved organics, ammonia and nitrate. The WAS stream contains 25.6% and 23.7% of influent O and H mass loads, of which 0.4% and 0.9% are in soluble form. Of the influent O mass, 113.7% is added as oxygen demand and the bio-processes generate 4200 kg of water (0.028% of influent flow), which adds 125.5% and 59.9% of influent O and H mass load to the effluent.

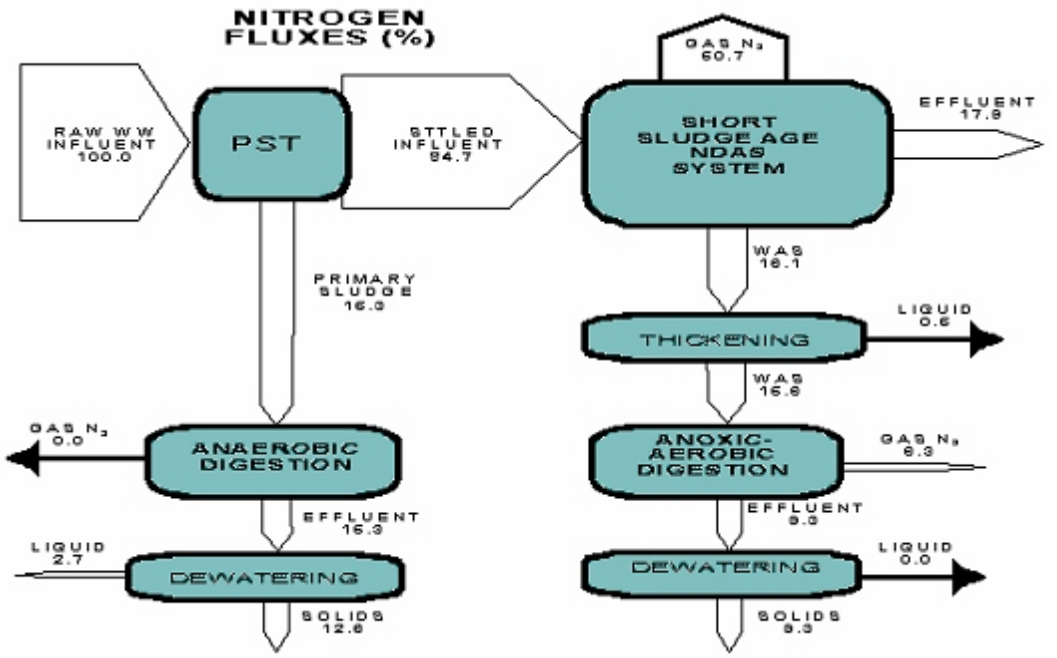


Figs 4 and 5: *Carbon (Fig 4, top) and Nitrogen (Fig 5, bottom) exit routes for 3 WWTP schemes at 14°C: (1) Long sludge age (30d) NDAS treating raw wastewater with direct discharge of waste activated sludge (WAS) to dewatering/drying beds (left bar), and short sludge age (8d) NDAS treating settled wastewater with PSAD, flotation thickening of WAS with (2) anoxic-aerobic digestion of WAS (centre bar) or (3) AD of WAS (right bar) (In legend S = Soluble, P = Particulate, G = Gas, Thick = to thickener and disposal).*

