

# Integrated biological, chemical and physical processes kinetic modelling Part 1 – Anoxic-aerobic C and N removal in the activated sludge system

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## Abstract

The biological kinetic Activated Sludge Model No. 1 (ASM1, Henze et al., 1987; Dold et al., 1991) for carbon (C) and nitrogen (N) removal is integrated with the mixed weak acid/base model of Musvoto et al. (1997, 2000a,b,c) to extend application of ASM1 to situations where an estimate for pH is important. Because chemical precipitation is generally not significant when treating municipal wastewaters for C and N removal, only gas and liquid phase processes were considered for this integrated model. The biological processes in ASM1 were modified to take into account the effect of the interaction of the weak acid/base species of the ammonia, carbonate and phosphate systems and pH on heterotrophic and autotrophic organism behaviour, which includes generation and utilisation  $\text{CO}_2$  in metabolism, use of specific weak acid/base species for organism growth and generation and utilisation of  $\text{H}^+$ . With these modifications, simulations with the model were compared with those of ASM1 and experimental data in the literature; a good correlation was obtained. However, these comparisons are only a preliminary validation, because, despite their inclusion, the weak acid/bases and pH do not have a significant effect on the biological processes in the cases considered (i.e. well buffered wastewater). A difficulty in calibrating this model is selection of the  $k_{\text{LA}}$  value for the aeration system, which affects the pH in the anoxic and aerobic reactors through  $\text{CO}_2$  gas exchange. Aerobic reactor outflows from two full-scale wastewater treatment plants with fine bubble aeration systems were found to be around 20% supersaturated with  $\text{CO}_2$ . The performance of a ND activated sludge system with low influent alkalinity is evaluated.

**Keywords:** Activated sludge, weak acid/base chemistry, integrated modelling, N removal

## Abbreviations

ACP	Amorphous calcium phosphate
ADL	Anaerobic digester liquor
Alk	Alkalinity
ANO	Autotrophic nitrifier organism
AS	Activated sludge
ASim	A computer simulation programme for NDBEPR systems (Gujer, 1998)
ASM1 & 2d	Activated Sludge Models No. 1 and 2d
ATP	Adenosine triphosphate
BA	Biological activated sludge processes name prefix
BEPR	Biological excess phosphorus removal
C	Carbon
CED	Chemical equilibrium dissociation
CIP	Chemical ion pairing
COD	Chemical oxygen demand
CP	Chemical/physical
CPB	Chemical/physical/biological
DO	Dissolved oxygen
IWA	International Water Association
IAWPRC	International Association for Water Pollution Research and Control (former IWA)
N	Nitrogen
ND	Nitrification/Denitrification
OHO	Ordinary heterotrophic organism
OUR	Oxygen utilisation rate

P	Phosphorus
pH	-ve log of the hydrogen ion ( $\text{H}^+$ ) activity
PGE	Physical gas exchange
PMP	Physical mineral precipitation
RBCOD	Readily biodegradable COD
SBCOD	Slowly biodegradable COD
SBR	Sequencing batch reactor
SCFA	Short chain fatty acid
T	Temperature
TDS	Total dissolved solids
TKN	Total Kjeldahl nitrogen
TN	Total inorganic nitrogen (FSA+nitrate+nitrite)
TOC	Total organic carbon
UCTOLD	A computer simulation programme for ND AS systems (see Dold et al., 1991)
UCTPHO	A computer simulation programme for NDBEPR AS systems (see Wentzel et al., 1992 and Dold et al., 1991)
VSS	Volatile suspended solids
W	Watts

## Symbols

b	Endogenous respiration/death rate of organisms. Subscripts A and H denote rates for ANOs and OHOs respectively
$C_{\text{T}}$	Total inorganic carbon
$D_{\text{LCO}_2}, D_{\text{LO}_2}$	Liquid phase molecular diffusion coefficient for $\text{CO}_2$ and $\text{O}_2$
$f_{\text{E}}$	Endogenous residue fraction of biomass
$f_{\text{ZE,P}}$	P content of endogenous residue fraction of OHOs
$f_{\text{ZB,N}}$	N content of the OHOs

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$f_{ZB,P}$	P content of the OHOs
$f_{ZE,P}$	P content of endogenous residue fraction of OHOs
$f_{xm}$	Maximum unaerated sludge mass fraction for nitrification
${}^{(1)}H_c$	Dimensionless Henry's law constant.
$k_G$	Gas phase individual mass transfer coefficient
$K$	Half saturation coefficient in process switching functions
${}^{(1)}K_H, {}^{(1)}K'_H$	Henry's law constant. Prime (') denotes value corrected for ionic strength effects.
$K_I, K_{II}$	Inhibition constants for pH effect on growth of ANOs
$k_L$	Liquid phase individual mass transfer coefficient
${}^{(1)}K_{La}$	Overall liquid phase mass transfer rate coefficient.
$K_{max}$	Inhibition constant for pH effect on growth of ANOs
${}^{(2)}K_n$	ANO half saturation coefficient.
${}^{(1)}K_P, {}^{(1)}K_r$	Weak acid/base forward (f) and reverse (r) dissociation rate constants. Prime (') denotes value corrected for ionic strength effects.
$n$	Diffusivity coefficient
$N_{obs}, N_{obsi}$	Biodegradable soluble organic N, and in influent
$p_{CO_2}, p_{N_2}, p_{O_2}$	Partial pressure of $CO_2$ , $N_2$ and $O_2$ gases
$R$	Universal gas constant
$R_{sm}$	Minimum sludge age for nitrification
$S_{bl,lost}$	Biodegradable COD lost when nitrate is N source for growth
$Y_{ZA}$	ANO yield coefficient
$Y_{ZH}, Y'_{ZH}$	OHO yield coefficient under aerobic and anoxic conditions respectively
${}^{(2)}\mu_A$	ANO maximum specific growth rate
$\theta_{ns}$	pH sensitivity coefficient for ANOs for $pH < 7.2$
[ ]	denotes compound concentration in mol/l
${}^{(1)}$	Additional subscripts $O_2, CO_2, NH_3$ and $N_2$ are the coefficients for $O_2, CO_2, NH_3$ and $N_2$ respectively.
${}^{(2)}$	Additional subscripts pH, 7.2, T and 20 are the values at pH, $pH=7.2$ , T and $T=20^\circ C$ respectively.

## Introduction

A number of mathematical models describing the kinetics of the biological processes for carbon (C), nitrogen (N) and phosphorus (P) removal by the activated sludge system have been developed, e.g. the C and N removal models of van Haandel et al. (1981) and Activated Sludge Model No. 1 (ASM1, Henze et al., 1987), and the C, N and P removal models UCTPHO (Wentzel et al., 1992) and ASM2 and 2d (Henze et al., 1995, 1999). These models are commonly used in research, design, operation and system development and can be coded into computer shell packages such as ASim (Gujer, 1993) and Aquasim (Reichert, 1998) and various versions of them are commercially available.

In all these models, it is assumed that the biological processes operate in an aqueous phase of constant pH, i.e. that there is sufficient buffer capacity in the aqueous phase to absorb or supply the protons ( $H^+$ ) required or generated directly or indirectly (via e.g. the weak acid base species) by the biological processes without a change in pH. For most applications with municipal wastewater, where the concentrations of C, N and P are low, this is a reasonable assumption. In fact, in some models, the parameter Alkalinity is included to check that this condition remains true (e.g. ASM1, Henze et al., 1987; UCTOLD and IAWPRC, Dold et al., 1991). However, in the treatment of a number of wastewaters this assumption is not valid, e.g. in the nitrification of wastewaters with low buffer capacity and/or high nitrogen

(N) concentrations, or in the treatment of wastewaters where the generation or utilisation of short-chain fatty acids (SCFA) is significant.

In this paper, the biological processes of C and N removal in activated sludge systems are integrated into the three phase mixed weak acid/base chemical-physical kinetic model developed by Musvoto et al. (1997, 2000a,b,c). This chemical-physical model includes kinetic descriptions for:

- (i) the ionic equilibrium reactions of the important weak acid/base systems that govern pH in wastewater treatment systems, i.e. the ammonia, carbonate (inorganic carbon), short chain fatty acid (SCFA), phosphate and water systems,
- (ii)  $CO_2$  and  $NH_3$  gas exchange between aqueous and gas phases,
- (iii) ion pairing and
- (iv) precipitation of common minerals associated with Calcium (Ca), Magnesium (Mg), carbonate and phosphate system species.

Because in the activated sludge system, mineral precipitation usually is not significant, only parts (i) and (ii) of the model, i.e. the aqueous and gas phase processes, are considered. Furthermore, because of the complex interaction between pH and biological excess P removal (BEPR), only the biological processes of C and N removal are included into the integrated model at this stage. In Part 2, the biological processes of anaerobic digestion are incorporated into the model, but initially also only in two (aqueous-gas) phases (Söttemann et al., 2005). In subsequent model extensions, BEPR and the third (solid) phase of mineral precipitation will be incorporated into the models to develop the components required for an integrated chemical, physical and biological process kinetic model for the whole wastewater treatment plant.

## Model development

Central to the mixed weak acid base chemical-physical model of Musvoto et al. (1997, 2000a,b,c) is that the hydrogen ion ( $H^+$ ) is included explicitly as a compound. Integrating the biological processes of C and N removal of ASM1 into this chemical-physical model requires a number of interactions between the chemical and biological processes to be defined, such as:

- the influence of the biological processes on the weak acid/base systems species and  $H^+$  concentrations, i.e. production and/or utilisation of  $H^+$ ,  $CO_2$ , ammonia and phosphate in the growth and death (endogenous respiration) processes, and
- the effect of pH on the biological process rates where these are expected to be significant, e.g. on the autotrophic nitrifier organism (ANO) maximum specific growth rate.

Additionally, interactions with the physical processes require consideration, such as:

- production of  $N_2$  and loss of this species via gas exchange and
- input of  $O_2$  via aeration and use of this in biological processes.

The mixed weak acid base kinetic model of Musvoto et al. (1997) comprises (see their Table 1):

- (1) The aqueous phase forward and reverse dissociation chemical processes of the ammonia, carbonate, phosphate, SCFA and water weak acid/base system species, i.e. processes 1-6 and 9-18 involving compounds 1-5 and 7-14.

TABLE 1 Petersen matrix overview of the integrated chemical-physical-biological processes model for simulating wastewater treatment plant unit operations						
Integrated CPB model matrix structure		Compounds				
		Chemical (C)		Physical (P)	Biological (B)	
		Equilibrium dissociation (CED)	Ion pairing (CIP)	Gas exchange (PGE)	Activated sludge (BA)	Anaerobic digest (BD)
PROCESSES	CHEMICAL	Equilibrium Dissociation	15 compounds of the 6 weak acid base systems: C1-C5 <sup>a</sup> , C7-C14 <sup>a</sup> , C28-C29 <sup>d</sup>  18 chemical equilibrium dissociation processes of the 6 weak acid base systems: C1-C6 <sup>a</sup> , C9-C18 <sup>a</sup> , C47-C48 <sup>d</sup>	13 compounds associated with 22 ion pairing processes including Ca and Mg: C15-C27 <sup>b</sup>	3 compounds CO <sub>2</sub> gas P1 (C6) <sup>a</sup> O <sub>2</sub> and N <sub>2</sub> gases P2-P3 <sup>c</sup>	13 compounds for activated sludge (A) : A1 - A14; 13 from ASM1 minus A10 (FSA = C1+C2) plus A14 (dissolved N <sub>2</sub> gas) and replacing in A13 S <sub>lost</sub> for Alk now obsolete  8 compounds for anaerobic digestion (D): D1-D7 and P4. CH <sub>4</sub> (P4) is produced directly as a gas due to its insolubility and H <sub>2</sub> (D3) is completely utilised as a dissolved gas
		Ion Pairing	22 chemical ion pairing processes (CIP) of 11 ion pairs: C20-C41 <sup>b</sup>			
		Mini Pptn	5 physical mineral precipitation processes (PMP): P1 (C19) <sup>a</sup> , P2-P5 (C42-C45) <sup>b</sup> No additional compounds - all included with CIP			
	PHYSICAL	Gas Exchange	4 physical gas exchange (PGE) dissolution and expulsion processes; 2 for CO <sub>2</sub> and 2 for N <sub>2</sub> , P6-P7 <sup>c</sup> (C7-C8) <sup>a</sup> and P9-P10 <sup>c</sup> . 1 physical gas exchange (PGE) expulsion process for NH <sub>3</sub> ; P8 <sup>c</sup> (C46) <sup>a</sup> 1 physical gas exchange (PGE) dissolution process for O <sub>2</sub> ; P11 <sup>c</sup> CH <sub>4</sub> in BD produced directly as a gas (insoluble). H <sub>2</sub> in BD considered soluble and negligible with respect to CO <sub>2</sub> and CH <sub>4</sub> K <sub>La</sub> rates different with aeration (active) or not (passive).			
		Actvd Sludge	12 biological (B) activated sludge (BA) processes, i.e. all 8 of ASM1 plus aerobic and anoxic heterotrophic growth with nitrate (A1b and A2b) <sup>c</sup> and anoxic hydrolysis of slowly biodegradable organics (COD, S <sub>bp</sub> ) (A9) <sup>c</sup> and organic N (N <sub>obp</sub> , A10) <sup>c</sup> .			
BIOLOGICAL	Anaer Digst	10 biological (B) anaerobic digestion (BD) processes. <sup>d</sup>				

**Notes:** 1 <sup>a</sup> see Table 1 of Musvoto et al. (1997); <sup>b</sup> see Tables 1b, 1c and 3 of Musvoto et al. (2000a); <sup>c</sup> see Tables 2 and 3 in this paper; <sup>d</sup> see Table 2 in Sötemann et al. (2005);  
2 Only reactant compounds are specified. Product and inert (unbiodegradable) are omitted but implicit, e.g. mineral precipitates, water, non-reactive sink gases and unbiodegradable COD and OrgN.

