Enhanced polyphosphate organism cultures in activated sludge systems. Part III: Kinetic model

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Abstract

A mathematical model is presented that describes the kinetics and stoichiometry of biological excess phosphorus (P) removal phenomena. The mathematical model is developed from the conceptual mechanistic model, set out in **Part II** of this series of papers. In the mathematical model 12 compounds and 13 processes are identified as essential to describe the biological excess P removal phenomena. The process rates and stoichiometry are formulated mathematically and displayed in matrix form for ready visualisation and systematic computation. The kinetic and stoichiometric constants in the model are evaluated directly or indirectly from experimental observations. The behaviour predicted by the model conforms closely to that observed experimentally.

Introduction

In **Part I** of this series of papers (Wentzel *et al.*, 1988), procedures have been set out whereby enhanced cultures of polyphosphate (polyP) organisms can be developed in the Bardenpho and UCT systems. In **Part II** (Wentzel *et al.*, 1989) using experimental observations made on these enhanced culture systems and on batch tests in which mixed liquors drawn from the systems are subject to a variety of conditions, a conceptual mechanistic model has been proposed to describe the biological excess P removal phenomena.

In this paper, using the mechanistic model as a basis, a mathematical model is developed that describes the stoichiometry and kinetics of the biological excess P removal phenomena. (In the paper, it is necessary to make frequent reference to the first two papers in the series. For simplicity, reference will be made to '**Part I**' or '**Part II**'.)

Model development

The mechanistic model, described in **Part II**, deals specifically with enhanced polyP organism cultures receiving acetate only as substrate. Furthermore, the model hypothesises behaviour only under anaerobic and aerobic states. The anoxic state has not been included because, for reasons not yet understood, the enhanced culture systems have shown minimal denitrification propensity. As a consequence, the biological excess P removal processes and compounds that can be hypothesised to be involved in the anoxic state cannot be tested experimentally. It was thought preferable therefore, to omit these processes from the mechanistic model and hence also from the mathematical model. In due course, when information on the anoxic processes becomes available, these can be incorporated.

The mechanistic model identifies 11 compounds associated with 12 processes as being directly involved in biological excess P removal in enhanced culture systems. However, in these enhanced culture P removal systems, nitrification inevitably takes place and it is not possible to calibrate the model without taking due cognisance of it. Consequently nitrification is included. To describe nitrification, 2 extra compounds and 2 extra processes are needed.

In developing the mathematical model for enhanced culture behaviour the final objective for modelling biological excess P removal must be kept in mind; this is, to extend the model to the mixed cultures usually encountered in nutrient removal systems treating municipal wastewater. Clearly, there will be interactions between the polyP and non-polyP organism populations in such systems. For example: Acetate and other short-chain fatty acids must be generated by the non-polyP organisms for sequestration by the polyP organisms (Wentzel *et al.*, 1985); and certain conceptual problems exist in regard to the death-regeneration behaviour of polyP and non-polyP organisms.

With regard to death-regeneration, there is substantial evidence that indicates polyP organisms are not predated in mixed cultures, or only insignificantly so, and suffer endogenous mass loss only for maintenance:

- Wentzel *et al.* (1985) found that, in mixed cultures, P release and uptake observed at different sludge ages could be explained only if the endogenous mass loss rate for polyP organisms is far lower than that for non-polyP organisms.
- In enhanced polyP organism cultures, although ample opportunity exists for predator growth, this does not happen as is evident from the high specificity of the organism mass and the low endogenous mass loss rates, see **Part II**.

Thus, in the mixed culture systems, the polyP and non-polyP organism populations appear to behave relatively independently with only two significant links between the two populations:

- Conversion of readily biodegradable COD to short-chain fatty acids by the non-polyP organisms for sequestration by the polyP organisms. The kinetics of conversion have been described by Wentzel *et al.* (1985) who indicate that the conversion rate is independent of the polyP organism mass; hence this link is one-directional. In anticipation of the model being developed further to apply to situations where sewage and not acetate serves as substrate, this process is included, with one extra compound.
- Apparently unbiodegradable soluble COD is generated by the polyP organisms during endogenous mass loss in the enhanced culture systems. However, in mixed cultures, this apparently unbiodegradable material very likely serves as a substrate source for the non-polyP organisms. This process of assimilation concerns the non-polyP organisms and only need be incorporated in the non-polyP kinetic model – again it is an undirectional link.

Taking the above into account, a total of 14 compounds

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TABLE 1
PROCESS KINETICS AND STOICHIOMETRY FOR BIOLOGICAL EXCESS P REMOVAL