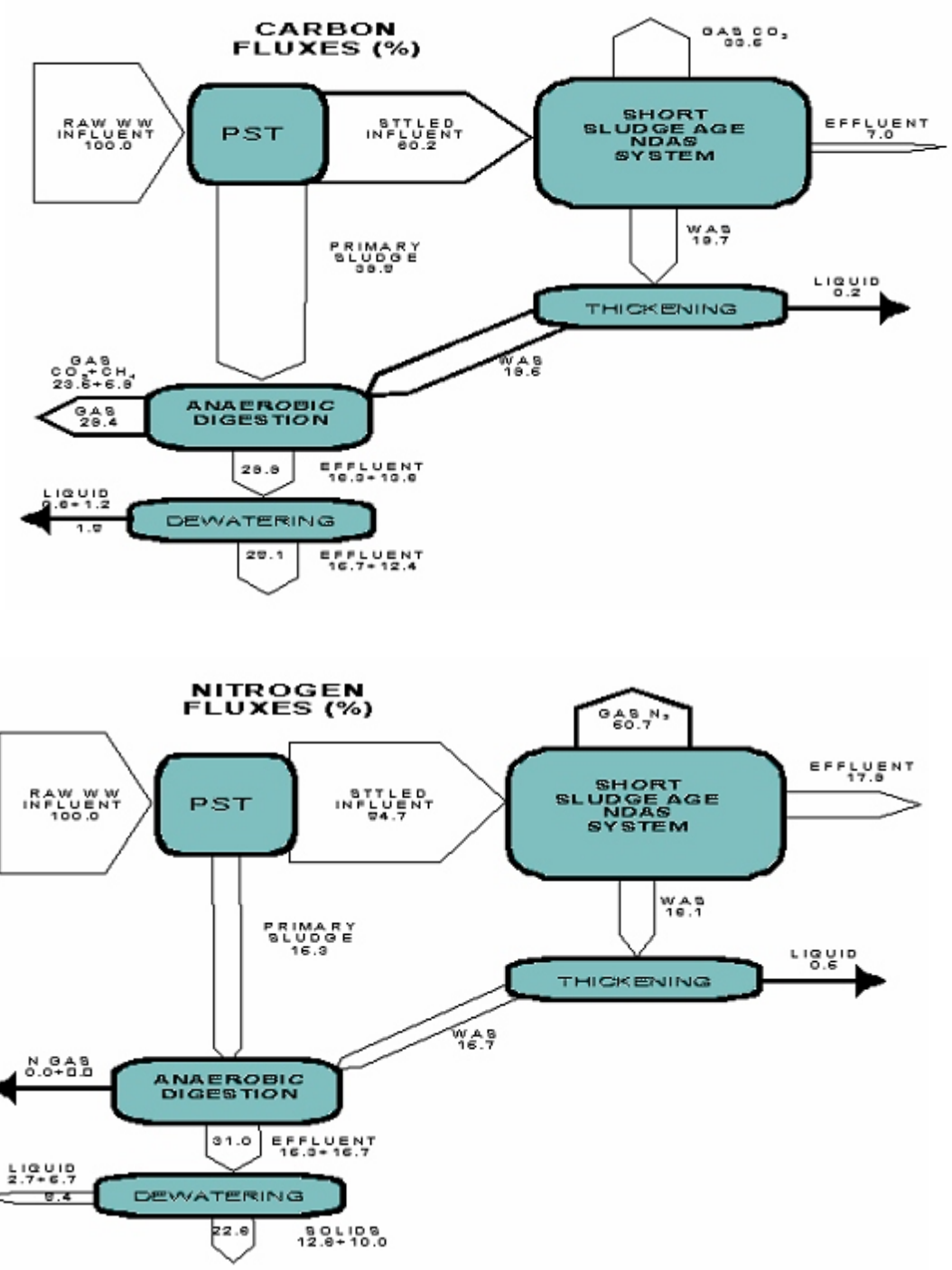


Figs 6a and b*: Carbon (Fig 6a, top) and nitrogen (Fig 6b, bottom) mass flows (fluxes, as % raw wastewater influent fluxes) through and exiting as solid, liquid and gas from the long sludge age (30d) extended aeration nitrification denitrification activated sludge system treating raw wastewater at 22°C. The width of the arrows give show the relative magnitudes of the fluxes.*





***Figs 7a and b**: Carbon (Fig 7a, top) and nitrogen (Fig 7b, bottom) mass flows (fluxes, as % raw wastewater influent fluxes) through and exiting as solid, liquid and gas from the example short sludge age (8d) nitrification denitrification activated sludge system treating settled wastewater at 22°C with anaerobic digestion of primary sludge and anoxic-aerobic digestion of waste activated sludge. The width of the arrows give show the relative magnitudes of the fluxes.*



***Figs 8a and b**: Carbon (Fig 8a, top) and nitrogen (Fig 8b, bottom) mass flows (fluxes, as % raw wastewater influent fluxes) through and exiting as solid, liquid and gas from the example short sludge age (8d) nitrification denitrification activated sludge system treating settled wastewater at 22°C with anaerobic digestion of primary sludge and waste activated sludge. The width of the arrows give show the relative magnitudes of the fluxes.*

7.4.4 For the settled wastewater short sludge age (8d) NDAS system at 14°C, of the influent O and H, 29.3% and 14.4% exits via the effluent in dissolved organics, ammonia and nitrate. Of the influent O mass, 67.0% is added as oxygen demand in the NDAS system and the bio-processes generate 2994 kg of water (0.020% of influent flow), which adds 89.5% and 42.7% of influent O and H mass load to the effluent. From PSAD, of the influent O mass load, 2.5%, 11.8% and 30.7% (as CO_2) exits in soluble, particulate and gaseous forms and of the influent H mass load, 1.0%, 10.8% and 22.8% (as CH_4) exits in soluble, particulate and gaseous forms. In PSAD, 455 kg of water is consumed, which provides some of the O and H for the CO_2 and CH_4 gas. 0.8% and 0.4% of influent O and H mass load exits via the flotation WAS thickener supernatant. In anoxic-aerobic digestion of WAS, of the influent O and H mass load, 0.0% and 0.0% exits in soluble form and 9.1% and 8.2% exits in particulate form. Of the influent O mass, 6.1% is added as oxygen demand and the bio-processes generate 430 kg of water, which adds 12.9% and 6.1% of influent O and H mass load to the effluent. In AD of WAS, of the influent O and H mass load, 10.8% (mostly dissolved CO_2) and 2.6% (mostly in NH_4^+ form) exits in soluble form and 5.7% and 9.0% exits in particulate form. 275 kg of water is consumed, which provides some of the O and H for the CO_2 and CH_4 production, which contain 7.6% and 6.7% of the influent O and H loads.