(2) The gas and solid phase physical processes of the carbonate system, i.e. CO<sub>2</sub> gas exchange (dissolution and expulsion) and CaCO<sub>3</sub> precipitation, i.e. processes 7, 8 and 19 respectively involving compounds 3, 6 and 15.

Keeping the same numbering of processes and compounds, Musvoto et al. (2000a) extended this model to include (see their Tables 1b and 3):

(3) Ion pairing of Ca and Mg with hydroxide and the various species of the carbonate and phosphate systems; this added 22 processes, i.e. the aqueous phase forward and reverse dissociation chemical processes of the 11 ion pairs (processes 20-41) and 12 compounds, i.e. Mg and 11 ion pair species (compounds 16-27) respectively (see their Table 1b).

(4) The gas and solid phase physical processes of the ammonia, carbonate and phosphate systems, i.e. ammonia gas strip-

ping and mineral precipitation of four additional minerals associated with Ca and Mg and species of the ammonia, carbonate and phosphate systems, i.e. struvite (MgNH<sub>4</sub>PO<sub>4</sub>), newberyite (MgHPO<sub>4</sub>), amorphous calcium phosphate [ACP, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>] and MgCO<sub>3</sub>; this added 5 additional processes i.e. 42 to 46 but no new compounds as the precipitated minerals were not included explicitly (see their Table 3).

Before incorporating the biological processes of ASM1 into the mixed weak acid/base chemical physical (CP) model of Musvoto et al. (1997, 2000a), all the processes and compounds were categorised into chemical (C), physical (P) and biological (B) groups and subgroups (Table 1). This was done for ease of discussion of the assembly of a particular integrated chemical-physical-biological (CPB) processes model, be it aerobic or anaerobic. For easy cross reference to the source chemical physical (CP) and biological (B) models, the numbers of the processes and compounds were not changed from those in the source models. The

following general groups and subgroups of processes and compounds were adopted, which are summarised in Table 1:

- (1) The chemical (C) processes, which comprise those of equilibrium dissociation (CED - forward and reverse weak acid base dissociation) and ion pairing (CIP). These are processes 1-41 in the Musvoto et al. (2000a) CP source model, but the physical (P) processes 7, 8 and 19 are excluded. These processes have the same numbers as in the source model, but the prefix C is added, i.e. C1-C41. The 27 compounds associated with these chemical processes are also numbered identically to the source model, but have the prefix C added, i.e. compounds C1-C5 and C7-C14 involved in the equilibrium dissociation (CED) processes and compounds C4, C5, C8, C10-C12 and C15-C27 involved in the ion pairing (CIP) processes. The only compound that does not belong to this group is the CO<sub>2</sub> gas (C6). CO<sub>2</sub> is included with the compounds associated with the physical (P) processes and so is labelled P1.
- (2) The physical (P) processes, which comprise those of mineral precipitation (PMP) and gas exchange (PGE). The five mineral precipitation processes 19 and 42 to 45 in the Musvoto et al. (2000a) CP source model are renumbered P1 to P5. Since the precipitants are not explicitly included, these processes involve only existing compounds in the model (viz. C1, C5, C11, C12, C15 and C16) and so add no new compounds. Physical gas exchange (PGE) combines gas dissolution (forward) and expulsion (reverse) processes. The two physical gas exchange processes for CO<sub>2</sub> (dissolution, 7 and expulsion, 8) of Musvoto et al. (1997), are numbered P6 and P7, but from the link with the inter-phase mass transfer developed by Musvoto et al. (1997), the rate formulations are expressed directly in terms of the more conventional mass transfer rate coefficient and the CO<sub>2</sub> partial pressure (p<sub>CO<sub>2</sub></sub>) (Table 3). Summing these two processes (P6 and P7) is directly equivalent to the conventional inter-phase mass transfer gas exchange. For ammonia, the expulsion ("stripping") process (46) of Musvoto et al. (2000a) is numbered P8 (Table 3). For this gas, the gas phase is accepted to contain zero ammonia (infinite sink) and hence a gaseous ammonia compound is omitted and so also a dissolution process. Added to the PGE processes of the source model to form the integrated CPB activated sludge model are the gas exchange processes for N<sub>2</sub> (dissolution P9 and expulsion P10) formulated in the same manner as for CO<sub>2</sub>. Also added is the process for O<sub>2</sub> dissolution by aeration, P11 (Table 3). The new compounds associated with these additional PGE processes are the dissolved and gaseous compounds of oxygen and nitrogen. Dissolved oxygen (A8) and nitrogen (A14) are compounds of the biological processes part of the model (see below) so only 2 physical compounds need to be added for the CPB activated sludge model, i.e. gaseous oxygen (P2) and gaseous nitrogen (P3).

No additional physical gas exchange processes would need to be added to incorporate the biological processes of anaerobic digestion, only one gaseous compound methane (CH<sub>4</sub>) - it can be assumed that because CH<sub>4</sub> is very insoluble, CH<sub>4</sub> gas is formed directly by the biological processes. Also in anaerobic digestion, dissolved hydrogen is produced and utilised but hydrogen gas production is negligible compared with CO<sub>2</sub> and CH<sub>4</sub> and hence hydrogen need be included only as a dissolved species (Table 1).

In model application, the gas exchange processes can

be passive (no gas bubbling) or active (with gas bubbling, e.g. aeration). For both cases, the gas exchange formulations apply, including that of O<sub>2</sub> dissolution (P11), which specifically requires aeration. However, the values of the gas exchange constants (K<sub>La</sub>) differ significantly for the two situations.

- (3) The biological (B) processes comprise the biological C and N removal process of activated sludge (ASM1) with prefix A and in Söttemann et al. (2005) of anaerobic digestion with prefix D (Table 1). Also for the biological processes and compounds of the activated sludge model, the same numbers of ASM1 were retained, except the prefix A was added to each, i.e. processes A1 to A8 and compounds A1 to A13. However, two biological processes are added, viz. aerobic and anoxic growth of heterotrophs (OHOs) with nitrate as N source (Dold and Marais, 1985), because these two processes affect reactor pH and these were numbered A1b and A2b. Of the 13 compounds in ASM1, two become redundant in the integrated CPB model - the free and saline ammonia (FSA, A10) because NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> are in the chemical compounds group and the Alkalinity (A13), which is now obsolete. Apart from the ammonium (NH<sub>4</sub><sup>+</sup>, C1), three other compounds in the source CP model are also involved with the biological processes, i.e. H<sub>2</sub>CO<sub>3</sub>\* (C3) through CO<sub>2</sub> generation or uptake, H<sup>+</sup> (i.e. pH, C7) through ammonification, nitrification, denitrification and OHO growth/death and HPO<sub>4</sub><sup>2-</sup> through uptake for OHO growth and release from OHO death. Details of the biological processes of anaerobic digestion are given by Söttemann et al. (2005).

Following the grouping and numbering system above (Table 1), the integrated two phase (aqueous-gas) chemical physical biological (CPB) activated sludge model for C and N removal was assembled by including:

- (1) The chemical equilibrium dissociation (CED) processes for the weak acid/bases (C1-C6 and C9-C18) with associated compounds C1-C5 and C7-C14 (Table 1 of Musvoto et al., 1997, not repeated here). Although the SCFA weak acid/base system is included, in the application here the SCFA are set to zero (see below).
- (2) The biological activated sludge processes (BA) of C and N removal from ASM1 (A1 to A8), including aerobic and anoxic OHO growth on ammonium (processes A1a and A2a) and nitrate (processes A1b and A2b), with their associated new compounds NH<sub>4</sub><sup>+</sup> (C1), H<sub>2</sub>CO<sub>3</sub>\* (C3), H<sup>+</sup> (C7), HPO<sub>4</sub><sup>2-</sup> (C11) and the remaining original 11 activated sludge system compounds (A1-A9, A11-A12) (see Table 2).
- (3) The physical gas exchange (PGE) processes of ammonia (C46/P8), carbon dioxide (P6 and P7) and nitrogen (P9 and P10) gases and aeration dissolution of oxygen (P11) with their associated compounds dissolved ammonia (C2) and dissolved and gaseous carbon dioxide (C3 and C6), oxygen (A8 and P2) and nitrogen (A14 and P3). A gaseous ammonia compound is not included, because the gas stream is accepted to contain zero ammonia (Table 3).

Not included in the integrated CPB activated sludge model are the chemical ion pairing (CIP) processes (C20-C41), because this was not considered important for activated sludge systems treating municipal wastewater (TDS < 1 000 mg/l); and the physical mineral precipitation (PMP) processes (C19, C42-C45 or P1-P5), because only the gas and aqueous phases are considered in this first integrated AS model.

TABLE 2

Matrix representation of the biological processes of ASM1, including anoxic and aerobic growth of OHOs on nitrate (processes A1b and A2b), combined with parts of the mixed weak acid base chemical-physical model of Musvoto et al. (2000a) to yield the two phase (aqueous-gas) integrated chemical-physical-biological (CPB) processes activated sludge system model for C and N removal (see Table 3 for physical processes).