Compound i →		1	2	3	4	5	6	7	8	9	10	11	12	13	14	Process rate, ρ_j $ML^{-3}T^{-1}$
j	Process ↓	$Z_{B,A}$	$Z_{B,G}$	Z_E	S_{anm}	S_{phb}	P_{polyP}	$S_{bs,c}$	$S_{bs,a}$	N_{h3}	$N_{O,bs}$	N_{O3}	P_s	S_{us}	0	
1	Aerobic growth of $Z_{B,G}$ on S_{phb} with N_{h3}		1			$-\frac{1}{Y_G}$	$\frac{f_{p,upt}}{Y_G}$			$-f_{ZBG,N}$			*A		$\frac{-1-Y_G}{Y_G}$	$\hat{\mu}_{G_1}\left[\frac{S_{phb}/Z_{B,G}}{(K_{sG1})+S_{phb}/Z_{B,G}}\right]\left[\text{Air on}\right]\left[\frac{NH_3}{\text{limit}}\right]\left[\frac{P}{\text{limit}}\right]Z_{B,G}$
2	Aerobic growth of $Z_{B,G}$ on S_{phb} with N_{O3}		1			$-\frac{1}{Y_G}$	$\frac{f_{p,upt}}{Y_G}$					$-f_{ZBG,N}$	*B		$\frac{-1-Y_G}{Y_G}$	$\hat{\mu}_{G_1}\left[\frac{S_{phb}/Z_{B,G}}{(K_{sG1})+S_{phb}/Z_{B,G}}\right]\left[\text{Air on}\right]\left[\frac{1-NH_3}{\text{limit}}\right]\left[\frac{P}{\text{limit}}\right]Z_{B,G}$
3	j_1 if P_s limited		1			$-\frac{1}{Y_G}$	$-f_{ZBG,P}$			$-f_{ZBG,N}$					$\frac{-1-Y_G}{Y_G}$	$\hat{\mu}_{G_2}\left[\frac{S_{phb}/Z_{B,G}}{(K_{sG2})+S_{phb}/Z_{B,G}}\right]\left[\text{Air on}\right]\left[\frac{NH_3}{\text{limit}}\right]\left[\frac{1-P}{\text{limit}}\right]Z_{B,G}$
4	j_2 if P_s limited		1			$-\frac{1}{Y_G}$	$-f_{ZBG,P}$					$-f_{ZBG,N}$			$\frac{-1-Y_G}{Y_G}$	$\hat{\mu}_{G_2}\left[\frac{S_{phb}/Z_{B,G}}{(K_{sG2})+S_{phb}/Z_{B,G}}\right]\left[\text{Air on}\right]\left[\frac{1-NH_3}{\text{limit}}\right]\left[\frac{1-P}{\text{limit}}\right]Z_{B,G}$
5	Aerobic decay of $Z_{B,G}$		−1	$f_{Ep,G}$						*C	*D		*E	$f_{Es,G}$	*F	$b_G Z_{B,G}$ (Air on)
6	Lysis of P_{polyP} for j_5						−1						1			$\rho_5(P_{polyP}/Z_{B,G})$
7	Lysis of S_{phb} for j_5					−1			1							$\rho_5(S_{phb}/Z_{B,G})$
8	Anaerobic decay of $Z_{B,G}$		−1	$f_{Ep,G}$						*G	*H		*I	$(1-f_{Ep,G})$		$b_G Z_{B,G}$ (Air off)
9	Lysis of P_{polyP} for j_8						−1						1			$\rho_8(P_{polyP}/Z_{B,G})$
10	Lysis of S_{phb} for j_8					−1			1							$\rho_8(S_{phb}/Z_{B,G})$
11	Anaerobic cleavage of P_{polyP} for maintenance						−1						1			$b_{pp}P_{polyP}$ (Air off)
12	Conversion $S_{bs,c}$ to $S_{bs,a}$							−1	1							$K_C S_{bs,c} Z_{B,H}$ (Air off)$(1-N_{O3}$ limit)
13	Sequestration of $S_{bs,a}$					1	$-f_{p,rel}$		−1				$-f_{p,rel}$			$K_p Z_{B,G}$ (Ac limit)(PolyP limit)
14	Aerobic growth of Autotrophs	1								$-f_{ZBA,N}$ $-1/Y_A$		$\frac{1}{Y_A}$	$-f_{ZBA,P}$		*J	$\hat{\mu}_{A}\left[\frac{N_{h3}}{K_{NH}+N_{h3}}\right]$(Air on)$(N_{h3}$ limit$)Z_{B,A}$
15	Decay of Autotrophs	−1		$f_{Ep,A}$	$1-f_{Ep,A}$						*K	*L				$b_A Z_{B,A}$

*A = $-f_{ZBG,P}-f_{P,upt}/Y_G$
*B = $-f_{ZBG,P}-f_{P,upt}/Y_G$
*C = $f_{ZBG,N}-f_{Ep,G}f_{ZBG,N}-f_{Es,G}f_{EsG,N}$
*D = $f_{Es,G}f_{EsG,N}$
*E = $f_{ZBG,P}-f_{Ep,G}f_{ZBG,P}$
*F = $-(1-f_{Ep,G}-f_{Es,G})$
*G = $f_{ZBG,N}-(f_{Ep,G}f_{ZBG,N}+f_{Es,G}f_{EsG,N})$
*H = $f_{Es,G}f_{EsG,N}$

*I = $f_{ZBG,P}(1-f_{Ep,G})$
*J = $\frac{4.57-Y_A}{Y_A}$
*K = $f_{ZBA,N}-f_{Ep,A}f_{ZEA,N}$
*L = $f_{ZBA,P}-f_{Ep,A}f_{ZEA,P}$

associated with 15 processes are identified for inclusion in the mathematical model.

Model presentation

In the mathematical model, the process rates are formulated mathematically as are the stoichiometric relationships between the processes and compounds. The large number of complex interactions between compounds and processes necessitates that these be clearly presented. Following the proposals of the IAWPRC Task Group (1987) on *Mathematical Modelling of Wastewater Treatment*, the matrix format is used to present the model. This matrix format facilitates clear and unambiguous presentation of the processes and compounds of the model and their interaction. The setting up of such a matrix, how to interpret it and how it is incorporated in the mathematical solution procedure is described briefly in **Appendix I.**

Model description

The matrix for the mathematical model is set out in Table 1. The compounds, "i" in number, are listed across the top of the matrix; the processes, "j" in number, are listed down the left hand side of the matrix. Following the IAWPRC recommendation, VSS is expressed in COD units; yields and all other relevant constants are similarly expressed, see **Appendix I.**

To facilitate discussion, the processes described in the matrix can be grouped into five categories:

(1) conversion of "complex" readily biodegradable COD to acetate (j = 12);
(2) sequestration of acetate (j = 13);
(3) growth (j = 1 to 4);
(4) endogenous mass loss (j = 5 to 11); and
(5) nitrifier growth and decay (j = 14 to 15).

(1) ***Conversion of "complex" readily biodegradable COD to acetate (j = 12)*** This process is included for completeness. It does not operate when only acetate, or other short-chain fatty acids, serve as influent, as in the enhanced culture systems. This process will be implicated in the polyP organism growth in mixed culture systems when the influent contains readily biodegradable COD other than short chain fatty acids. It functions, therefore, as a link when incorporating polyP organism behaviour into the general activated sludge model. Development of the stoichiometry and kinetics of this process is as described by Wentzel *et al.* (1985).