7.4.5 For the raw WW extended aeration NDAS system at 14°C, a total of 2210 kg CO_2-C (59.4% of influent TOC) is generated (~20 g C/person/d).

7.4.6 For the settled wastewater short sludge age (8d) NDAS system with anoxic-aerobic digestion of WAS at 14°C, a total of 1868 kg CO_2-C (50.2% of influent TOC) and 533 kg CH_4-C (14.3%) is generated, total 2400 kg C (64.5%). With AD of WAS, a total of 1636 kg CO_2-C (44.0% of influent TOC) and 719 kg CH_4-C (19.3%) is generated, a total of 2355 kg C (63.3%). If all the CH_4 is combusted (beneficially or flared), it can be seen that the WWTP type makes little difference to the % influent TOC converted to CO_2.

7.5 Conclusions from the stoichiometric modelling

Much interesting information can be generated by the integrated steady state kinetic and stoichiometric models. This part of the research project:

7.5.1 provides a basis for and demonstrates the strength of including steady state mass balances based kinetic and stoichiometric models in plant wide WWTP models for design and operation.

7.5.2 shows that while COD balances no longer apply when including the autotrophic nitrification process, C, H, O, N and TOD mass balances must strictly apply and should be used to verify model development and outputs.

7.5.3 demonstrates that much useful information can be generated with relatively simple steady state models to aid WWTP layout design and track the different products exiting the WWTP via the solid, liquid and gas streams, such as aerobic versus anaerobic digestion of WAS, N loads in recycle streams, methane production for energy recovery and green house gas (CO_2, CH_4) generation.

8. AEROBIC DIGESTION OF WAS FROM BIOLOGICAL EXCESS PHOSPHORUS REMOVAL SYSTEMS (Objective 7 and 8) – Mebrahtu et al. (2007)

Aerobic batch digestion of waste activated sludge (WAS) from a laboratory scale nitrification denitrification biological excess P removal (NDBEPR) system was carried out with controlled pH (7.20) and in the temperature regulated (20˚C) water research laboratory of the University of Cape Town. The parent NDBEPR system operated at 20 days sludge age and high mixed liquor suspended solids (MLSS) concentration in the aerobic reactor (16 to 20 g/ℓ) because submerged panel membranes effected the solid-liquid separation step. The influent COD concentration was 1000 mg COD/ℓ, of which 200 mg COD/ℓ was added acetate to increase the BEPR in the system. Eight aerobic batch digestion tests were conducted on aerobic reactor sludge harvested from this system; seven (BT1 to7) at high MLSS concentration (~16 to 20 g/ℓ) and one (BT8) at low MLSS concentration (~ 4 g/ℓ).

Both the NDBEPR parent system and the eight batch digestion tests were simulated with Activated Sludge Model No. 2 (ASM2, Henze et al., 1995), modified to include the ISS model of Ekama and Wentzel (2004). This ASM2 model was calibrated against the parent NDBEPR system data as follows: From the measured influent COD characteristics, i.e. RBCOD and unbiodegradable soluble COD fraction ($f_{S'us}$), the unbiodegradable particulate COD fraction ($f_{S'up}$) was selected such that the predicted VSS concentrations in the system matched those measured – an average value of $f_{S'up}$ of 0.183 was obtained, which is in the range of values obtained in the past. Next, the influent RBCOD split between the OHOs and PAOs was determined to match the predicted P removal to that measured. This was done in two ways, by changing the (i) influent RBCOD anaerobic fermentation rate to VFA or (ii) the PAO polyphosphate uptake rate. These have the effect of (i) changing PAO mass at a fixed PAO P content (~0.38 mg P mg PAO/VSS) or (ii) changing the PAO content for a fixed PAO mass. Finally, the influent ISS concentration was selected such that the predicted ISS mass in the system matched that measured. This was an iterative process because of the interaction between the predicted variables such as the P removal and system ISS concentration. Once calibrated against the measured NDBEPR system performance, the predicted results were used as initial conditions for the simulation of the batch test data. The calibration established for the parent system was used unchanged for the batch tests. The two different ways of calibrating the P removal made negligible difference to the predicted P concentrations in the batch tests. From these simulations, the P content of the PAOs was known because it account for the observed P removal in the parent UCT NDBEPR system. Also from Fukase et al. (1982), Arvin and Christensen (1985), Comeau et al. (1985) and Wentzel et al. (1989), the cation and P content of polyphosphate is Mg:K:Ca:P = 0.0275:0.295:0.05:1, which gives an ISS/P ratio of 3.19 mg ISS/mg P. This closely matched the 3.286 ISS/P ratio found by Ekama and Wentzel in their ISS model. This indicated that the Mg, K and Ca concentrations expected in the bulk liquid can be calculated from the simulated P release.