No. j	No. i	C3	C7	C11	A1	A2	A3	A4	A5	A6	A7	A8	A9	C1/A10	A11	A12	A13	A14	Process rate, P <sub>j</sub>
	Compounds Processes	H <sub>2</sub> CO <sub>3</sub> *	H <sup>+</sup>	HPO <sub>4</sub> <sup>2-</sup>	S <sub>i</sub>	S <sub>bs</sub>	X <sub>i</sub>	S <sub>enn</sub>	Z <sub>BH</sub>	Z <sub>BA</sub>	Z <sub>E</sub>	O <sub>2</sub> dissolved	NO <sub>3</sub> *	NH <sub>4</sub> <sup>+</sup>	N <sub>obs</sub>	N <sub>opp</sub>	S <sub>lost</sub>	N <sub>2</sub> dsivld	
A1a	Aerobic growth of Z <sub>BH</sub> with NH <sub>4</sub> <sup>+</sup>	$\frac{(1-Y_{ZH})}{(3Y_{ZH})}$	$\frac{f_{ZBP}N/14}{2f_{ZBP}P/31}$	-f <sub>ZBP</sub>	-1/Y <sub>ZH</sub>	-1/Y <sub>ZH</sub>			1			$-\frac{(1-Y_{ZH})}{N_{ZH}}$	-f <sub>ZBN</sub>	-f <sub>ZBN</sub>					$\mu_H \left[ \frac{S_{bs}}{K_{SH} + S_{bs}} \right] \left[ \frac{HAir}{On} \right] \left[ \frac{NH_4^+}{limit} \right] Z_{BH}$
A1b	Aerobic growth of Z <sub>BH</sub> with NO <sub>3</sub> *	F*	$\frac{f_{ZBP}N/14}{2f_{ZBP}P/31}$	-f <sub>ZBP</sub>	-1/Y <sub>ZH</sub>	-1/Y <sub>ZH</sub>			1			$-\frac{(1-Y_{ZH})}{N_{ZH}}$	-f <sub>ZBN</sub>				$-\frac{64}{f_{ZBN}}$		$\mu_H \left[ \frac{S_{bs}}{K_{SH} + S_{bs}} \right] \left[ \frac{HAir}{On} \right] \left[ \frac{1-NH_4^+}{limit} \right] \left[ \frac{NO_3}{limit} \right] Z_{BH}$
A2a	Anoxic growth of Z <sub>BH</sub> with NH <sub>4</sub> <sup>+</sup>	$\frac{(1-Y_{ZH})}{(3Y_{ZH})}$	A*	-f <sub>ZBP</sub>	-1/Y <sub>ZH</sub>	-1/Y <sub>ZH</sub>			1				$-\frac{(1-Y_{ZH})}{(2.86Y_{ZH})}$	-f <sub>ZBN</sub>				D*	$\mu_H \left[ \frac{S_{bs}}{K_{SH} + S_{bs}} \right] \left[ \frac{HAir}{Off} \right] \left[ \frac{NH_4^+}{limit} \right] \left[ \frac{NO_3}{limit} \right] Z_{BH} \eta_G$
A2b	Anoxic growth of Z <sub>BH</sub> with NO <sub>3</sub> *	F*	C*	-f <sub>ZBP</sub>	-1/Y <sub>ZH</sub>	-1/Y <sub>ZH</sub>			1				B*				$-\frac{64}{f_{ZBN}}$		$\mu_H \left[ \frac{S_{bs}}{K_{SH} + S_{bs}} \right] \left[ \frac{HAir}{Off} \right] \left[ \frac{1-NH_4^+}{limit} \right] \left[ \frac{NO_3}{limit} \right] Z_{BH} \eta_G$
A3	Aerobic growth of Z <sub>BA</sub>	-3/8	$\frac{f_{ZBP}N/14}{1/(7Y_{ZB})}$						1			$-\frac{(4.57-Y_{ZB})}{Y_{ZB}}$	1/Y <sub>ZB</sub>	$-\frac{(1-Y_{ZB})}{f_{ZBN}}$					$\mu_A \left[ \frac{NH_4^+}{K_{SA} + NH_4^+} \right] \left[ \frac{A\ Air}{On} \right] Z_{BA}$
A4	Death of Z <sub>BH</sub>		$\frac{2(f_{ZBP}P)}{f_{ZBP}P/31}$	f <sub>ZBP</sub> f <sub>ZEP</sub>	1-f <sub>E</sub>	1-f <sub>E</sub>		1-f <sub>E</sub>	-1		f <sub>E</sub>				f <sub>ZBN</sub> <sup>2</sup> f <sub>ZEN</sub>				b <sub>H</sub> Z <sub>BH</sub>
A5	Death of Z <sub>BA</sub>				1-f <sub>E</sub>	1-f <sub>E</sub>		1-f <sub>E</sub>	-1		f <sub>E</sub>				f <sub>ZBN</sub> <sup>2</sup> f <sub>ZEN</sub>				b <sub>A</sub> Z <sub>BA</sub>
A6	Ammonification of N <sub>obs</sub>		-1/14											1	-1				K <sub>R</sub> N <sub>obs</sub> Z <sub>BH</sub>
A7	Hydrolysis of S <sub>enn</sub>				1			-1											E* ;
A8	Hydrolysis of N <sub>opp</sub>														1	-1			E* (N <sub>opp</sub> /S <sub>enn</sub> )
	Units	gC/m <sup>3</sup>	gH/m <sup>3</sup>	gP/m <sup>3</sup>	gCOD/m <sup>3</sup>	gCOD/m <sup>3</sup>	gCOD/m <sup>3</sup>	gCOD/m <sup>3</sup>	gCOD/m <sup>3</sup>	gCOD/m <sup>3</sup>	gCOD/m <sup>3</sup>	gCOD/m <sup>3</sup>	gCOD/m <sup>3</sup>	gN/m <sup>3</sup>	gN/m <sup>3</sup>	gN/m <sup>3</sup>	gCOD/m <sup>3</sup>	gN/m <sup>3</sup>	

$$A^* = -\frac{1-Y_{ZH}}{14 \cdot 2.86 Y_{ZH}} + \frac{f_{ZBN} - 2 \cdot \frac{f_{ZBP}}{31}}{14} \quad B^* = -\frac{1-Y_{ZH}}{2.86 Y_{ZH}} + f_{ZBN} \quad C^* = -\frac{1-Y_{ZH}}{14 \cdot 2.86 Y_{ZH}} \quad D^* = \frac{1-Y_{ZH}}{2.86 Y_{ZH}} \quad E^* = K_H \left[ \frac{S_{enn} Z_{BHP}}{K_x + (S_{enn} Z_{BHP})} \right] \left[ \frac{HAir}{On} \right] + \eta_s \left[ \frac{HAir}{Off} \right] \left[ \frac{NO_3}{limit} \right] Z_{BH} \quad F^* = \frac{1-Y_{ZH}}{3 Y_{ZH}} + \frac{64}{14 \cdot 3 \cdot f_{ZBN}}$$

Notes: (1) Compound A1-A13 numbered identically to ASM1, except NH<sub>4</sub><sup>+</sup>, which is C1 in Musvoto et al. (1997) and 10 in ASM1. NH<sub>4</sub><sup>+</sup> in ASM1 is actually the free (NH<sub>3</sub>) and saline (NH<sub>4</sub><sup>+</sup>) ammonia (FSA), where here it is only the saline. H<sub>2</sub>CO<sub>3</sub>\* alkalinity (compound 13) is no longer required. Ammonium (C1), dissolved CO<sub>2</sub> (C3) and dinitrogen (A14), H<sup>+</sup> (C7) and mono-hydrogen phosphate (C11) are included here because they are involved with the biological activated sludge processes. Y<sub>ZH</sub> = Y<sub>ZH</sub> for aerobic, Y<sub>ZH</sub> = Y<sub>ZH</sub> for anoxic.

No	Compound-Process†	C2 NH <sub>3</sub> dissolved	C3 H <sub>2</sub> CO <sub>3</sub> * CO <sub>2</sub> diss	A8 O <sub>2</sub> dissolved	A14 N <sub>2</sub> dissolved	P1(C6) CO <sub>2</sub> gas	P2 O <sub>2</sub> gas	P3 N <sub>2</sub> gas	Rate
P6	Gas exchange of CO <sub>2</sub> - dissolution		+1			-1			$K_{La-CO_2} P_{CO_2} K_{H-CO_2}$
P7	Gas exchange of CO <sub>2</sub> - expulsion		-1			+1			$K_{La-CO_2} [H_2CO_3^*]$
P8	Gas exchange of NH <sub>3</sub> - expulsion	-1							$K_{La-NH_3} [NH_{3diss}]$
P9	Gas exchange of N <sub>2</sub> - dissolution				+1			-1	$K_{La-N_2} P_{N_2} K_{H-N_2}$
P10	Gas exchange of N <sub>2</sub> - expulsion				-1			+1	$K_{La-N_2} [N_{2diss}]$
P11	Aeration - dissolution of O <sub>2</sub>			+1			-1		$K_{La-O_2} ([O_{2sat}] - [O_{2diss}])$
	Units	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	mol/l	

For brevity, only the biological (B) and physical gas exchange (PGE) processes parts of the integrated CPB activated sludge model with their associative compounds are shown in the Petersen matrix of the model (Tables 2 and 3). Because the chemical and physical parts of the model have units mol/l, these were changed to reflect the usual units in biological models, viz. gC/m<sup>3</sup>, gN/m<sup>3</sup> and gP/m<sup>3</sup>. Hence, when the H<sup>+</sup> interacts with C, N or P species, it was divided by the molar mass of C, N and P respectively. Also, the kinetic rate equations for the biological processes were modified to take into account the effect of H<sup>+</sup> where this effect is significant. This was done in two ways:

- Where there is a direct influence of pH on the biological process rate, pH was included in the kinetic rate formulation, and
- the kinetic rates of the biological processes were reformulated to utilise specific species of the weak acid/base systems – stoichiometric coefficients were added and existing ones modified to take this into account.

The modifications outlined above were developed for the two organism groups included in ASM1, i.e. ordinary heterotrophic (OHOs) and autotrophic nitrifier (ANOs) organisms. For both groups, information in the literature on their behaviour was used for the modifications and the derivation of the stoichiometric coefficients of the integrated model are discussed briefly below. A review of bioenergetics and activated sludge model development is not given since these topics are already covered in detail in the literature (e.g. McCarty, 1964, 1972; Dold et al., 1980; van Haandel et al., 1981; Henze et al., 1987; Ohron et al., 1996; Casey et al., 1999; Sperandio et al., 1999). Only aspects relevant to the integration are discussed to clarify the additions and changes to the stoichiometric coefficients and kinetic rates in Tables 2 and 3.

## Modifications to the ASM1 to accomplish integration

### Ordinary heterotrophic organisms (OHOs)

The processes that involve the OHOs in ASM1 are growth (A1 and A2), death (A4), hydrolysis of enmeshed particulate biodegradable organics (A7) and associated particulate biode-

gradable organic nitrogen (A8) and ammonification of soluble biodegradable organic nitrogen (A6). The growth of OHOs is described by four processes, two under aerobic conditions using either ammonia (A1a) or nitrate (A1b) as N source, and two under anoxic conditions also using either ammonia (A2a) or nitrate (A2b) as N source. These processes were modified to include:

- production of CO<sub>2</sub> in metabolism,
- uptake or release of specific weak acid/base N and P species for growth and death, and
- utilisation or production of H<sup>+</sup>.

### OHO metabolism

The bioenergetics of OHO growth are quantified in terms of the lumped electron donating capacity parameter COD, because in wastewater treatment the different organics involved in the growth processes are not known. This is possible because the free energy released per electron (e<sup>-</sup>) transferred in the breakdown of different types of organics varies in the narrow range 105 to 121 kJ/e<sup>-</sup> eq. The integrated model requires a carbon balance to be made over the activated sludge system. Thus the mass CO<sub>2</sub> generated in the growth process needs to be known, which requires the COD/TOC ratio of the wastewater organics to be known. For the range of different organics listed in Table 4, the COD/TOC ratio was calculated and varies between 2.67 and 4.0. Because most of the organics in wastewater are of carbohydrate/sugar type with a relatively small proportion of organics with high COD/TOC ratios, an average COD/TOC ratio would seem to be around 3.0. Because CO<sub>2</sub> is generated only in catabolism, the CO<sub>2</sub> generation is proportional to the oxygen utilised, i.e.

$$O_2 \text{ utilised in producing 1 g OHOs as COD} = (1 - Y_{ZH}) / Y_{ZH} \quad (1a)$$

where:

$$Y_{ZH} = \text{OHO yield coefficient (mg COD OHOs formed/mg COD organics utilised)}$$

$$\text{Hence the CO}_2 \text{ generated in producing 1 g OHOCOD} \\ = O_2 \text{ utilised} / (\text{COD/TOC ratio}) = (1 - Y_{ZH}) / (3.0 Y_{ZH}) \quad (1b)$$

The CO<sub>2</sub> released during metabolism is in the dissolved form and accepted to add to the H<sub>2</sub>CO<sub>3</sub>\* concentration in the bulk liquid.

Organic compound	Formula	COD/TOC ratio
Carbohydrates	$C_n(H_2O)_n$	2.67 for all n
Sugars	$C_n(H_2O)_{n-2}$	2.67 for all n
<sup>1</sup> Carboxylic acids (SCFA and LCFA)	$CH_3(CH_2)_nCOOH$	$4(3n+2)/[3(n+1)]$ = 3.33 for n=1; = 3.94 for n=20
Primary amines	$CH_3(CH_2)_nNH_2$	4 for all n
Amino acids	$H(CH_2)_nC_2H_4O_2N$	$4(n+1)/(n+2) < 4$
Alkanes	$H(CH_2)_nH$	$4(3n+1)/3n \approx 4$
Alcohols	$H(CH_2)_nOH$	4 for all n
<sup>1</sup> Unsaturated fats have slightly lower COD/TOC ratio because for every double C bond (C=C), there are 2 Hs fewer		

Hence, the stoichiometric coefficient  $(1-Y_{ZH})/(3Y_{ZH})$  is added to the compound  $H_2CO_3^*$  in the integrated model matrix (Table 2).