(2) ***Sequestration of acetate (j = 13)*** The compound acetate (i = 8) is taken up and stored as PHB. The rate of acetate uptake is modelled as being zero order with respect to the acetate concentrations (i = 8) and first order with respect to the polyP organism concentration (i = 2), as observed in **Part II.** The specific rate constant for sequestration is K_p. Every acetate COD that is taken up appears as PHB (i = 5). Concomitantly, stored polyP (i = 6) is cleaved and P released to the bulk liquid (i = 12). The polyP cleavage and P release is modelled as being directly proportional to the acetate uptake, the stoichiometric constant of proportionality being $f_{P,rel}$. Should either the acetate concentration (i = 8), or the stored polyP (i = 6) become limiting, the sequestration process terminates. This is achieved by using the switching functions (Ac limit and polyP limit) respectively. The sequestration reaction is modelled to occur only in the absence of oxygen, in accordance with the arguments presented in **Part II.** This is achieved by using the switching function (Air off). The sequestration process is applicable to both the first and second phase P release described in **Part II**, only the kinetic and stoichiometric constants, K_p and $f_{P,rel}$, differ in the two phases. To model the data assembled in the batch tests, a function (P Switch) is utilised to change the constants from the first phase values to the second phase values. However, in "normal" application of the model the first phase only is expected to be operative.

(3) ***Growth (j = 1 to 4)*** In line with the experimental observations in **Part II**, modelling of aerobic growth needs to consider whether soluble P is limiting or not, and whether ammonia or nitrate is used as a nitrogen source for cell synthesis. All possible combinations of these give rise to four processes for growth, as shown in Table 1. However, modelling of these processes has a number of common factors. Following the proposals in **Part II**, PHB (i = 5) serves as the only substrate source for polyP organism growth. Being an internally stored polymer, the specific rate of utilisation is modelled as a surface saturation type reaction, similar to that proposed for the rate of utilisation of particulate material in the general activated sludge model (Dold *et al.*, 1980) with maximum specific growth rate $\hat{\mu}_{G1}$ and half saturation coefficient K_{sG1}. This function has the same basic structure as the Monod function with this exception; because the substrate is stored the rate of reaction is not proportional to the "free" substrate concentration, but rather proportional to the substrate concentration per unit organism mass. Utilisation of PHB (i = 5) increases the polyP organism mass (i = 2). If sufficient soluble P (i = 12) is available, a fraction of the PHB is oxidised to provide energy for growth and for taking up P (i = 12) and storing it as polyP (i = 6). P (i = 12) also is taken up for cell synthesis (j = 1 and 2). The P uptake is modelled as being proportional to the PHB utilisation, in accordance with the mechanistic model in **Part II**, the constants of proportionality being $f_{P,upt}$ for P uptake and for polyP storage, and $f_{ZBG,P}$ for cell synthesis. The oxidation of PHB (i = 5) causes a decrease in the oxygen concentration (i = 14).

Should soluble P become limiting, P uptake for polyP (i = 8) formation ceases, but growth continues with the P requirements for cell synthesis supplied from the polyP pool (j = 1 and 4). Growth under conditions where soluble P is limiting has different kinetic rate constants, ($\hat{\mu}_{G2}$ and K_{sG2}), than when P is not limiting. The change from one growth process to the other is achieved by the switching functions (P limit) and (1 – P limit).

Ammonia (i = 9) is used as a nitrogen source for synthesis (j = 1 and 3). Should ammonia become limiting, nitrate (i = 11) can serve as an alternative nitrogen source for synthesis (j = 2 and 4), as observed in **Part II.** This is accomplished by incorporating switching functions, (NH_3 limit) and (1 – NH_3 limit), dependent on the ammonia concentration. A further switching function (Air on) ensures that the growth processes (j = 1 to 4) only operate if oxygen is present.

(4) ***Endogenous mass loss (j = 5 to 11)*** In the mechanistic model set out in **Part II**, to account for endogenous mass loss, two situations were identified:

(i) When the predator action is significant, such as in mixed cultures, cell death produces lysed biodegradable material in excess of that required for maintenance and this excess is used for regeneration of active mass. In

this situation, for the purposes of modelling, the death-maintenance-regeneration is reduced to a death-regeneration approach, i.e. the maintenance energy requirement is "merged" with the energy for regeneration, because maintenance energy is a relatively small fraction of the energy requirement for regeneration.

(ii) When predator action is absent or insignificant, such as in pure cultures, cell death produces just sufficient lysed biodegradable material for satisfying the maintenance energy requirement, i.e. the rate of death is controlled by the maintenance energy requirement. Because the maintenance energy requirement is proportional to the active mass, the endogenous mass loss can be modelled without passing through a death-maintenance cycle. One may simply allocate a fraction of the endogenous mass loss (the biodegradable material) to the oxygen demand, to account for maintenance energy requirements, and allocate the balance (the unbiodegradable material) to some form(s) of inert material(s), the total being equal to the "maintenance death mass loss rate" for the organisms. Death now is the fractional reduction in the active mass. This is equivalent to the endogenous mass loss behaviour as conceived by McKinney and Ooten (1969).

Approach (ii) is adopted to deal with endogenous mass loss for the polyP organism enhanced cultures with the difference that not only is a particulate inert fraction generated (as in McKinney and Ooten, 1969) but also an apparently inert soluble fraction insofar as the polyP organisms are concerned. (In a mixed culture this apparently inert soluble material probably will serve as a substrate source for the non-polyP organisms).

The endogenous mass loss is modelled separately for the aerobic (j = 5 to 7) and anaerobic (j = 8 to 11) states. In the aerobic state the polyP organism mass (i = 2) decreases (j = 5) generating a particulate endogenous residue (i = 3) and a soluble "unbiodegradable" COD (i = 13), that is, unbiodegradable with respect to the polyP organisms. The balance is oxidised to provide energy for cell maintenance, decreasing the oxygen (i = 14). The rate of mass loss is first order with respect to the polyP organism mass (i = 2). The ammonia (i = 9) increases by the difference between the amount released from endogenous mass loss, and the amount associated with the two unbiodegradable fractions generated. The stored polyP (i = 6) content of the mass lost is released to the bulk liquid (j = 6), so also the stored PHB (j = 7) (see **Part II** as to the reasons for this).