8.1 A lag of two to four days was observed experimentally before the onset of a endogenous behaviour during the aerobic digestion process. This possibly was caused by an apparent growth during the early period of the digestion, for the phosphorus accumulating organisms (PAOs), on the stored polyhydroxyalkanoates (PHA) and for the ordinary heterotrophic organisms (OHOs) on slowly biodegradable substrate enmeshed in the sludge harvested from the NDBEPR system. This behaviour was not observed theoretically – the predicted concentration of stored PHA in the PAOs and enmeshed SBCOD were low in the aerobic reactor.

8.2 Similar trends and rates of volatile suspended solids (VSS) destruction and total suspended solids (TSS) reduction were observed in the aerobic digestion tests, and the VSS/TSS ratio remained almost constant with digestion time. The parallel reduction in VSS and TSS implies that there is also a reduction in inorganic suspended solids (ISS). This reduction is both qualitatively and quantitatively described by the ISS model of Ekama and Wentzel (2004). The calibrated ASM2 model predicted closely the observed decrease in VSS and TSS with time in the batch digestion tests.

8.3 Although subject to some variation, the filtered COD was observed to increase, on average, about 30 mg/ℓ indicating a very low generation of residual filtered unbiodegradable COD during the aerobic digestion process. Considering the very high total COD concentration at which seven batch tests were done (17,000 to 20,000 mg COD/ℓ) this increase is negligible. The total COD reductions obtained were comparable to the VSS destructions. The COD/VSS ratio remained approximately constant during aerobic digestion. While no unbiodegradable soluble COD is generated in the model, the simulated COD and COD/VSS ratio for the batch tests matched closely those observed.

8.4 The highest percentage VSS destruction and total COD reduction were obtained at the longest batch detention times. However, experimentally there was some variation in that the percentage VSS reduction did not consistently follow the aerobic digestion time for all eight batch tests. For the percentage COD reduction consistency was observed. The removal efficiency of VSS was slightly higher than that of the COD, indicating a slight increase in COD/VSS ratio of the remaining solids. Because this increase was small, the correlation between the predicted and measured COD/VSS ratio was good.

8.5 With complete mixing and adequate aeration (2-5 mg O/ℓ) complete nitrification was observed in all the batch tests. The FSA concentrations in the bulk solution at the end of the digestion period were all well below 1 mg N/ℓ. This was also predicted by the model.

8.6 Similar TKN reductions with respect to VSS destruction and TSS reduction were observed. The almost identical TKN reductions with respect to VSS destruction and TSS reduction and continuous increase in nitrate concentration with cumulative total oxygen utilized during the digestion period indicates, as expected from the model, that the source of the released N was the solubilization of the organic N in the sludge mass. This N release is solely associated with the degradation of OHO and PAO biodegradable organics. Moreover, the nitrogen content of the WAS was almost constant throughout the digestion period, i.e., at an average of 0.087 mg N/mg VSS for the eight batch tests. The calibrated ASM2 model predicted reasonably well the measured ammonia and nitrate concentrations with time, indicating that the observed OHO death and PAO endogenous respiration rates matched those of the ASM2 model. The observed increase in soluble (unbiodegradable) organic N was extremely low in relation to the total TKN reduction in unfiltered TKN and validates the ASM2 model (zero generation) in this respect.

8.7 A direct relationship was observed between the supernatant ortho phosphate (OP) concentration in the batch tests and the initial P content in the solids; the higher the initial P content, the higher the supernatant OP concentration with time. The P release was significantly more than from biomass P content only, indicating that PAO poly phosphate was released during aerobic digestion. The calibrated ASM2 in which all the stored polyphosphate of the PAOs that have “died” in the endogenous respiration as well as the

biomass P content of the PAOs and OHOs that have "died", was used to assess the magnitude of the P release observed in the batch tests.

8.8 Compared with the ASM2 predicted OP concentration with time, the observed OP concentration was much lower, by 2 to 3 times, for the seven concentrated TSS batch tests (16-20 g TSS/ℓ). The only batch test for which the predicted OP concentration with time matched that observed was the diluted one (BT-8, 4 g TSS/ℓ). Although complete nitrification kept the FSA concentration low (< 1 mg N/ℓ), the ionic product of the measured Mg, OP and FSA was close to the solubility product for struvite during digestion time indicating that, for the concentrated batch tests, mineral precipitation was possible. From the composition of polyphosphate, at least as much Mg release as P release on a mass concentration basis is expected. The ASM2 predicted P concentration after 15d digestion exceeded 600 mg P/ℓ and so without mineral precipitation, Mg concentrations of this magnitude should be observed. The observed Mg (and calcium) concentrations were an order of magnitude lower, only ~ 60 mg/ℓ Although the measured Ca, Mg and OP concentrations increased progressively with digestion time in the concentrated batch tests, it was concluded that struvite precipitation took place in these tests, which would account for the much lower observed OP release than predicted by the ASM2 model. For all other parameters, the correlation between predicted and observed results was reasonable considering the complexity of the system being modelled.