The COD/TOC ratio accepted will not significantly influence the activated sludge system mixed liquor pH. This is because in the breakdown of the organics listed in Table 4, no direct release of  $H^+$  is envisaged to take place. The  $CO_2$  is generated as  $H_2CO_3^*$  but with aeration this is mostly stripped from the bulk liquid, which is controlled by gas exchange (higher partial pressure than the atmosphere). Hence, the  $CO_2$  generated is mostly lost to the gaseous phase. Further, if some final dissolved  $CO_2$  state is achieved (e.g. equilibrium with the atmosphere or super-saturation) then any COD/TOC ratio variation is essentially absorbed by the gas phase, not to the bulk liquid and hence does not cause a significant pH change. In contrast, on oxidation the proteins release their N content as  $NH_3$ , which at pH between 6.5 and 8.0, will take up a  $H^+$  to form  $NH_4^+$ , a process called ammonification. This increases the alkalinity of the bulk liquid and at constant  $CO_2$  partial pressure ( $p_{CO_2}$ ) will produce a pH increase. In contrast to the  $CO_2$ , significant  $NH_3$  loss to the gas phase does not occur (see later). Therefore, in the breakdown of organics, it is not the generation of  $CO_2$  that affects the pH so much as the uptake of a  $H^+$  by the  $NH_3$  released from the breakdown of organic N (proteins). Hence, to predict the pH correctly, the COD/TOC ratio does not need to be known accurately, but the organic N content of the wastewater and its ammonification do need to be known accurately.

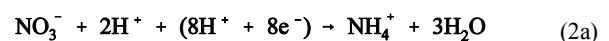
Under anoxic conditions, nitrate ( $NO_3^-$ ) serves as terminal electron acceptor and the specific yield coefficient is decreased to ~80% of the aerobic value. With nitrate as electron acceptor approximately the same quantity of free energy from the organics is available to the organism as when oxygen is the electron acceptor, but *ideally* only 2 ATP moles are formed per pair of electrons transferred to the nitrate (Payne, 1981) compared with 3 ATP moles per pair of electrons with oxygen. Measurements by Orhon et al. (1996), Sperandio et al. (1999) and Muller et al. (2003) confirm this reduction in yield experimentally with artificial and real domestic wastewaters. This reduction in yield under anoxic conditions is not recognised in early activated sludge models like UCTOLD (Dold et al., 1991), ASM1 (Henze et al., 1987), UCTPHO (Wentzel et al., 1992) and ASM2 (Henze et al., 1995), but is accepted in later models like ASM2d (Henze et al., 1999) and Biowin (Barker and Dold, 1997). This reduction also has been accepted in the model developed here, so that under anoxic conditions, about 20% less OHO biomass and 40% more  $CO_2$  are generated than under aerobic conditions (Table 5). As mentioned earlier, this lower  $CO_2$  generation does not affect the reactor pH but the lower loss of  $CO_2$  to the gas phase (no aeration) does increase the pH above that of the aerobic reactor.

#### **Use of specific weak acid/base species for OHO growth**

The nitrogen required for OHO synthesis is obtained from either ammonia (processes A1a and A2a) or, in the absence of ammonia, nitrate (processes A1b and A2b). Phosphorus is also incorporated in OHO mass. The concentrations of N and P required for synthesis are quantified in ASM1 and similar biological models as the N and P content of the active biomass i.e.  $f_{ZB,N} = 0.068$  mgN/mgOHOCOD and  $f_{ZB,P} = 0.020$  mgP/mgOHOCOD respectively, but it is not specified which of the ammonia and phosphate weak acid/base system species are taken up for synthesis.

From the literature on bioenergetics, it is accepted that the non-ionic ammonia and phosphate system species are taken up for synthesis, i.e.  $NH_3$  and  $H_3PO_4$ . However, it has been accepted in the model that the most abundant species of the systems in the pH range typical for activated sludge systems of 6.5 to 8.5,  $NH_4^+$  and  $HPO_4^{2-}$ , are taken up, releasing one and taking up two protons respectively during cell synthesis. In this operating pH range, the concentrations of  $NH_3$  and  $H_3PO_4$  are extremely low and their use in kinetic models for synthesis can lead to numerical instability.

When ammonia is depleted,  $NO_3^-$  is taken up by the OHOs as the N source for growth. However, the  $NO_3^-$  must be first reduced to  $NH_4^+$  by accepting  $8H^+$  and  $8e^-$ , which are supplied by the biodegradable organics and two additional  $H^+$  are taken up from the bulk liquid, viz.



One of the two  $H^+$  is returned to the bulk liquid when  $NH_4^+$  is taken up for growth, but the other is required in the reduction reaction and therefore increases the bulk liquid pH. Hence, the net change in  $H^+$  concentration with  $NO_3^-$  as N source and P uptake as  $HPO_4^{2-}$  for OHO growth is

$$= -f_{ZB,N}/14 - 2f_{ZB,P}/31 \text{ mgH}^+/\ell \quad (2b)$$

The biodegradable organics that supply the  $8H^+$  and  $8e^-$  for the nitrate reduction (Eq. 2a) are "lost" from the system, i.e. are no longer available for growth, which is shown quantitatively in Fig. 1. Even though nitrate reduction (Eq. 2a) thermodynamically is an energy generating reaction, bioenergetically the OHOs get no energy from it. It is, therefore, not correct to change the yield coefficient to account for this additional  $H^+$  and  $e^-$  consumption. Accordingly, the yield coefficients under aerobic and anoxic conditions remain  $Y_{ZH} = 0.67$  and  $Y'_{ZH} = 0.54$  mgOHOCOD formed/mgCOD organics utilised. To take account of the COD

**TABLE 5**  
**Stoichiometric and matrix representation of the aerobic and anoxic growth processes with ammonia and nitrate as N source taking account of the substrate required for the reduction of nitrate to ammonia in the chemical-physical-biological (CPB) processes model for C and N removal in the activated sludge system (see Table 2 for biological processes)**

No	A2 S <sub>bs</sub> C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> Growth	A13 S <sub>lost</sub> C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> Reductn	C1 A10 NH <sub>4</sub> <sup>+</sup> Growth	C7 H <sup>+</sup> Denit	A9 NO <sub>3</sub> Denit	C7 H <sup>+</sup> Growth	A9 NO <sub>3</sub> Growth	A8 O <sub>2</sub> Growth	A5 C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> N Biomass	C3 CO <sub>2</sub> Growth	C3 CO <sub>2</sub> Reductn	A14 N <sub>2</sub> Denit	H <sub>2</sub> O Growth	H <sub>2</sub> O Reductn	H <sub>2</sub> O Denit
A1a	-1	0	-y	0	0	+y	0	-(6-5y)	+y	+(6-5y)	0	0	+(6-2y)	0	0
A1b	-1	-y/3	0	0	0	-y	-y	-(6-5y)	+y	+(6-5y)	+2y	0	+(6-2y)	+y	0
A2a	-1	0	-y'	$-\frac{8}{10}(6-5y')$	$-\frac{8}{10}(6-5y')$	+y'	0	0	+y'	+(6-5y')	0	$+\frac{4}{10}(6-5y')$	+(6-2y')	0	$+\frac{4}{10}(6-5y')$
A2b	-1	-y'/3	0	$-\frac{8}{10}(6-5y')$	$-\frac{8}{10}(6-5y')$	-y'	-y'	0	+y'	+(6-5y')	+2y'	$+\frac{4}{10}(6-5y')$	+(6-2y')	+y'	$+\frac{4}{10}(6-5y')$
<b>Units</b>	<b>mol</b>	<b>mol</b>	<b>mol</b>	<b>mol</b>	<b>mol</b>	<b>mol</b>	<b>mol</b>	<b>mol</b>	<b>mol</b>	<b>mol</b>	<b>mol</b>	<b>mol</b>	<b>mol</b>	<b>mol</b>	<b>mol</b>
A1a	$-\frac{1}{Y_{ZH}}$	0	$-f_{ZBN}$	0	0	$\frac{f_{ZBN}}{14}$	0	$-\frac{(1-Y_{ZH})}{Y_{ZH}}$	+1	$\frac{(1-Y_{ZH})}{3Y_{ZH}}$	0	0	-	-	-
A1b	$-\frac{1}{Y_{ZH}}$	$-\frac{64}{14}f_{ZBN}$	0	0	0	$-\frac{f_{ZBN}}{14}$	$-\frac{f_{ZBN}}{14}$	$-\frac{(1-Y_{ZH})}{Y_{ZH}}$	+1	$\frac{(1-Y_{ZH})}{3Y_{ZH}}$	$\frac{64}{14 \times 3}f_{ZBN}$	0	-	-	-
A2a	$-\frac{1}{Y_{ZH}}$	0	$-f_{ZBN}$	$-\frac{(1-Y_{ZH})}{14 \times 2.86 Y_{ZH}}$	$-\frac{(1-Y_{ZH})}{2.86 Y_{ZH}}$	$\frac{f_{ZBN}}{14}$	0	0	+1	$-\frac{(1-Y_{ZH})}{3Y_{ZH}}$	0	$\frac{(1-Y_{ZH})}{2.86 Y_{ZH}}$	-	-	-
A2b	$-\frac{1}{Y_{ZH}}$	$-\frac{64}{14}f_{ZBN}$	0	$-\frac{(1-Y_{ZH})}{14 \times 2.86 Y_{ZH}}$	$-\frac{(1-Y_{ZH})}{2.86 Y_{ZH}}$	$-\frac{f_{ZBN}}{14}$	$-\frac{f_{ZBN}}{14}$	0	+1	$-\frac{(1-Y_{ZH})}{3Y_{ZH}}$	$\frac{64}{14 \times 3}f_{ZBN}$	$\frac{(1-Y_{ZH})}{2.86 Y_{ZH}}$	-	-	-
<b>Units</b>	<b>gCOD</b>	<b>gCOD</b>	<b>gN</b>	<b>gH</b>	<b>gN</b>	<b>gH</b>	<b>gN</b>	<b>gO</b>	<b>gCOD</b>	<b>gC</b>	<b>gC</b>	<b>gN</b>	<b>gN</b>	<b>gC</b>	<b>gN</b>

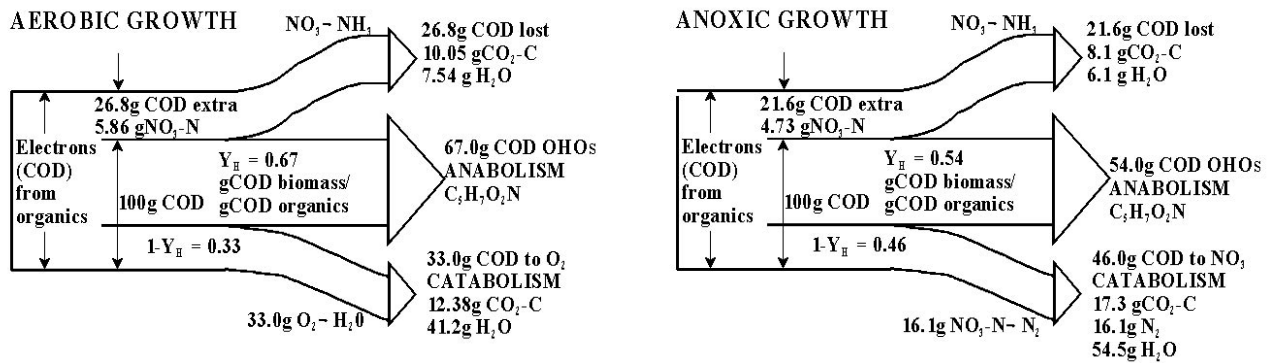
**Notes:**

(1) For an aerobic yield coefficient ( $Y_{ZH}$ ) of 0.67 mgOHO/COD/mgCOD organics  $y = Y_{ZH} \times 192/160 = 0.67 \times 192/160 = 0.804$  mol OHO/mol organics.