In the anaerobic state the polyP organism mass (i = 2) also decreases (j = 8) generating particulate endogenous residue (i = 3) and soluble "unbiodegradable" COD (i = 13). However, as no electron acceptor (oxygen) is available, energy generation from oxidation of substrate no longer is possible and the balance of the mass loss is accumulated as soluble unbiodegradable COD (i = 13), that is, "unbiodegradable" with respect to the polyP organisms (see **Part II** for a detailed discussion). PolyP is cleaved (j = 11) to supply maintenance energy requirements — cleavage is modelled as being first order with respect to the polyP organism mass (i = 2). The ammonia (i = 9) increases by the difference between the amount released from endogenous mass loss, and the amount associated with the two unbiodegradable fractions generated. Furthermore, the stored polyP (i = 6) content of the mass lost is released to the bulk liquid as soluble P (j = 9), so also the stored PHB as acetate (j = 10).

(5) ***Nitrifier growth and decay (j = 14 to 15)*** This is modelled as in the general model (Dold *et al.*, 1980; Dold and Marais, 1986).

Transport terms

The matrix presentation of the processes, compounds and the rates defines the behaviour at a single point in the system. To obtain the behaviour or any system (e.g. single completely mixed or plug flow reactor, or series of such reactors) the transport terms (e.g. mass flows and compounds into, and out of, the reactors) must be included to obtain a solution, see IAWPRC Task Group Report (1987). This is accomplished by setting up mass balances in time and/or space for every compound in every reactor and then solving the resultant set of equations. Details of how to set up mass balances using the matrix and solution techniques to solve the equations are described in **Appendix I.**

Model calibration

Calibration of the model requires that the stoichiometric and kinetic constants be quantified. These constants are listed in Tables 2 and 3. Essentially there are three ways whereby these constants can be quantified: From a test in which the constant is isolated and directly measured; from a test in which the effect of the constant is completely dominant compared to the effects of other constants; and by "curve fitting", using a range of system and batch operating conditions — this approach can be applied only if most of the other constants have been evaluated. All three methods were used to evaluate the constants.

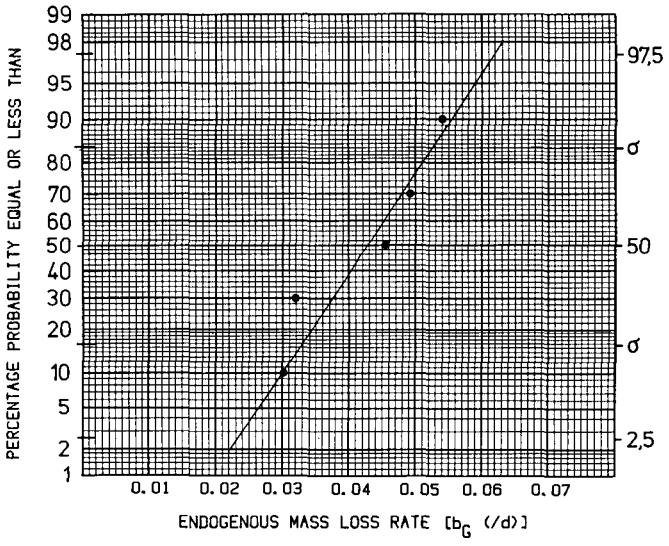

Figure 1
Statistical plot of endogenous mass loss rates (b_G) obtained from a number or aerobic digestion batch tests, such as in Part II, Fig. 3.

In discussing the methods used to determine the constants, it is necessary to refer repeatedly to experimental observations reported in **Part II**. (For simplicity, the following method will be used to refer to a specific data set: **Part II**, Fig. –).

(1) Direct determination

The following constant were quantified by direct determination:

(i) *Specific endogenous mass loss rate (b_G)* This constant was determined from the slope of the semilog plot, log (OUR) versus time, obtained from aerobic digestion batch tests, see **Part II**, Fig. 3. The b_G values from a number of such tests are shown plotted on normal probability paper in Fig. 1, giving a mean value for b_G of 0,04/d with a standard deviation of the mean of ± 0,004/d.

(ii) *COD/VSS ratio (f_{cv})* An aliquot of mixed liquor was

TABLE 2
DESCRIPTION AND VALUES OF STOICHIOMETRIC CONSTANTS IN THE MATRIX (Table 1).

Constant		Range of values	Units
Symbol	Description		
	A – PolyP organisms		
Y_G	Yield	0,639	mgCOD volatile mass/mgCOD
$f_{P,upt}$	Ratio P uptake/COD stored substrate utilised	0,9–1,1	mgP/mgCOD
$f_{ZBG,N}$	Nitrogen content of active mass	0,07	mgN/mgCOD active mass
$f_{ZEG,N}$	Nitrogen content of endogenous mass	0,07	mgN/mgCOD active mass
$f_{EsG,N}$	Nitrogen content of soluble unbiodegradable COD	0,07	mgN/mgCOD
$f_{ZBG,P}$	Phosphorus content of active mass (excluding polyP)	0,02	mgP/mgCOD active mass
$f_{ZEG,P}$	Phosphorus content of endogenous mass	0,02	mgP/mgCOD endogenous mass
$f_{Ep,G}$	Fraction of active mass that remains as particulate unbiodegradable residue	0,25	mgCOD endogenous mass/mgCOD active mass
$f_{Es,G}$	Fraction of active mass that remains as soluble unbiodegradable residue	0,20	mgCOD/mgCOD active mass
$f_{P,rel1}$	Ratio P release/acetate uptake for phase 1 sequestration	0,48–0,55	mgP/mgCOD
$f_{P,rel2}$	Ratio P release/acetate uptake for phase 2 sequestration	0,8–1,0	mgP/mgCOD
PSwitch	Changes acetate sequestration from phase 1 to phase 2, i.e. $f_{P,rel1}$ to $f_{P,rel2}$ and K_{p1} to K_{p2}	0,32	mgP/mgCOD active mass
f_{cv}	Ratio COD/VSS	1,42	mgCOD/mgVSS
	B – Autotrophs (nitrifiers)		
Y_A	Yield	0,15	mgCOD volatile mass/mgCOD
$f_{ZBA,N}$	Nitrogen content of active mass	0,068	mgN/mgCOD active mass
$f_{ZEA,N}$	Nitrogen content of endogenous mass	0,068	mgN/mgCOD endogenous mass
$f_{ZBA,P}$	Phosphorus content of active mass	0,02	mgP/mgCOD active mass
$f_{ZEA,P}$	Phosphorus content of endogenous mass	0,02	mgP/mgCOD endogenous mass
$f_{Ep,A}$	Fraction of active mass that remains as particulate unbiodegradable residue	0,08	mgCOD endogenous mass/ mgCOD active mass

TABLE 3
DESCRIPTION AND VALUES OF KINETIC CONSTANTS IN THE MATRIX (Table 1).