8.9 Struvite precipitation in the concentrated (2% TSS) batch tests is supported by (i) the much lower OP concentration in the undiluted BT-7 compared with the diluted BT-8 "corrected" for dilution and (ii) the only batch test which the OP concentration could be correctly predicted was diluted BT-8 – all the other undiluted batch tests had predicted OP concentrations 2 to 3 times higher than the measured OP concentrations and (iii) the measured Mg concentration was only about 1/3rd of that expected from the polyphosphate content and batch test simulation model precdicted OP concentration. From Mg:K:Ca:P = 0.275:0.295:0.05:1 content of polyphosphate, the predicted bulk liquid cation concentrations from the predicted final OP concentration of around 700 mg P/ℓ should be 192:206:35:700. The observed final concentrations were significantly below these predicted concentrations from the P content of the PAOs at around 60: - :30:300. In hindsight, K should have been measured also because it does not readily precipitate. High and increasing K concentrations with digestion time would have provided further evidence that P was being released by the PAOs but Mg and OP remained low in the bulk liquid due to struvite precipitation.

8.10 The absence of a consistent high difference between the observed percentage daily incremental P release with respect to the total P release in the batch tests suggest that the polyphosphate (PP) content of the remaining live PAOs remains approximately constant during the digestion process. An initial very high release of P by all the live PAOs until their P content is the same low value as OHOs before the endogenous respiration commences was not observed. Therefore, it seems reasonable to accept, as is done in the ASM2 model, that P is released by PAOs during aerobic digestion as they die at their endogenous rate, i.e. as their VSS mass decreases, though validation of this may entail further investigation due to the confounding issue of mineral precipitation in the batch tests.

8.11 The predicted OUR declined much more rapidly over the first 2 to 3 days than observed. The theoretical (predicted) nitrate and OP concentrations versus cumulative oxygen utilized (OU) was linear. Due to the high initial observed OUR, the observed nitrate versus cumulative OU has an initial lag but thereafter becomes linear at the same slope as that predicted. This confirms that the nitrate generated is due to the OHO and PAO death/endogenous processes. There was also a lag for the observed OP concentration versus cumulative OU. However, the observed slope did not become linear but continued to increase with digestion time. This suggests that PAOs die/release P faster as digestion progresses but this observation cannot be validated due to the high likelihood of P precipitation in the concentrated batch tests.

8.12 Except for the initial OUR where a marked difference between the predicted and measured values were observed over the first 2 to 4 days of the batch test, the calibrated ASM2 model acceptably predicted the COD, TKN, FSA, VSS and nitrate concentrations. With regard to the OP concentration, it would appear that ASM2 can predict the potential supernatant OP concentration correctly for low concentration (~ 4 g TSS/ℓ) aerobic digestion, but whether the high predicted OP concentration will be actually observed in high concentration (>20 g TSS/ℓ) aerobic digestion seems unlikely due to struvite precipitation. Therefore, once calibrated, the ASM2 model can be used to simulate aerobic digestion systems to estimate the nitrate and maximum OP concentrations in digester liquor. From simulation runs with anoxic-aerobic digestion (50% aerobic time with 2 or 3 hour air on), near complete denitrification can be obtained (nitrate < 2 mg N/ℓ) in the aerobic digester. This also helps keep digester alkalinity and pH up without chemical dosing (Warner et al., 1986).

8.13 A steady state aerobic digestion model for NDBEPR WAS was developed based on the OHO and PAO active fractions of the VSS. With the widely accepted endogenous respiration rates of OHOs (0.24 /d) and PAOs (0.04 /d) this steady state model, including nitrification and extended to include the ISS and TSS concentration, yielded closely similar VSS, TSS, ortho P and nitrate concentrations with time in batch aerobic digestion as ASM2. The steady state aerobic digestion model, therefore, acceptably describes the aerobic digestion of WAS from BEPR AS systems.

8.14 The average values of the endogenous respiration (b) rate for OHOs obtained from the initial part (6-8 days) of the observed batch tests (where the OHO activity is expected to be the highest) with the different measured test parameters, such as COD, OUR, VSS and nitrate, was very variable and differed widely from the commonly accepted values of b_{H20} = 0.24/d due to variability in measured data. The b rate of the OHOs determined from the ASM2 batch test simulated OUR was 0.13/d. This is between the commonly accepted b_{H20} (0.24/d) and b_{G20} (0.04/d) rates, which is reasonable considering that the PAO active fraction is higher due to the acetate dosing to the parent system resulting in a high PAO OUR also at the start of the batch test. The b rate obtained for the PAOs from the simulated results of the last part of the batch tests (where the OHO activity is expected to have ceased) was quite consistent and close to the commonly accepted value b_{G20} = 0.04/d. It was concluded from this that the b_H and b_G rates cannot be determined experimentally from aerobic batch tests on sludge harvested from NDBEPR systems.

8.15 Generally, VSS reduction is accepted as a measure of residual biodegradability in treated sludge, in which sludges with > 38% reduction in VSS and 20-30% VSS are considered

stable. Specific oxygen utilization rate (SOUR) of sludges has recently gained in acceptance as a method of measuring aerobic digester effectiveness. For land disposal, the biosolids must achieve a SOUR value of less than 1.5 mg O/(g TSS.h) for biosolids treated by an aerobic process (Tonkovic, 1999) and generally, SOUR < 1 mg O/(g VSS.h) are considered well-stabilized sludges. The SOUR observed at the end of the batch tests were all below the SOUR < 1 mg O/(g VSS.h) threshold value, signifying that the aerobically digested waste activated sludge was well stabilized.