(2) For an anoxic yield coefficient of ( $Y'_{ZH}$ ) 0.54 mgOHO/COD/mgCOD organics  $y' = 0.54 \times 192/160 = 0.648$  mol OHO/mol organics.

(3) The water production is included in the molar stoichiometric part of the table (upper) to allow element (C, H, O, N) mass balance checks. The COD based stoichiometry in the lower half is calculated from the molar stoichiometry, e.g. y mol biomass (160 gCOD/mol) is synthesised from 1 mole glucose (192 gCOD/mol), so 1 gCOD biomass requires 192/(160y) g glucose; substituting  $y = Y_{ZH} \times 192/160$  from (1) above yields 1 gCOD biomass requires  $1/Y_{ZH}$  gCOD glucose (-ve for consumption) and y mol biomass (160 gCOD/mol) production yields (6-5y) mol CO<sub>2</sub> in growth process, so 1 gCOD biomass produces 12 (6-5Y<sub>ZH</sub>192/160)/(192Y<sub>ZH</sub>) gCO<sub>2</sub>-C = +72(1-Y<sub>ZH</sub>)/(192Y<sub>ZH</sub>) where 72/192 = TOC/COD ratio of glucose; for a TOC/COD ratio of 1/3 this = (1-Y<sub>ZH</sub>)/(3Y<sub>ZH</sub>).





**Figure 1**  
Schematic and quantitative representation of aerobic (left) and anoxic (right) OHO growth using nitrate as nitrogen source (assimilative denitrification) taking account of the organics (electrons) required to reduce nitrate to ammonia.

“lost” by nitrate reduction for growth, the compound  $S_{b,lost}$  (A13) is added to the model as a compound so that (i) the magnitude of this “lost” COD is tracked and (ii) COD balances can still be used to verify the model. Integrating the stoichiometry of the reduction of nitrate to ammonia into the growth processes using glucose as an example substrate is shown in Table 5. The Petersen matrix coefficients of the aerobic and anoxic growth processes (1 and 2) in Table 2 were calculated from Table 5. It can be seen that (i) additional  $CO_2$  is generated when nitrate is utilised as N source for growth, but this additional  $CO_2$  generation does not affect the reactor pH, and (ii)  $H^+$  are taken up from the bulk liquid in the reduction of  $NO_3^-$  to  $NH_3$  which will cause a pH increase.

In completely mixed single aerobic reactor systems, the ammonia is unlikely to be depleted sufficiently for  $NO_3^-$  to be utilised as the N source – this situation is more likely to occur in plug flow type and sequencing batch reactor (SBR) systems. In anoxic reactors, whether completely mixed or plugflow, invariably ammonia is present in excess of synthesis requirements. In completely mixed nitrifying aerobic digestion of waste activated sludge there always should be sufficient ammonia for growth because the ammonia released in OHO death always is greater than that taken up for OHO growth on the slowly biodegradable (SB) COD released in OHO death, but in application of the model nitrate utilisation for OHO growth nevertheless can occur. This also can occur with model application to aerobic digestion of primary sludge even when sufficient ammonia is dosed for net OHO biomass production from the primary sludge particulate biodegradable organics. This apparent ammonia deficiency in the model arises because the rate of nitrification is faster than the rate of OHO growth, which is limited by the supply rate of SBCOD from the OHO death process. This leads to uptake of nitrate for OHO growth, but to the release of ammonia in OHO death. This released ammonia is then nitrified with an associated OUR for nitrification. The consequence is an incorrectly predicted high nitrification OUR from the continual supply of ammonia nitrogen from the death process, nitrogen that is taken up as nitrate by the OHOs. This problem is eliminated in the model by reducing the switching function K value which controls the switch from ammonia to nitrate uptake for OHO growth to a very low value (0.0001 mgN/l). This prevents the OHO growth process from slowing down when the ammonia concentration gets low, allowing it to successfully “compete” for ammonia against the nitrification process. This problem therefore has nothing to do with ammonia deficiency but everything to do with the relative rates of processes competing for the same compounds, in this case ammonium ( $NH_4^+$ ). *K values of switch-*

*ing functions on processes competing for the same compounds therefore require very careful scrutiny in simulation models.*

### Utilisation and generation of $H^+$ in OHO growth and death (endogenous respiration)

When  $NH_4^+$  (or  $NO_3^-$ ) and  $HPO_4^{2-}$  are taken up for synthesis, a proton is released (or taken up) and two protons taken up respectively to convert these species to their unionised forms  $NH_3$  and  $H_3PO_4$ . This changes the  $H^+$  concentration which has to be taken into account, viz.:

$$\begin{aligned} \text{Concentration } NH_4^+ \text{ (or } NO_3^-) \text{ taken up for synthesis} \\ = f_{ZB,N} \text{ (gN/gOHOCOD)} \end{aligned} \quad (3a)$$

$$\begin{aligned} \text{Concentration } HPO_4^{2-} \text{ taken up for synthesis} \\ = f_{ZB,P} \text{ (gP/gOHOCOD)} \end{aligned} \quad (3b)$$

$$\begin{aligned} \text{Hence the change } H^+ \text{ concentration in synthesis with} \\ NH_4^+ = f_{ZB,N} / 14 - 2 f_{ZB,P} / 31 \text{ mgH}^+ / \ell \end{aligned} \quad (3c)$$

$$\begin{aligned} \text{and the change } H^+ \text{ concentration in synthesis with} \\ NO_3^- = -f_{ZB,N} / 14 - 2 f_{ZB,P} / 31 \text{ mgH}^+ / \ell \end{aligned} \quad (3d)$$

If the unionised N and P species ( $NH_3$  and  $H_3PO_4$ ) are used instead for synthesis, virtually the same net effect on  $H^+$  will occur, due to the redistribution of the weak acid/base species via the CED kinetic processes.

In organism death, since the death-regeneration approach is followed (Dold et al., 1980), the difference in N contents of the active biomass lost and the endogenous residue formed is released as biodegradable particulate organic N. Hence, this process has no direct influence on the  $H^+$  concentration. In contrast, to reduce complexity in phosphorus compounds, the corresponding P is released as  $HPO_4^{2-}$ , with associated  $H^+$  to maintain neutrality. This changes the  $H^+$  concentration which has to be taken into account, viz.:

$$\begin{aligned} \text{Concentration } HPO_4^{2-} \text{ released in OHO death} \\ = f_{ZB,P} - f_E f_{ZE,P} \text{ (gP/gOHOCOD)} \end{aligned} \quad (4a)$$

$$\begin{aligned} \text{Associated change } H^+ \text{ concentration} \\ = +2(f_{ZB,P} - f_E f_{ZE,P}) / 31 \end{aligned} \quad (4b)$$

### Ammonification of soluble organic nitrogen

Ammonification is the process mediated by OHOs (A6) whereby biodegradable soluble organic nitrogen ( $N_{obs}$ ), which is in the unionised “ $NH_3$ ” form, is converted to saline ammonia ( $NH_4^+$ ). Associated with ammonification therefore is a decrease in the  $H^+$  concentration of the bulk liquid due to uptake of a  $H^+$  by the

NH<sub>3</sub> to form NH<sub>4</sub><sup>+</sup>. The H<sup>+</sup> taken up in ammonification is 1/14 gH<sup>+</sup>/gN Organic N ammonified.

In ASM2, the ammonification process is omitted. Instead, the conversion of soluble biodegradable organic N (N<sub>obs</sub>) to ammonia is linked to the utilisation of readily biodegradable organics (RB COD) of which it is part. So if a wastewater has an influent biodegradable soluble organic N to RBCOD ratio (N<sub>obs</sub>/S<sub>bs</sub>) of say 0.03 (i<sub>NSF</sub> in ASM2), the ammonia (NH<sub>3</sub>) release rate is 0.03 times the rate of RBCOD utilisation. The release of ammonia from the particulate biodegradable organic N is modelled in the identical way in ASM1 and ASM2. Two models were developed and compared, one conforming strictly to ASM1 including the ammonification process, and the other linking the release of ammonia from the soluble organic N to the utilisation of RBCOD. No significant differences were noted between the predictions of the two model versions, provided the ammonification kinetic rate constants were correctly selected.

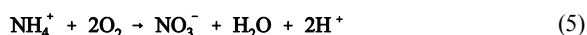
#### A note on the utilisation of SCFA in OHO growth

Inclusion of the SCFA weak acid/base system in the model arises from the earlier application of the chemical-physical part of the model to aeration treatment of anaerobic digester liquor (ADL) (Musvoto, 2000a,c), where it was required to establish the correct pH. Practically, the SCFA are not explicitly required in this integrated CPB model because the influent SCFA concentration usually is very low and hence is included in the RBCOD. However, if the SCFA concentration is significant, such as with activated sludge treatment of anaerobic digester liquor, then SCFA utilisation will influence the pH significantly and will need to be explicitly included in the model. This will require that the SCFA are modelled separately as a subfraction of the RBCOD and that four processes be added to the model, viz. processes A1c and A1d - aerobic growth of OHOs on acetate with ammonia (A1c) and nitrate (A1d) as N source, and processes A2c and A2d which are the anoxic equivalents. These processes will have identical stoichiometry as growth on RBCOD, but the substrate utilisation is deducted from the HAc species of the SCFA system. Also, the SCFA concentration would need to be deducted from the RBCOD to correctly reflect the RBCOD as the remaining fermentable RBCOD, as is done in UCTPHO (Wentzel et al., 1992) or ASM2 (Henze et al., 1995), where SCFA is modelled separately from the fermentable RBCOD for biological P removal.

#### Autotrophic nitrifier organisms (ANOs)

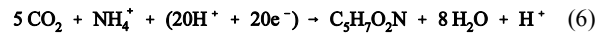
##### Autotrophic metabolism

Although mediated by a number of different ammonia oxidising and nitrite oxidising organisms in two sequential steps from ammonia to nitrite and nitrite to nitrate, in ASM1 nitrification is modelled as a single step from ammonia to nitrate by a generic group of autotrophic nitrifier organisms (ANOs). The nitrification rate is defined by the slower process rate of the sequence, which under most circumstances is the ammonia oxidation. Stoichiometrically, nitrification of saline ammonia requires 2 mol (64 gO) oxygen and produces 1mol nitrate and 2 mol protons, i.e.



The ANOs obtain their anabolic carbon requirements from dissolved CO<sub>2</sub> (H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>) and their catabolic energy (e<sup>-</sup>) requirements from oxidising ammonia to nitrate. Accepting that C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>N represents the C, H, O and N content of the ANOs and has a COD content of 160 g/mol, then five mol CO<sub>2</sub> are required

to synthesise one mol ANOs viz.



which includes also the ammonia requirement for cell synthesis.

The catabolic ammonia (e<sup>-</sup> and H<sup>+</sup>) requirement is determined from the ANO yield coefficient, i.e.

$$Y_{ZA} = 0.15 \text{ (gANOCOD synthesised/gNH}_4^+\text{-N nitrified)} \\ = 0.15 \cdot 14/160 \text{ (mol ANOs/mol NH}_4^+\text{-N nitrified)}$$

From Eq. 6, the mol CO<sub>2</sub> required is 5 times the mol of ANOs formed. Hence:

$$\text{CO}_2 \text{ required} = (5 \times 12/160) = 3/8 \text{ (gCO}_2\text{-C/gANOCOD synthesised)} \quad (7)$$

This stoichiometric ratio for CO<sub>2</sub> utilised by the ANOs is added to the model, accepting that the CO<sub>2</sub> taken up is in the dissolved form and represented as H<sub>2</sub>CO<sub>3</sub><sup>\*</sup> (Table 2).

The ANOs are conventionally considered to use the NH<sub>4</sub><sup>+</sup> species because this is the most abundant species in the optimum pH range for nitrification, i.e. 7.2 to 8.5. However, Suzuki (1974), in studies on *Nitrosomonas europae* concluded that the NH<sub>3</sub> species is used in the oxidation process. Also, Drozd (1976) argued that *Nitrosomonas* uses the NH<sub>3</sub> form because a rapid decrease in pH was noticed in the medium in growing cultures suggesting that a proton remains on the exterior of the cell wall in the medium. In this integrated model, it has been accepted that the unionised NH<sub>3</sub> species is used in oxidation, but that NH<sub>4</sub><sup>+</sup> species is taken up from solution with the release of H<sup>+</sup>. In the operating pH range for nitrification, the NH<sub>3</sub> concentration is extremely low and its use in the model can lead to numerical instability.