Constant		Range of values	Units
Symbol	Description		
	A – PolyP organisms		
$\hat{\mu}_{G1}$	Maximum specific growth rate with no soluble P limit	0,9 – 1,1	/d
$\hat{\mu}_{G2}$	Maximum specific growth rate with soluble P limit	0,42	/d
K_{sG1}	Growth rate half saturation coefficient with no soluble P limit	0,18	mgCOD/ℓ
K_{sG2}	Growth rate half saturation coefficient with soluble P limit	0,18	mgCOD/ℓ
b_G	Specific endogenous mass loss rate	0,03 – 0,04	/d
b_{pp}	Specific polyP cleavage rate for anaerobic "maintenance" energy generation	0,03	/d
K_c	Specific rate for conversion of "complex" readily biodegradable COD to short chain acids	0,04	mgCOD/mgCOD active mass.d
K_{p1}	Specific rate of acetate uptake for first phase sequestration	6,0	mgCOD/mgCOD active mass.d
K_{p2}	Specific rate of acetate uptake for second phase sequestration	2,6	mgCOD/mgCOD active mass.d
	B – Autotrophs (nitrifiers)		
$\hat{\mu}_A$	Maximum specific growth rate	± 0,35	/d
K_{NH}	Growth rate half saturation coefficient	1,0	mgN/ℓ
b_A	Specific decay rate	0,04	/d

drawn from the last aerobic reactor of the enhanced culture system. A sample was taken for VSS and TSS determinations. A further sample was diluted appropriately with distilled water and macerated in a high speed blender and the COD of the resultant macerated liquor measured. From the two results, f_{cv} was determined. A number of f_{cv} values were determined on the enhanced culture systems over a period of two months during steady state conditions. These are shown plotted on normal probability paper in Fig. 2, giving a mean value f_{cv} = 1,42 mgCOD/mgVSS with a standard deviation of the mean of ± 0,013. This mean value conforms to the theorethical value obtained for the empirical stoichiometric formulation for biological sludge of $C_5H_7O_2N$ (WRC, 1984).

(iii) ***Fractional nitrogen content of active*** ($f_{ZBG,N}$) ***and endogenous*** ($f_{ZEG,N}$) ***masses*** The fractional nitrogen content of active ($f_{ZBG,N}$) and endogenous ($f_{ZEG,N}$) masses are given by the TKN/COD ratio provided it is assumed that the ratio is the same for the active and endogenous masses. Furthermore, the COD/VSS ratio can be assumed to be constant and equal 1,42 mgCOD/mgVSS, as shown above. Hence, the TKN/COD ratio can be determined from TKN and VSS measurements on the mixed liquor, the latter measurement being more simple than direct measurement of COD. The TKN/VSS values from a number of such tests are shown plotted on probability paper in Fig. 3, giving a mean value of 0,102 mgN/mgVSS with a standard deviation of the mean of 0,0013. The TKN/COD ratio then is equal to (TKN/VSS)/1,42 i.e. 0,072 mgN/mgCOD. The TKN/COD ratio of the soluble unbiodegradable endogenous residue ($f_{EsG,N}$) is assumed to be equal to this value.

(iv) ***Fractional phosphorus content of active*** ($f_{ZBG,P}$) **and endogenous** ($f_{ZEG,P}$) **masses** This phosphorus content excludes the polyP. Values for these constants were obtained from the literature due to the difficulty in separating the polyP from the normal cell phosphorus content. Values in the literature range from 0,01 to 0,03 mgP/mgVSS (Mino *et al.*, 1984; WRC, 1984). The value 0,02 mgP/mgVSS is accepted.

(2) Dominant behaviour

Constants obtained from dominant behaviour were the following:

(i) ***Ratio P release/Acetate uptake*** ($f_{P,rel}$) This ratio was obtained from the anaerobic batch tests with acetate addition, see **Part II**, Figs. 7 and 8, for both the first (f_{P,rel_1}) and the second (f_{P,rel_2}) phases of sequestration; it is assumed that the rate of acetate sequestration in these tests is so rapid that endogenous effects can be taken as negligible. The ratios are obtained by plotting acetate concentration versus P concentration, the slope of the line defining $f_{P,rel}$. Values from a number of such plots are shown plotted on probability paper, Figs. 4 and 5, for f_{P,rel_1} and f_{P,rel_2} respectively, giving mean values of f_{P,rel_1} = 1,09 mmol P/mmol acetate and f_{P,rel_2} = 1,81 mmolP/mmol acetate with standard deviations of the means as ± 0,038 and ± 0,072 respectively. This implies that in the second phase more P must be released to sequester one unit of acetate than in the first phase. Converting units, f_{P,rel_1} = 0,52 mgP/mgCOD (HAc) and f_{P,rel_2} = 0,88 mgP/ mgCOD (HAc).