8.16 Aerobic digestion, modified to include intermittent aeration to promote nitrate removal and lime addition to enhance mineral precipitation, is a simple stabilization system for NDBEPR WAS producing a low N and P dewatering liquor for recycle to the biological reactor.

In this research mineral precipitation in aerobic digestion of concentrated NDBEPR sludge was not expected and resulted in significantly (by 2 to 3 times) lower OP concentration in the bulk liquid. While this is a major advantage practically, because it leads to much lower OP concentrations in digester dewatering liquors, it is an aspect that requires confirmation by further investigation. Perhaps it is possible to integrate the biological processes of ASM2 into a 3 phase mixed weak acid base chemistry model so that mineral precipitation can be modelled also. ASM-1 and a variant of Anaerobic Digestion Model No. 1 (UCTADM1) have been integrated into a two phase (aqueous gas) mixed weak acid base model (Sötemann *et al*., 2005a and b) but not into three phase weak acid base chemistry models yet.

9. PROJECT CONCLUSIONS AND FURTHER RESEARCH

This project made significant advances towards developing steady state mass balances based integrated WWTP models which link primary sedimentation, nitrification denitrification activated sludge and aerobic or anaerobic digestion of primary and waste activated sludges. The most significant of these developments is the finding that particulate organics that are unbiodegradable in the activated sludge reactor, i.e. those from the influent wastewater and from the endogenous process generated in the reactor, are also unbiodegradable under anaerobic digestion conditions. Activated sludge and anaerobic digestion simulation models can therefore be linked with common compounds at the link to form plant wide WWTP models. Such plant wide models are large, complex and require significant modelling skills, experience and understanding to master and use effectively. Furthermore, such models are not compatible with design because they require all the reactor sizes and inter-connecting flows to be quantitatively defined. Steady state models are more practical for design, because they allow reactor sizes and interconnecting flows to be simply determined. Steady state models of WWTP unit operations are therefore a very useful complement to the complex simulation ones. Development of a mass balances based steady state model for the entire WWTP comprising primary settling, ND activated sludge and aerobic or anaerobic digestion of primary and waste activated sludge was completed in this project. Mass balance carbon (C), nitrogen (N), oxygen (O), hydrogen (H) and total oxygen demand (TOD) stoichiometry was also developed to complement the steady state models so that the different products exiting the WWTP via the solid, liquid and gas streams can be calculated, such N loads in recycle streams, methane production for energy recovery and green house gas (CO_2, CH_4) generation.

Not considered in this project were the behaviour of the phosphorus accumulating organisms (PAO) from biological excess P removal (BEPR) activated sludge systems under anaerobic digestion conditions. The release rates of N and P from the cell bound phase to the dissolved phase under anaerobic digestion conditions needs to be investigated to include anaerobic digestion of BEPR WAS into plant wide WWTP models to determine potential N and P concentrations in digester dewatering liquor. Also, it is not clear whether anaerobic digestion of WAS together with primary sludge (PS) has a beneficial effect on the hydrolysis rate of WAS compared with anaerobically digesting the WAS by itself. Hence the main objectives of further research are:

(1) Determine the P release processes and kinetics of BEPR WAS in AD.
(2) Determine the hydrolysis rates of WAS from nitrification denitrification (ND) and NDBEPR activated sludge systems when anaerobically digested by itself and when co-digested with PS.

9.1 Experimental research work.

To achieve this the following experimental programme is envisaged:

- Operate three continuous flow activated sludge (AS) systems and four flow-through ADs – one AS system as a membrane UCT NDBEPR system and two Modified Ludzack-Ettinger (MLE) ND systems to generate WAS for the three of the four ADs.
- Feed raw wastewater to one MLE system and settled wastewater to the other MLE and membrane UCT systems.
- Make the raw wastewater from the settled wastewater fed to the MLE and UCT systems by adding a predetermined concentration of primary sludge (PS). Feed the same PS to the fourth AD.

- Operate the four ADs at three sludge ages (10, 18 and 25d) to determine the sludge hydrolysis rate and at a very long sludge age (60d) to determine the sludge unbiodegradable fraction.
- Conduct anaerobic batch tests on mixtures of sludge harvested from the ADs and AS reactors to measure the P and N release rates.
- Calibrate the ASM1 (for ND) and ASM2 (for NDBEPR) with the two MLE and one UCT system data such that these models simulate the performance of these systems accurately. The predicted mixed liquor concentrations then reflect the initial concentrations and WAS sludge characteristics fed to the anaerobic digesters.
- With the measured AD performance data, calibrate and simulate the flow through ADs with the steady state and simulation (UCTADM1) AD models. Does the predicted performance match that observed? If yes then the AS and AD models are a good representation of the processes in the systems. If not, find reasons for the differences and appropriately modify the models to accurately simulate the observed data.