##### Production/utilisation of H<sup>+</sup> in ANO growth and death

The change in H<sup>+</sup> during nitrification (NH<sub>4</sub><sup>+</sup> oxidation and uptake for ANO growth) is derived from Eqs. 5 and 6 and the stoichiometric coefficient for NH<sub>4</sub><sup>+</sup> in the ASM1 model is:

$$\text{Concentration of NH}_4^+\text{-N nitrified to produce 1 gANOCOD/m}^3 \\ = 1/Y_{ZA} \\ \text{From Eq. 5, 14 g of NH}_4^+\text{-N nitrified produce 2g H}^+ \\ \text{So } 1/Y_{ZA} \text{ g NH}_4^+\text{-N nitrified produces } 1/(7Y_{ZA}) \text{ gH}^+$$

Also, from Eq. (5), the NH<sub>4</sub><sup>+</sup> incorporated into ANO biomass during synthesis releases a H<sup>+</sup>. The concentration of N incorporated into ANO mass is defined by the N content of the ANOs, which is accepted to be equal to that of the OHOs, i.e. f<sub>ZB,N</sub> = 0.068 mgN/mgANOCOD. So from Eq. 6:

$$14 \text{ g NH}_4^+\text{-N incorporated into ANOs releases 1 g H}^+ \\ \therefore f_{ZB,N} \text{ g NH}_4^+\text{-N incorporated into ANOs releases } f_{ZB,N}/14 \text{ g H}^+$$

Thus in total, during nitrification 1/(7Y<sub>ZA</sub>) + f<sub>ZB,N</sub>/14 gH<sup>+</sup> are released per gANOCOD generated. For ANO death, N transformations are as for OHOs above.

Because the ANO mass constitutes such a small part of the measured reactor COD (or VSS) concentration and the endogenous respiration rate is so low, P uptake and release in ANO growth and death respectively are ignored as negligibly small. However, these can be readily incorporated if required, by following the concepts of the OHOs developed above.

### Effect of pH on maximum specific growth rate of ANOs

The maximum specific growth rate of nitrifiers  $\mu_A$  is very sensitive to pH, with nitrification rates declining sharply outside the optimum pH range of 7.0 to 8.5. In the activated sludge system treating reasonably well buffered wastewaters, quantitative modelling of the effect of pH on nitrification is not critical because pH reduction can be limited or completely obviated by including anoxic zones thereby ensuring alkalinity recovery via denitrification. However, in poorly buffered wastewaters, or wastewaters with high influent N (such as anaerobic digester liquors), the interaction between the biological processes, pH and nitrification is the single most important one for the N removal activated sludge system. Hence, it is essential to include the effect of pH on the nitrification rate in the integrated model to simulate this important interaction.

Quantitative modelling of the effect of pH on  $\mu_A$  has been hampered by a lack of information and the general expected trends have been formulated based on empirical assumptions. Many studies have shown that  $\mu_A$  can be expressed as a percentage of the highest value at optimum pH. Accepting this approach and that  $\mu_A$  is highest and remains approximately constant in the pH range for  $7.2 < \text{pH} < 8.5$  and decreases as the pH decreases below 7.2 (Downing et al., 1964; Loveless and Painter, 1968), WRC (1984) modelled the  $\mu_A$  - pH dependency as:

$$\text{For } 7.2 < \text{pH} < 8.5, \mu_{\text{ApH}} = \mu_{\text{A}7.2} \quad (8a)$$

$$\text{For } 5 < \text{pH} < 7.2, \mu_{\text{ApH}} = \mu_{\text{A}7.2} \theta_{\text{ns}}^{(\text{pH}-7.2)} \quad (8b)$$

where:

$$\theta_{\text{ns}} = \text{sensitivity coefficient} \approx 2.35$$

WRC (1984) considered additionally an increase in half saturation concentration ( $K_n$ , mgN/l) with decrease in pH, i.e.  $K_{\text{npH}} = K_{\text{n}7.2} q_{\text{ns}}^{(7.2-\text{pH})}$  with  $q_{\text{ns}}$  also = 2.35. They did this because Marais and Ekama (1976) observed an increase in effluent ammonia concentration as the reactor pH decreased with increasing sludge age. It is simple to include this additional effect into the model, but it was omitted because very little data could be found in the literature on the effect of pH on  $K_n$  to support the observation of Marais and Ekama (1976), probably because the effect of pH on nitrification was observed as an effect on  $\mu_A$ , rather than an effect on  $\mu_A$  and  $K_n$  individually.

WRC (1984) did not consider cases where  $\text{pH} > 8.5$ . Declining  $\mu_A$  values at  $\text{pH} > 8.5$  have been observed and it has been noted that nitrification effectively ceases at a pH of about 9.5 (Malan and Gouws, 1966; Wild et al., 1971; Antoniou et al., 1990). Accordingly, for  $\text{pH} > 7.2$  an additional formulation is proposed to model the decline in the maximum specific growth rate from  $\text{pH} > 7.2$  to 9.5 as a function of  $\mu_{\text{A}7.2}$  using inhibition kinetics as follows:

$$\mu_{\text{ApH}} = \mu_{\text{A}7.2} K_I \frac{K_{\text{max}} - \text{pH}}{K_{\text{max}} + K_{\text{II}} - \text{pH}} \quad (9)$$

where:

$$K_I = 1.13, K_{\text{max}} = 9.5, K_{\text{II}} \approx 0.3.$$

The overall effect of pH on  $\mu_A$  is modelled by combining Eqs. (8) and (9), giving the maximum specific growth rate at any pH between 5.5 and 9.5 as a fraction of the maximum rate at  $\text{pH} = 7.2$ , Eq. 10, which is shown graphically in Fig 2. It can be seen that in the range  $\text{pH} = 7.2$  to 8.3, the change in  $\mu_{\text{ApH}}$  is small, with  $\mu_{\text{ApH}}/\mu_{\text{A}7.2} > 0.9$ .

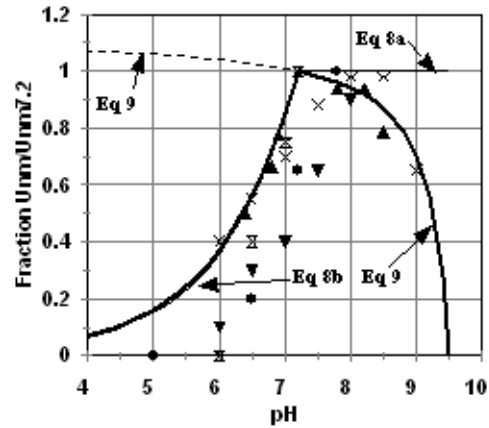


Figure 2

The effect of pH on the maximum specific growth rate of autotrophic nitrifying organisms at 20°C ( $\mu_{\text{nm}20}$ ).

— Model (Eqs 8-10); • Malan & Gouws (1966)

▼ Sawyer et al. (1973) ◻ Downing et al. (1966)

× Wild et al. (1971) ▲ Antoniou et al. (1990)

$$\mu_{\text{ApH}} = \mu_{\text{A}7.2} 2.35^{(\text{pH}-7.2)} K_I \frac{K_{\text{max}} - \text{pH}}{K_{\text{max}} + K_{\text{II}} - \text{pH}} \quad (10)$$

where:

the term  $2.35^{(\text{pH}-7.2)}$  is set = 1 for  $\text{pH} > 7.2$ ,

the term  $K_I \frac{K_{\text{max}} - \text{pH}}{K_{\text{max}} + K_{\text{II}} - \text{pH}}$  is set = 1 for  $\text{pH} < 7.2$  and

$\mu_{\text{ApH}} = 0$  for  $\text{pH} > 9.5$ .

Experimental data from the literature are also shown in Fig. 2 to provide some quantitative support for Eq. 10. At low pH ( $< 7.2$ ) data from Wild et al. (1971) and Antoniou et al. (1990) fit the equation reasonably well. Very little data are available for  $\text{pH} > 8.5$ , but the few points from Antoniou et al. (1990) show reasonable agreement with Eq. 10. Accordingly, Eq. 10 was accepted to calculate  $\mu_{\text{ApH}}$  in the integrated model in the pH range 5.5 to 9.5. From Eq. 10 the minimum sludge age for nitrification ( $R_{\text{sm}}$ ) at different pH and temperature (T) and un-aerated mass fraction ( $f_{\text{xm}}$ ) is given by:

$$R_{\text{sm}} = 1 / [\mu_{\text{ApHT}}(1 - f_{\text{xm}}) - b_{\text{nT}}] \text{ days} \quad (11)$$

The problem with nitrification in low alkalinity wastewater is that the pH obtained is not known, because it is interactively established between the degree of nitrification, loss of alkalinity, pH and  $\mu_{\text{ApHT}}$  (see below).

## Modelling gas exchange in the integrated model

### Modelling approach

In the three phase carbonate system weak acid/base model of Musvoto et al. (1997), the physical (P) processes of carbon dioxide gas exchange (passive) with the atmosphere were included. They did this by modelling the expulsion (reverse,  $K'_{\text{rCO}_2}$ ) and dissolution (forward,  $K'_{\text{fCO}_2}$ ) rates of diffusion separately and linking the two rates through the Henry's law constant for  $\text{CO}_2$  ( $K_{\text{HCO}_2}$ ), i.e.  $K'_{\text{fCO}_2} = K'_{\text{rCO}_2} K'_{\text{HCO}_2} / RT$ . They showed this approach yielded identical results to the usual interphase gas mass transfer equation with an overall liquid phase mass transfer rate coefficient  $K_{\text{LaCO}_2}$ , where  $K_{\text{LaCO}_2} = K'_{\text{rCO}_2}$ . In their model application, the actual  $\text{CO}_2$  expulsion rate constant value ( $K'_{\text{rCO}_2}$ ) was not important, because they considered final steady state conditions only, not the transient dynamic conditions to the final steady state.

Musvoto et al. (2000a), Van Rensburg et al. (2003) and Loewenthal et al. (2004) extended this chemical physical (CP) model to include three phase mixed weak acid base systems to simulate multiple mineral precipitation and active gas exchange of CO<sub>2</sub> and NH<sub>3</sub> during aeration of anaerobic digester liquor and swinery wastewater. Because they simulated transient (dynamic) conditions, the gas exchange and mineral precipitation rates were important and these were determined from the experimental batch test results.

In this integrated CPB processes model of the activated sludge system, four gases need to be considered, viz. ammonia, carbon dioxide, nitrogen and oxygen. Because measurements of pH and H<sub>2</sub>CO<sub>3</sub>\* alkalinity in aerobic reactors of full-scale activated sludge systems showed that equilibrium between the aqueous and gas (atmosphere) CO<sub>2</sub> phases is not reached during aeration in the aerobic reactor, the gas exchange (active) rates of the first three gases and the dissolution rate of oxygen by aeration are important for the simulation results, so that the K<sub>La</sub> rate constants for the four gases had to be determined (Table 3).

For active gas exchange (stripping or dissolution), if the dimensionless Henry's law constant of a gas, H<sub>c</sub> [= 1/(K<sub>H</sub>RT)] is > 0.55, then oxygen can be used as a reference gas and the overall liquid phase mass transfer (expulsion/dissolution) rate coefficient K<sub>La</sub> (= K'<sub>L</sub>) for the other gases can be accepted to be in a fixed relationship to the K<sub>La</sub> rate for oxygen (K<sub>LaO2</sub>) dependent on the relative magnitudes of the diffusivity of the other gases to oxygen (see Eq. 12) (Munz and Roberts, 1989). Of the four gases, only ammonia has a H<sub>c</sub> < 0.55 (= 0.011 at 20 °C, see Table 6), so the K<sub>LaNH3</sub> (= K'<sub>LNH3</sub>, Musvoto et al., 2000a) needs to be determined independently of the K<sub>La</sub> rate of oxygen. However, because negligibly little ammonia is expelled from the aqueous phase with aeration in the pH range 6.5 to 8 for activated sludge systems, ammonia expulsion could have been omitted from the integrated model without loss of accuracy.