(ii) ***Specific rate of acetate sequestration*** (K_p) This constant was obtained by linear regression analysis of the acetate decrease during the same anaerobic batch tests with acetate addition as in (2)(i) above. Again it is assumed that the rate of acetate sequestration is so rapid that offer effects can be neglected. Specific rate constants, i.e. rate per unit VSS, from a number of such tests are shown plotted on probability paper in Figs. 6 and 7 for phase one (K_{p1}) and phase two

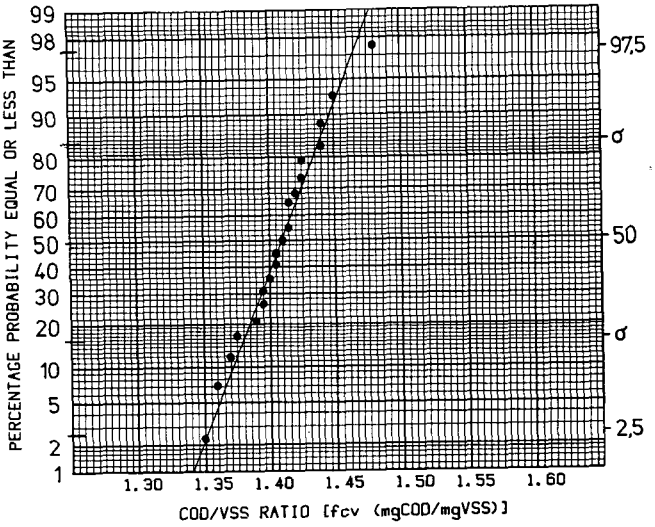

Figure 2
Statistical plot of COD/VSS ratios (f_{cv}) measured for mixed liquor from the polyP organism enhanced culture systems.

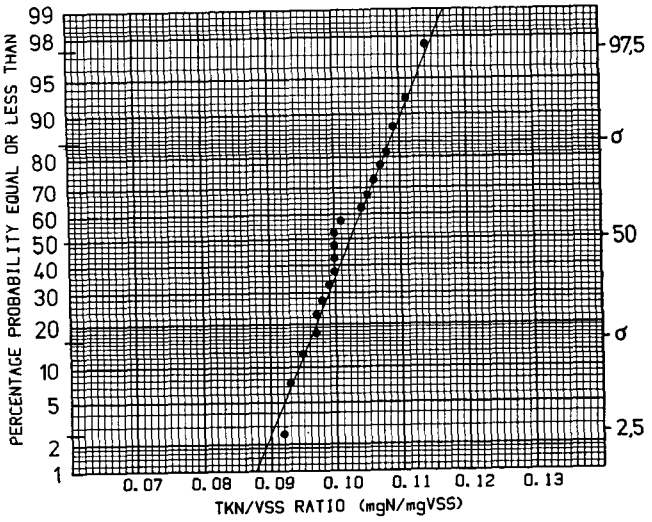

Figure 3
Statistical plot of TKN/VSS ratios measured for mixed liquor from the polyP organism enhanced culture systems.

(K_{p2}) sequestration respectively, giving means of K_{p1} = 6,7 mgHAc/mgVSS.d and K_{p2} = 2,91 mgHAc/mgVSS.d and standard deviations of the mean of ± 0,29 and ± 0,02 respectively. Recalculating, to take into account endogenous mass and to convert to COD units, K_{p1} = 6,07 mgCOD(HAc)/mgCOD active mass.d and K_{p2} = 2,67 mgCOD(HAc)/mgCOD active mass.d.

(iii) ***Change from first to second phase sequestration (PSwitch)*** The change from first to second phase sequestration was modelled to take place when the stored polyP/(polyP organism active mass) declined below the value, PSwitch. The value for PSwitch was obtained from the anaerobic batch tests described above by subtracting the mass of P released during first phase sequestration from the initial polyP concentration and dividing by the active mass of organisms. This gives a value PSwitch = 0,31 mgP/mgCOD active mass. The constant (PSwitch) comes into operation only in situations of high acetate loading, e.g. in batch tests. As described in **Part II**, the acetate loading rates

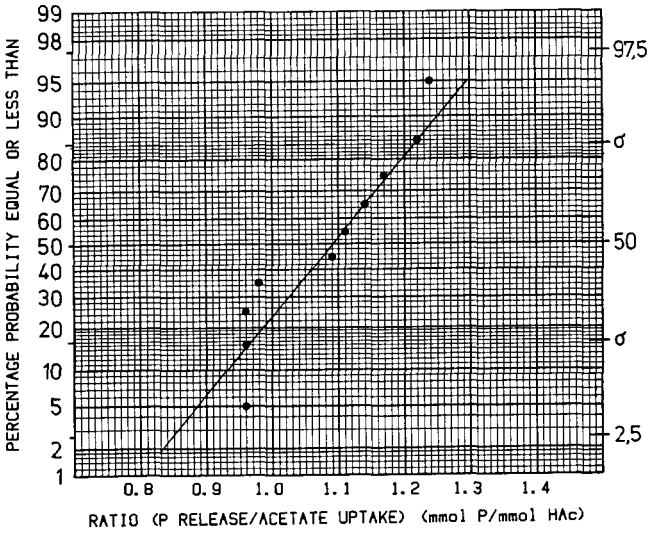

Figure 4
Statistical plot of first phase stoichiometric ratio between anaerobic P release and acetate uptake ($f_{P,rel1}$).

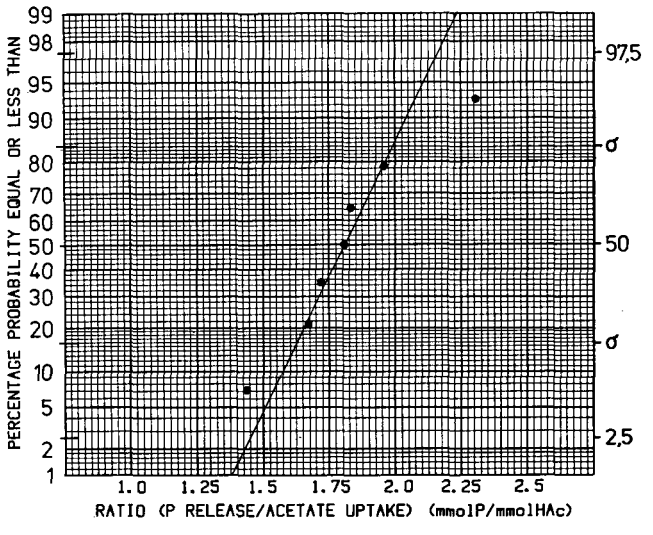

Figure 5
Statistical plot of second phase stoichiometric ratio between anaerobic P release and acetate uptake ($f_{P,rel2}$).