With this experimental set up, the following can be determined for plant wide WWTP modelling:

(1) Kinetics of P release from to BEPR WAS under anaerobic conditions.
(2) Does mineral precipitation take place in BEPR WAS ADs?
(3) Compare the P release in AD with that observed in aerobic digestion of this investigation.
(4) Confirm mineral precipitation in the aerobic digestion tests of this investigation.
(5) Confirm unbiodegradable fraction of primary sludge with two sources – mass balance round PST and PS AD.
(6) Confirm unbiodegradable fraction of ND system WAS from the MLE system performance data and AD of MLE system WAS for both raw and settled wastewater.
(7) Measure the hydrolysis rate of WAS co-digested with PS – does the much larger acidogen biomass generated with PS digestion assist in the hydrolysis of WAS leading to a faster hydrolysis rate of WAS compared with digesting it by itself.

9.2 Model development work.

ASM1 and UCTADM1 (a variant of the IWA ADM1) have been programmed into a two phase (aqueous-gas) mixed weak acid base framework to form two phase integrated mixed weak acid base chemical, physical and biological process models for the systems. This needs to be done also for ASM1, which includes the biological excess P removal. Then the biological processes of ASM2 and UCTADM1 need to be modelled in a three phase (aqueous-gas-solid) mixed weak acid base chemical-physical framework to form three phase integrated chemical, physical and biological process models. With these models, mineral precipitation in aerobic (as may have happened in this investigation) and anaerobic digestion of BEPR WAS (as may happen in this recommended research) can be investigated in greater depth by simulation.

9.3 Municipal WWTP investigations arising from this research project.

Research projects in the municipal wastewater treatment area emanating from this research project that require investigation are:

9.3.1 Biodegradability of toilet paper.

Waterborne sanitation systems cannot function without toilet paper – a low wet strength cleaning material. Most other cleaning materials such as high wet strength paper (e.g. newspaper) will block the system. Toilet paper is made from fibrous organic material and could make a significant contribution to the unbiodegradable particulate organics in

wastewater. The higher the unbiodegradable particulate organics in wastewater, the larger the activated sludge reactor and the higher the sludge production at the WWTP.

9.3.2 Effect of chemically enhanced primary treatment (CEPT) on biological nutrient removal performance and WWTP capacity.

Many WWTPs are overloaded with organics – high COD loads – as local authorities have under-invested in plant expansions over the past decade. CEPT increases COD removal in PSTs and diverts organics away from the secondary treatment (activated sludge) system to the PS treatment system, and so increases capacity or reduces organic load on secondary treatment. The higher PS production usually can be absorbed by anaerobic (or aerobic) digesters when PS is thickened because capacity of these systems is governed more by hydraulic flow than organic load. However, CEPT changes the wastewater characteristics by removing colloidal non-settleable particulate organics and this may affect the biological N and P removal performance of the activated sludge system.

9.3.3 Critical appraisal of sludge minimization practices.

The European Union has recently sponsored several research projects in Europe focused on WWTP sludge production minimisation practices and technologies (see IWA/WISA Conference on Management of Residues emanating from Water in Wastewater Treatment, Aug., 2005, Sandton, RSA). While some of these techniques show an improvement in solids removal in anaerobic digestion, the question arises whether this is due to conversion of unbiodegradable organics to biodegradable organics or due to a faster hydrolysis/utilization rate the existing biodegradable organics. Also, some of these sludge minimisation techniques are very energy intensive - several times that required for aeration. Because the greatest environmental impact of the WWTP is at the power generation plant, one questions the wisdom of reducing sludge production (and hence monetary cost) at the WWTP at a major increase in environmental cost at the power generation plant.

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APPENDIX A

UNIVERSITY OF CAPE TOWN
Department of Civil Engineering

Water Research Commission Project K5/1620
Mass balances and modelling of wastewater treatment plants

Appendix A - Publications from Project (2005-2006).

1.1 Journal papers - Published

*Sötemann SW, Musvoto EV, Wentzel MC and Ekama GA (2005) Integrated chemical, physical and biological processes kinetic modelling Part 1 – Anoxic and aerobic processes of carbon and nitrogen removal in the activated sludge system. *Water SA* **31**(4) 529-544.

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*Ekama GA, Wentzel MC and Sötemann SW (2006) Mass balances based plant wide wastewater treatment plant models – Part 2: Tracking the influent inorganic suspended solids. *Water SA* **32**(3) 277-285.

*Ekama GA, Sötemann SW and Wentzel MC (2006) Mass balances based plant wide wastewater treatment plant models – Part 3: Biodegradability of activated sludge organics under anaerobic conditions. *Water SA* **32**(3) 287-296.

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2.1 International conference papers – presented

Ekama GA and Wentzel MC (2005) A model for calculating the reactor inorganic suspended solids concentration in activated sludge systems. Procs 4th IWA Activated sludge population dynamics specialist conference, Brisbane, 17-20 July, 333.