In the CP model of Musvoto et al. (2000a), the concentration of *non-dissolved* CO<sub>2</sub> gas, CO<sub>2g</sub>, was essentially kept constant; CO<sub>2g</sub> was included as a compound in the model only for continuity. In this integrated CPB model, CO<sub>2g</sub> is not constant because dynamic variation in CO<sub>2</sub> production and consumption are considered. In implementation of the integrated CPB model, the CO<sub>2g</sub> and the other gas compounds can be dealt with as part of the bulk liquid or as in a separate gaseous phase. Since the gas exchanges occur with the atmosphere where the partial pressures of the gasses are essentially constant, and the head-space above activated sludge systems usually are not confined, both approaches should lead to near identical simulations, provided the gas exchange rates are independent of the corresponding gas concentration e.g. CO<sub>2g</sub>. Because the former approach is simpler to implement in the computer programme Aquasim (Reichert, 1998), this approach was followed here. To ensure that the gas exchange rates are independent of the corresponding gas concentration, the original gas exchange dissolution formulation of Musvoto et al. (1997) was changed, with the gas species (e.g. CO<sub>2g</sub>) concentration substituted for the relevant gas partial pressure and Henry's law constant (e.g. p<sub>CO2</sub> K<sub>HCO2</sub>, see Table 3). In effect this allows the gas species concentrations to vary and these are removed from the reactor hydraulically, i.e. with the effluent flow. If a separate gas phase implementation is required in Aquasim, the diffusive link can be used for the gas exchange equations in Table 3. This would be necessary in anaerobic digestion (Batstone et al., 2002).

Therefore, for CO<sub>2</sub>, N<sub>2</sub> and NH<sub>3</sub> gas exchange from the anoxic and aerobic reactors, the following approach was adopted (using CO<sub>2</sub> as example):

Transfer from dissolved form [H<sub>2</sub>CO<sub>3</sub>\*] to non-dissolved form CO<sub>2g</sub> is the sum of processes P6 and P7 in Table 3.

$$r_{gmtCO2} = K_{LaCO2} \left[ [H_2CO_3^*] - p_{CO2} K_{HCO2} \right] \text{ molCO}_2/(\text{m}^3\text{d}) \quad (\text{see Table 3}) \quad (12a)$$

where:

- r<sub>gmt</sub> = rate of gas mass transfer (mol gas/(m<sup>3</sup>d))
- [H<sub>2</sub>CO<sub>3</sub>\*] = concentration of dissolved CO<sub>2</sub> in aqueous phase (mol/l)
- p<sub>CO2</sub> = partial pressure of CO<sub>2</sub> in the atmosphere (atm)
- K<sub>HCO2</sub> = Henry's law constant for CO<sub>2</sub> (Table 6)
- K<sub>LaCO2</sub> = Overall liquid phase mass transfer rate coefficient for CO<sub>2</sub> (/d)

where:

$$K_{LaCO2} = K_{LaO2} \left[ \frac{D_{LCO2}}{D_{LO2}} \right]^n \left[ 1 + \frac{1}{\frac{k_G}{k_L} H_{cCO2}} \right]^{-1} \quad (/d) \quad (12b)$$

where:

- K<sub>La</sub> = Overall liquid phase mass transfer rate coefficient for CO<sub>2</sub> and O<sub>2</sub> (/d)
- D<sub>L</sub> = Liquid phase molecular diffusion coefficient for CO<sub>2</sub> and O<sub>2</sub> (cm<sup>2</sup>/s) (Table 6)
- k<sub>G</sub>, k<sub>L</sub> = Gas (k<sub>G</sub>) and liquid (k<sub>L</sub>) phase individual mass transfer coefficients (m/s)
- H<sub>cCO2</sub> = Dimensionless Henry's constant for CO<sub>2</sub> (Table 6)
- n = Diffusivity coefficient = 0.50

In Eq. 12b, the ratio k<sub>G</sub>/k<sub>L</sub> represents the relative contribution of the gas and liquid phases mass transfer resistance under turbulent mixing conditions. A value of 30 to 40 is recommended by Munz and Roberts (1989) for the high turbulent mixing conditions created by power inputs (P/V) greater than 70 W/m<sup>3</sup> characteristic of aerated activated sludge reactors. In the simulations the k<sub>G</sub>/k<sub>L</sub> ratio was set to 40. From simulation, it was found that the K<sub>LaO2</sub> rate affected the aerobic reactor dissolved oxygen (DO) and CO<sub>2</sub> (H<sub>2</sub>CO<sub>3</sub>\*) concentrations, but not the pH. As the K<sub>LaO2</sub> rate was decreased from 600/d to 100/d, the DO decreased from close to saturation (~7 mgO/l) to ~3.0 mgO/l and CO<sub>2</sub> (H<sub>2</sub>CO<sub>3</sub>\*) concentration increased from 1.7 mgCO<sub>2</sub>/l (~3x saturated at atmospheric p<sub>CO2</sub> = 0.00035) to 6.2 mgCO<sub>2</sub>/l (~10x saturated) but the pH remained around 7.0. However, the anoxic reactor pH increased from 7.7 to 8.0 as the K<sub>LaO2</sub> rate decreased due to increasing denitrification and so greater alkalinity generation resulting from recycling less DO to the anoxic reactor (at a mixed liquor recycle ratio of 1:1). Tests at 2 full-scale activated sludge plants with fine bubble aeration indicated the aerobic reactor effluents were about 20% supersaturated with dissolved CO<sub>2</sub>. So to get low dissolved CO<sub>2</sub> concentrations the K<sub>LaO2</sub> rate was set at 600/d. Since the H<sub>c</sub> for NH<sub>3</sub> is <0.55, the above equations cannot be applied for NH<sub>3</sub>. The mass transfer coefficient for ammonia (K<sub>LaNH3</sub>, Table 3) was set at a very low value of 3.2/d to ensure an extremely low loss of ammonia by aeration stripping. The partial pressure of the three gases in Table 3 were set at the standard atmospheric values i.e. p<sub>N2</sub> = 0.79165, p<sub>O2</sub> = 0.20800 and p<sub>CO2</sub> = 0.00035 atmospheres.

### The integrated two phase mixed weak acid/base chemical, physical and biological processes activated sludge model

All the changes to the processes of growth for the heterotrophs and autotrophs discussed above were made to ASM1. The amended biological model was combined with the two phase

**TABLE 6**  
**Dimensionless Henry's Law constants ( $H_c$ ) at 20°C, liquid phase diffusion coefficient ( $D_L$ ) at 20°C and liquid phase mass transfer rate coefficient ( $K_{La}$ ) for oxygen, the reference gas, nitrogen, carbon dioxide and ammonia (Perry and Green, 1997)**

Gas	Diffusivity at 20°C cm <sup>2</sup> /s	Dimensionless Henry's law constant $H_c$	Overall liquid phase mass transfer rate coefficient $K_{La}$
Oxygen, O <sub>2</sub>	202500	32.54	600/d *1
Nitrogen, N <sub>2</sub>	190000	64.2	Based on O <sub>2</sub> (Eq 12)
Carbon Dioxide CO <sub>2</sub>	175300	1.06	Based on O <sub>2</sub> (Eq 12)
Ammonia, NH <sub>3</sub>	-	0.011	3.2 /d*2

Note \*1: Model fitted value to obtain 20% CO<sub>2</sub> super-saturation in the aerobic reactor bulk liquid, i.e. partial pressure of CO<sub>2</sub> 20% higher than in the atmosphere ( $p_{CO_2}$  atmosphere = 0.00035 atm).

Note \*2: Arbitrary low value - actual low value not important because effectively zero ammonia gas strips from the aeration reactor by aeration.

$$K_{HCO_2} = 10^{-pK_{HCO_2}} \text{ mol}/(\ell \cdot \text{atm}); \quad pK_{HCO_2} = -\frac{2025.3}{T_K} - 0.0104 T_K + 11.365 \quad ; \quad H_{cCO_2} = \frac{1}{K_{HCO_2} R T_K}$$

$$K_{HN_{2T}} = K_{HN_{225}} \exp \left[ 1300 \left( \frac{1}{T_K} - \frac{1}{289.15} \right) \right] \quad \text{where} \quad K_{HN_{225}} = 0.000661 \text{ mol}/(\ell \cdot \text{atm})$$

$$r_{dissO_2} = K_{LaO_2} [O_{2sat} - O_{2reactor}] \quad \text{where} \quad O_{2sat} = 8.9 \text{ mgO}/\ell \text{ (0.000278 mol}/\ell) \text{ at } 20^\circ\text{C and } 1 \text{ atm,}$$

$O_{2reactor} = \sim 2.0 \text{ mgO}/\ell$  (0.000063 mol/l) and  $K_{LaO_2} = 600 /d$ .

$K_{HCO_2} = 0.03931$ . Hence CO<sub>2</sub> saturation concentration = 0.03931 \* 0.00035 = 13.76x10<sup>-6</sup> mol/l.

Molar mass of CO<sub>2</sub> = 44 g/mol. Hence CO<sub>2</sub> saturation concentration = 13.76x10<sup>-6</sup>x44000 = 0.60 mg/l.

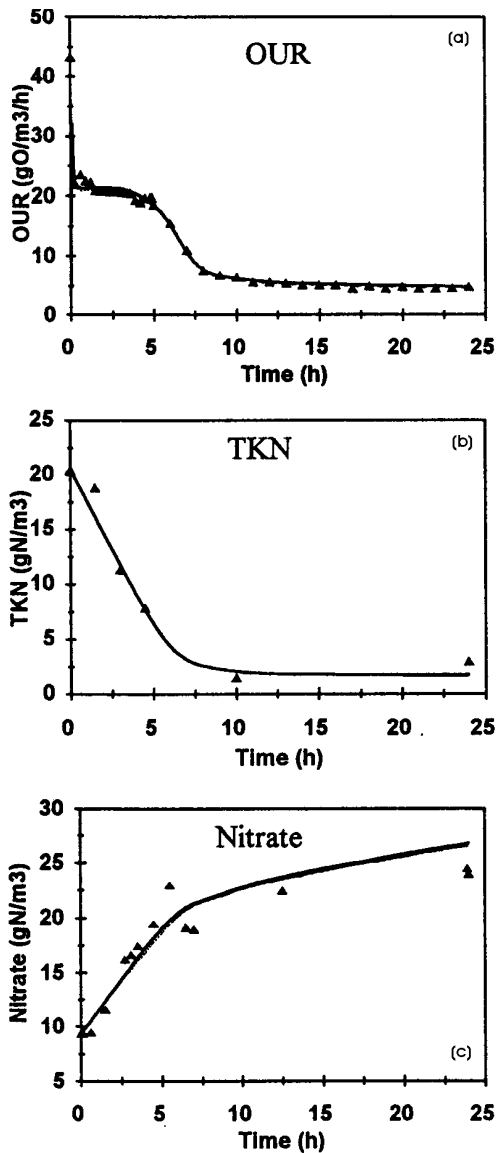
(aqueous-gas) mixed weak acid/base subset model (Musvoto et al., 2000a; b; c), to give the integrated two phase mixed weak acid/base chemical, physical and biological processes (CPB) activated sludge model shown in matrix form in Tables 2 and 3. This model was incorporated into the Aquasim computer programme (Reichart, 1998).

A number of simulations were done to verify the integrated CPB model, one of which, the aerobic batch test of Still et al. (1996), is shown in Fig. 3 as illustration. Additional details such as kinetic and stoichiometric constants, are given by Dold et al. (1991). Because the total species concentrations of the carbonate, phosphate and SCFA systems were not measured by Still et al. (1996), values for these parameters had to be estimated for input to the model – values for the SCFA concentration were accepted to be zero as discussed above. All the remaining input information was taken from Dold et al. (1991). The oxygen utilisation rate (OUR), nitrate and TKN concentrations predicted by the integrated model are compared with those predicted by the ASM1 (as given by Dold et al., 1991) and the experimental data in Figs. 3a, b and c. The predictions of the two models are identical and both compare very well with the experimental data. However, the integrated model predictions for the chemical physical processes could not be compared because ASM1 does not consider these processes, nor were they monitored experimentally in the batch test. Close correlation between predictions of the two models is expected because the simulations are for a municipal wastewater where the pH remained essentially constant so that, despite their inclusion in the integrated model, the weak acid/base systems (pH) have no significant effect on the biological processes. No suitable data on activated sludge treatment of municipal wastewaters where the weak acid/base

systems and pH play a significant role could be found in the literature to directly validate the model. Because the chemical-physical and biological processes parts of the integrated model had been validated independently, rigorous validation of the integrated model was not required except where the chemical physical processes affect the biological processes. In this regard, the principal interaction is the effect of pH on nitrification and this interaction was based and calibrated on literature information (Eqs. 8 to 10, Fig. 2).