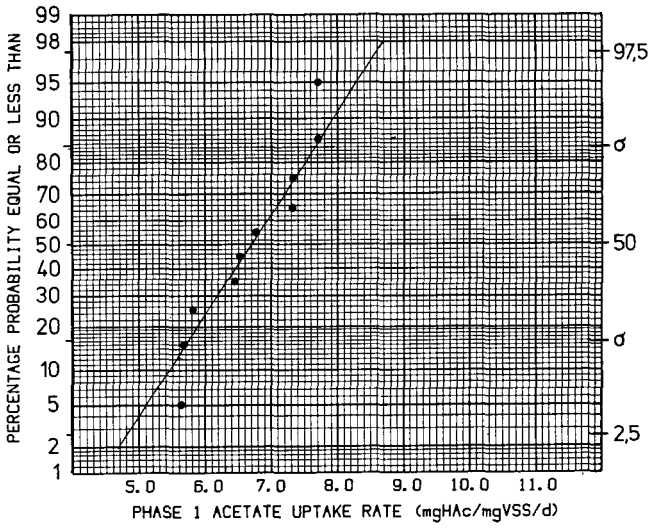

Figure 6
Statistical plot of first phase rates of acetate uptake (K_{p1}) in anaerobic batch tests such as in Part II, Fig. 7.

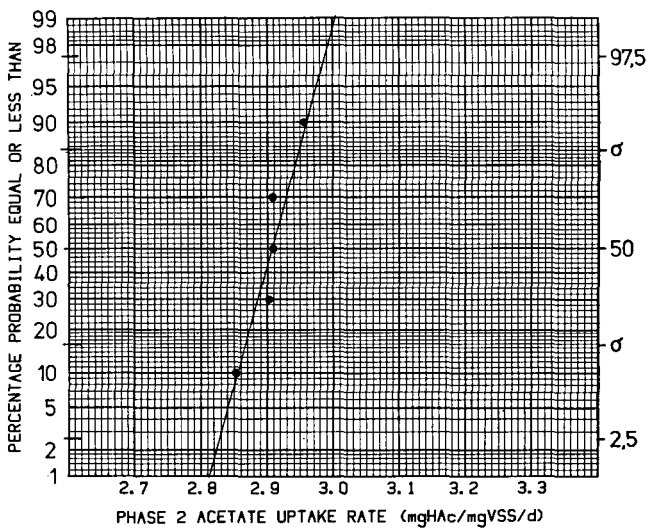

Figure 7
Statistical plot of second phase rates of acetate uptake (K_{p2}) in anaerobic batch tests such as in Part II, Fig. 8.

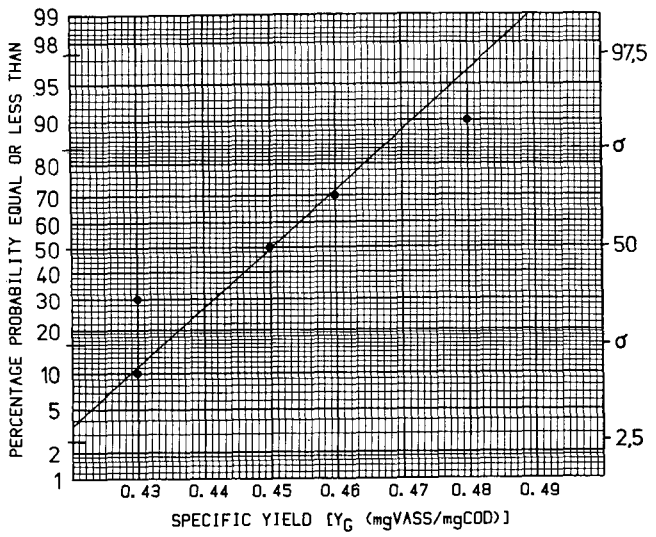

Figure 8
Statistical plot of yield (Y_G) values obtained from COD mass balances on aerobic batch tests following anaerobic acetate addition, such as in Part II, Fig. 12.

encountered in anaerobic reactors of enhanced culture systems probably will be insufficient to stimulate second phase P release.

(iv) ***Yield*** (Y_G) In **Part II** the difficulties associated with determining the actual specific yield were briefly described. However, where the substrate is completely biodegradable and soluble, a direct technique for determining the actual specific yield (Y_G) is possible by utilising the data obtained from the batch tests in which the batch is aerated following anaerobic acetate addition (**Part II**, Figs. 12 and 13). From the matrix (Table 1) it is evident that a COD mass balance must be obtained in the growth process. By monitoring the OUR, the mass of oxygen consumed for COD oxidation following anaerobic addition of a known mass of acetate can be calculated by integrating the OUR-time plot and subtracting the oxygen demand for nitrification and endogenous mass loss. The value for Y_G is determined to be the value that gives equality between the mass of COD added and the mass of COD recovered. Using this technique Y_G values were obtained from a number of such tests, shown plotted on probability paper in Fig. 8, giving a mean Y_G = 0,639 mgCOD active mass/mgCOD consumed and standard deviation of the mean of ± 0,0128. Dividing by the f_{cv}, measured earlier, gives Y_G = 0,45 mgVSS/mgCOD. This conforms to the values determined for general activated sludge by Dold *et al.* (1980).

(3) Curve fitting

The following constants were obtained by curve fitting:

(i) ***Maximum specific growth rate*** ($\hat{\mu}_G$) ***and half saturation coefficient*** (K_{sG}) The maximum specific growth rate ($\hat{\mu}_G$) and half saturation coefficient (K_{sG}) for PHB utilisation with no soluble P limitation ($\hat{\mu}_{G_1}$ and K_{sG_1} respectively) are obtained by fitting the predicted carbonaceous OUR to the carbonaceous OUR observed in the aerobic batch tests following anaerobic acetate addition, see Part II, Figs. 12 and 13; or Figs. 13 and 14 in this paper. The values for $\hat{\mu}_{G_1}$ and K_{sG_1} determine the shape of the OUR curve; only one pair of data values provide predictions that fit the observed curve. Furthermore, the effect of $\hat{\mu}_G$ and K_{sG} dominate completely in these tests so that selection of values for the constants is not influenced by other constant values. The range of values obtained for a number of such tests is listed in Table 3.