Ekama GA, Wentzel MC and Loewenthal RE (2005) Integrated chemical-physical processes kinetic modeling of multiple mineral precipitation problems. IWA specialized conference on nutrient management in wastewater treatment processes and recycle steams, Krakow, 18-21 Sept., 225-233.

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Ekama GA, Wentzel MC and Sötemann SW (2006) Tracking influent inorganic suspended solids through wastewater treatment plants. Procs. IWA world water congress and exhibition: Sustainable water management practises. Beijing. 10-14 Sept.

Ekama GA, Sötemann SW and Wentzel MC (2006) Biodegradability of waste activated sludge organics under anaerobic conditions. Procs. IWA world water congress and exhibition: Sustainable water management practises. Beijing. 10-14 Sept.

2.2 International conference papers – accepted

Brink IC, Wentzel MC and Ekama GA(2007) Using stoichiometry to build a plant wide mass balance based steady state WWTP model. Procs 10th IWA Design, operation and economics of large wastewater treatment plants, Vienna, 9-13 Sept.

Ekama GA, Wenbtzel MC and Brink IC (2007) Estimating greenhouse gas emissions from wastewater treatment plant with bioprocess stoichiometry. 2007 Association of Environmental Engineering and Science Professors (AEESP) conference, Virginia Tech, Blacksburg, USA, 27/7-1/8. (Invited paper).

2.3 Local conference papers – presented

Sötemann SW, Wentzel MC and Ekama GA (2006) Towards developing a mass balances based wastewater treatment plant model. Procs. 9th biennial WISA conference and exhibition, Durban, 21-25 May.

3 Reports

Mebrahtu MK, Wentzel MC and Ekama GA (2007) Aerobic digestion of waste activated sludge from biological N ad P removal systems. Research report No W126, Dept of Civil Eng., Univ of Cape Town, Rondebosch, 7701, Cape, RSA.

Ekama GA, Mebrahtu MK, Brink IC and Wentzel MC (2007) Mass balances and modelling over wastewater treatment plants. Final report to the WRC on Project K5/1620, Report 1620/1/11, Water Research Commission, Private Bag, 03, Gezina, 0031, Gauteng, RSA. (This report)

APPENDIX B

LIST OF SYMBOLS AND ABBREVIATIONS

Abbreviation	Description
AD	Anaerobic digestion
ADM1	Anaerobic digestion model No 1
ADWF	Average dry weather flow
AerD	Aerobic digestion
ANO	Autotrophic nitrifier organisms
AS	Activated sludge
ASM1	Activated Sludge Model No. 1
ASM2	Activated Sludge Model No. 2
BEPR	Biological excess phosphorus removal
BPO	Biodegradable particulate organics
BT	Batch test
C	Carbon
COD	Chemical oxygen demand
d	Day
FSA	Free and saline ammonia
F-RBO	Fermentable readily biodegradable organics
H	Hydrogen
h	Hour
ISS	Inert suspended solids
kg	Kilogram
Mg	Magnesium
mg	Milligram
Mℓ	Megalitre
MLE	Modified Ludzack Ettinger
N	Nitrogen
ND	Nitrifying / denitrifying
O	Oxygen
OHO	Ordinary heterotrophic organism
OP	Ortho phosphorus
OU	Oxygen utilized
OUR	Oxygen utilisation rate
P	Phosphorus
PAO	Polyphosphate accumulating organism
PHA	Phosphate accumulating organisms
PP	Polyphosphate
PS	Primary sludge
PST	Primary settling tank
RBCOD	Readily biodegradable COD
SBCOD	Slowly biodegradable COD
SOUR	Specific oxygen utilization rate
TKN	Total Kjeldahl nitrogen
TOC	Total organic carbon

TOD	Total oxygen demand
TP	Total phosphorus
TSS	Total suspended solids
UPO	Unbiodegradable particulate organics
USO	Unbiodegradable soluble organics
VFA	Volatile fatty acid
VSS	Volatile suspended solids
WAS	Waste activated sludge
WRC	Water Research Commission
WW	Wastewater
WWTP	Wastewater treatment plant
^{o}C	Degrees Celcius

Symbol	**Description**
b_H, b_{H20}	Endogenous respiration rate of OHOs (/d) and at 20^{o}C
b'_H, b'_{H20}	Death rate of OHOs (/d) and at 20^{o}C
b_G, b_{G20}	Endogenous respiration rate of PAOs (/d) and at 20^{o}C
f_{cv}	COD/VSS ratio of organics
$f_{AS'up}$	Unbiodegradable fraction of activated sludge
$f_{PS'up}$	Fraction of unbiodegradable COD in the primary sludge
$f_{ZB,N}$	N content of the OHOs
$_A$, $_{A20}$	ANO maximum specific growth rate, and at 20^{o}C
S_{bpi}	Influent biodegradable particulate organics concentration
S_{upi}	Influent unbiodegradable particulate COD concentration
Y_H	OHO yield coefficient in terms of VSS