#### **A note on the COD mass balance of the model**

Material mass balances (COD, C, N and P) are performed on model outputs and experimental systems to check model and data accuracy. Strictly, COD mass balances cannot be applied to the integrated model because inorganic C (CO<sub>2</sub>) is changed to organic nitrifier (ANO) VSS (COD) mass, unless this contribution to the calculated VSS (COD) is specifically excluded. Theoretically, this contribution to the VSS (COD) is large enough (2 to 4%) to indicate a modelling error (>0.5%), but practically, remains small enough to be considered negligible for normal domestic wastewater where the mass of ANOs is very small compared with the mass of OHOs. However, for wastewaters which have a high TKN/COD ratio, such as sludge treatment liquors, the mass of ANOs will be significant compared with the mass of OHOs and COD mass balances much greater than 100% will be obtained if the ANO VSS (COD) is not excluded from the sludge mass in the COD mass balance. For the C mass balance, the COD/TOC ratio of the influent organics need to be known and was accepted at 3.0 (see above). Similarly, the COD/TOC ratios of the OHO and ANO active masses and their endogenous



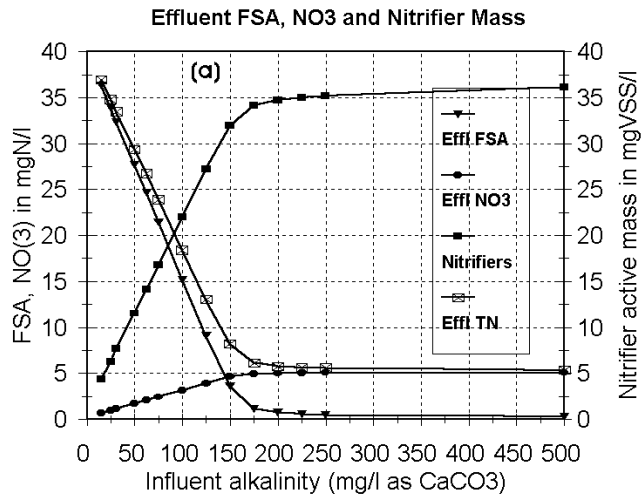
**Figure 3**

Comparison of the predicted oxygen utilisation rate (OUR), and nitrate and TKN concentrations with the IWA Activated Sludge Model No.1 (ASM1) and the integrated chemical, physical and biological processes model for the nitrification aerobic batch test of Still et al. (1996) (see also Dold et al., 1991). Dashed line ---- ASM1 (not visible, below solid line), solid line ----- Integrated model and  $\blacktriangle$  experimental data.

masses need to be known. For these, the active and endogenous masses were accepted to have the same stoichiometric formulation of  $C_5H_7O_2N$  (WRC, 1984) which gives a COD/TOC of 2.67 mgCOD/mgC.

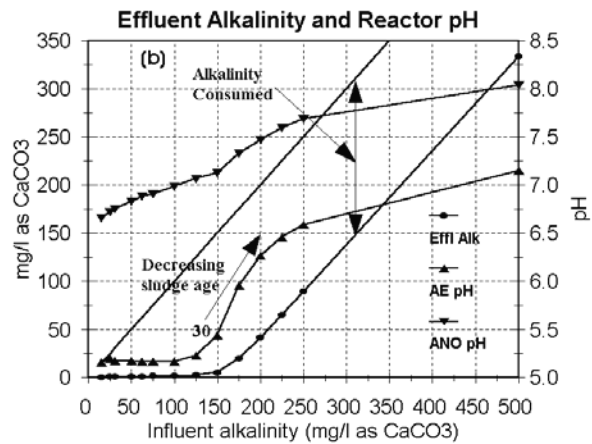
### Low alkalinity nitrifying/denitrifying (ND) system

To evaluate the performance of the integrated CPB model and illustrate the behaviour of ND activated sludge systems with low influent alkalinity, a Modified Ludzack Ettinger (MLE) anoxic-aerobic system was simulated. The influent wastewater characteristics (raw wastewater, COD=750 mgCOD/l, TKN=60 mgN/l, FSA=45 mgN/l, TP=11.27 mgP/l, SCFA=0 mg/l pH = 7.3) and the system design and operating conditions (sludge age 30 d, temperature 22°C, anoxic and aerobic mass fractions 0.35



**Figure 4a**

Effluent free and saline ammonia (FSA), nitrate ( $NO_3$ ) and total nitrogen ( $TN=FSA+NO_3$ ) and aerobic reactor autotrophic nitrifier organism (ANO) concentration versus influent  $H_2CO_3^*$  alkalinity concentration.



**Figure 4b**

Influent (diagonal) and effluent  $H_2CO_3^*$  alkalinity and aerobic and anoxic reactor pH versus influent  $H_2CO_3^*$  alkalinity.

and 0.65 and mixed liquor and sludge return recycles 3:1 and 1:1) were the same for each simulation. Also  $K_{LaO_2}$  was set at 600/d to maintain low dissolved  $CO_2$  concentrations (see above). Only the influent  $H_2CO_3^*$  alkalinity was varied from 500 down to 15 mg/l as  $CaCO_3$ . Effluent free and saline ammonia (FSA), nitrate ( $NO_3$ ), total nitrogen ( $TN=FSA+NO_3$ ) and  $H_2CO_3^*$  alkalinity (as  $CaCO_3$ ) concentrations and anoxic and aerobic reactor pH versus influent  $H_2CO_3^*$  alkalinity are shown in Fig. 4.

The ND system delivers < 1 mgFSA-N/l, ~5 mg $NO_3$ -N/l and ~5 mgTN-N/l for influent  $H_2CO_3^*$  alkalinity > 200 mg/l (all alkalinities as  $CaCO_3$ ) (Fig. 4a). Although the pH in the aerobic reactor (which is about 1 pH unit below that in the anoxic reactor due to the  $CO_2$  stripping by aeration) decreases with decreasing influent  $H_2CO_3^*$  alkalinity, it remains above 6.3 (Fig. 4b), at which pH the growth rate of the nitrifiers is still high enough for the long sludge age (30 d) to achieve complete nitrification. The difference between the influent and effluent  $H_2CO_3^*$  alkalinity is the  $H_2CO_3^*$  alkalinity consumed by the system and from Fig 4b this is about 150 mg/l when the influent  $H_2CO_3^*$  alkalinity is >200 mg/l. Once the influent  $H_2CO_3^*$  alkalinity decreases below 200 mg/l, the effluent  $H_2CO_3^*$  alkalinity drops below 50 mg/l and the aerobic reactor pH declines rapidly from 6.3 to

below 5.5 for an influent  $\text{H}_2\text{CO}_3^*$  alkalinity of  $<150 \text{ mg/l}$ . At pH 5.5 (influent  $\text{H}_2\text{CO}_3^*$  alkalinity =  $150 \text{ mg/l}$ ), nitrification is at the point of failure and for lower influent alkalinities, the effluent FSA and TN concentrations begin to increase sharply and the effluent nitrate concentration decreases due to the lower concentration of nitrate generated by nitrification. Thus in general, if the effluent  $\text{H}_2\text{CO}_3^*$  alkalinity from an activated sludge system, whether fully aerobic or ND, drops below  $50 \text{ mg/l}$ , the reactor pH will fall below 5.5, which will inhibit nitrification and consequently compromise N removal. This conclusion is not new – WRC (1984) stated the same conclusion and recommended that when the effluent  $\text{H}_2\text{CO}_3^*$  alkalinity falls below  $50 \text{ mg/l}$ , lime dosing should be considered to raise the aerobic reactor pH, or, for fully aerobic systems, denitrification in anoxic zones be introduced to decrease the overall  $\text{H}_2\text{CO}_3^*$  alkalinity consumption.

In this example, nitrification fails at the low pH of around 5.5 because the sludge age is very long (30 d). At this pH, the maximum specific growth rate of the ANOs ( $\mu_A$ ) is depressed so low that an operating sludge age of 30 d becomes lower than the minimum sludge age for nitrification ( $R_{sm}$ ) and the nitrifiers are washed out of the system. At shorter operating sludge ages, the pH at which nitrification fails will be higher (as indicated in Fig. 4b). So at low influent  $\text{H}_2\text{CO}_3^*$  alkalinity ( $<100 \text{ mg/l}$ ), the pH declines,  $\mu_A$  (Eq. 10) decreases and  $R_{sm}$  increases (Eq. 11). Once  $R_{sm}$  approaches the operating sludge age of the system ( $R_s$ ), nitrification becomes unstable and the effluent FSA begins to increase, particularly under cyclic loading conditions.

## Conclusion

The biological processes of the nitrification-denitrification (ND) activated sludge model No 1 (ASM1, Henze et al., 1987) were integrated into a two-phase (aqueous-gas) subset of the three phase mixed weak acid/base chemical-physical kinetic model of Musvoto et al. (2000a; b; c). In this integration, a number of additions were made to ASM1, such as production and/or utilisation of  $\text{CO}_2$ ,  $\text{H}^+$ ,  $\text{NH}_3$ , and  $\text{H}_3\text{PO}_4$  in heterotrophic (OHO) and autotrophic (ANO) growth and death (endogenous respiration); and the effect of pH (i.e.  $\text{H}^+$ ) on the biological processes, in particular on the autotrophic nitrifiers (ANOs).

The integrated chemical, physical and biological (CPB) processes activated sludge model simulations were compared with those of ASM1 (Dold et al., 1991) and experimental data in the literature. Identical simulation results were obtained with both models and the correlation of both models with experimental data was good. Strictly, these comparisons serve only as model verification because, although included, the weak acid/bases and pH have no significant effect on the biological processes in the cases considered. However, because the CPB model was developed by integrating previously individually validated models, rigorous independent experimental validation of the integrated model was not deemed necessary, except where the chemical-physical processes interact strongly with the biological processes. The principal interaction is the effect of pH on nitrification and this interaction was based on literature information and so is calibrated as best as possible. It is concluded from this integration that:

- the total organic carbon (TOC) to chemical oxygen demand (COD) ratio of the wastewater does not significantly influence the reactor pH, but
- the free and saline ammonia (FSA) to total Kjeldahl nitrogen (TKN) ratio and concentrations,

- nitrate uptake for OHO growth once ammonia is depleted (assimilative denitrification),
- extent of denitrification and
- the extent of  $\text{CO}_2$  stripping from the aerobic reactor by aeration do affect reactor pH.

Experimental determination of the inorganic carbon concentration ( $C_T$ ) in effluents from full-scale N removal activated sludge plants indicated that the effluents were about 20% supersaturated with  $\text{CO}_2$  gas so that  $\text{CO}_2$  gas exchange by aeration in the aerobic reactor does not yield  $\text{CO}_2$  equilibrium with the atmosphere.

From simulation of long sludge age nitrification-denitrification (ND) activated sludge systems with incrementally decreasing influent  $\text{H}_2\text{CO}_3^*$  alkalinity, when the effluent  $\text{H}_2\text{CO}_3^*$  alkalinity falls below about  $50 \text{ mg/l}$  as  $\text{CaCO}_3$ , the aerobic reactor pH drops below 6.3, which severely retards nitrification and causes the minimum sludge age for nitrification ( $R_{sm}$ ) to increase up to the operating sludge age of the system. Therefore, when treating low  $\text{H}_2\text{CO}_3^*$  alkalinity wastewaters, such as those from the Western and Southern coastal areas of South Africa, the minimum sludge age for nitrification ( $R_{sm}$ ) varies with temperature and reactor pH and for low effluent  $\text{H}_2\text{CO}_3^*$  alkalinity ( $< 50 \text{ mg/l}$  as  $\text{CaCO}_3$ ), nitrification becomes unstable and sensitive to dynamic loading conditions resulting in increases in effluent ammonia concentration and reduced N removal. For effluent  $\text{H}_2\text{CO}_3^*$  alkalinity  $< 50 \text{ mg/l}$ , lime should be dosed raise the aerobic reactor pH and stabilise nitrification.

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