The maximum specific growth rate and half saturation coefficient for PHB utilisation with a soluble P limitation ($\hat{\mu}_{G_2}$ and K_{sG_2} respectively) were obtained in a similar manner from an aerobic batch test (after anaerobic acetate addition) in which the soluble P reduced to zero, see Fig. 14 in Part II and Fig. 15 in this paper.

(ii) ***Ratio P uptake/stored COD utilisation*** ($f_{P,upt}$) This ratio was obtained from the P concentration changes observed in the aerobic batch tests described for (3)(i) above. It is assumed that the P concentration changes dominate over the changes due to endogenous respiration, so that the effect due to $f_{P,upt}$ is not influenced by predetermination of other constants. The range of $f_{P,upt}$ values obtained in this manner is listed in Table 2.

(iii) ***Specific polyP cleavage for anaerobic "maintenance" energy generation*** (b_{pp}) This rate was determined by trial curve fitting to the increase in the P in the anaerobic batch tests after the acetate concentration becomes zero, see **Part II**, Figs. 7 and 8, Figs. 10 and 11 in this paper. This requires that the endogenous mass loss rate (b_G) already is determined. Ranges of values obtained for b_{pp} are listed in Table 3.

(iv) ***Endogenous residue fractions*** ($f_{Ep,G}$ **and** $f_{Es,G}$) Both the particulate ($f_{Ep,G}$) and the soluble ($f_{Es,G}$) endogenous residue fractions were determined from the aerobic digestion batch tests, see **Part II**, Figs. 2 and 6. The magnitude of the soluble unbiodegradable COD fraction ($f_{Es,G}$) is determined by fitting the predicted data to the soluble COD time curve observed in the batch test, see Fig. 9(c). The particulate endogenous residue fraction ($f_{Ep,G}$) is determined by fitting the predicted OUR to that observed in the batch tests, see Fig. 9(a). By knowing b_G and $f_{Es,G}$ only one value of $f_{Ep,G}$ will provide conformity between predicted and observed OUR. Values obtained for $f_{Ep,G}$ and $f_{Es,G}$ are listed in Table 2.

(v) *Switching functions* The switching functions utilised in the model are set out in Table 4. Values for constants were determined by "curve fitting"; very small values are selected to meet the requirement that the function reduces to zero only at very low concentrations, see **Appendix I.**

With regard to the nitrifiers, the yield coefficient (Y_A), fractional N contents of the endogenous residue ($f_{ZEA,N}$) and the active mass ($f_{ZBA,N}$), the half saturation coefficient for growth (K_{NH}) and the specific endogenous mass loss rate (b_A) were taken from typical values accepted in the IAWPRC model (Dold and Marais, 1986). The nitrifier maximum specific growth rate ($\hat{\mu}_A$) was determined by "curve fitting", to the nitrification curve in aerobic batch tests after anaerobic acetate addition.

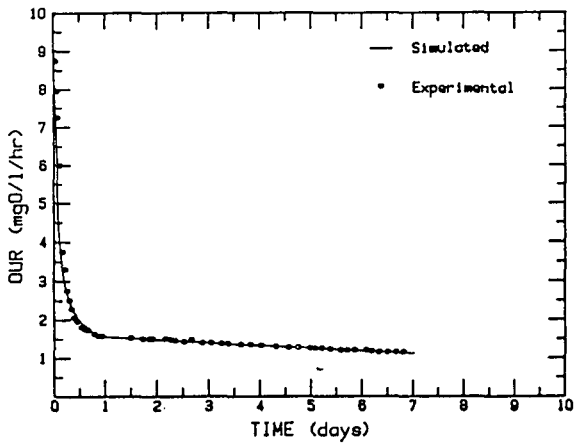

Figure 9(a)
Experimentally observed and simulated oxygen utilisation rate (OUR) response with time in a batch aerobic digestion of mixed liquor from the enhanced culture system (VSS = 1 096 mgVSS/ℓ).

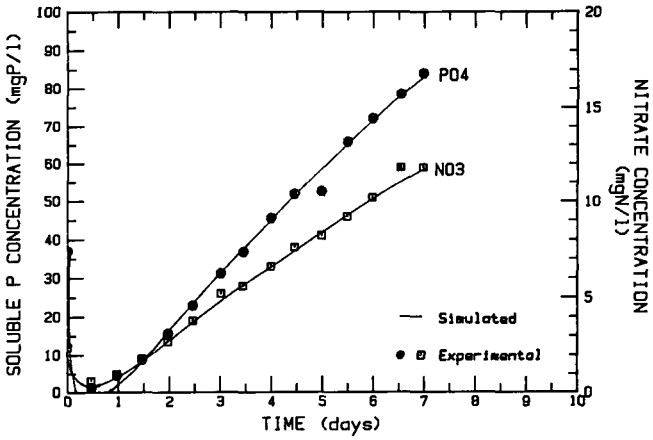

Figure 9(b)
Experimentally observed and simulated total soluble phosphorus (PO_4) and nitrate (NO_3) concentration-time profiles for the batch aerobic digestion in Fig. 9(a).

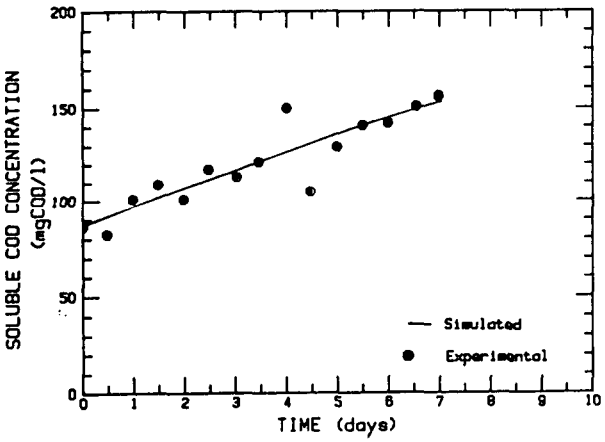

Figure 9(c)
Experimentally observed and simulated filtered COD concentration-time profiles for the batch aerobic digestion in Fig. 9(a).

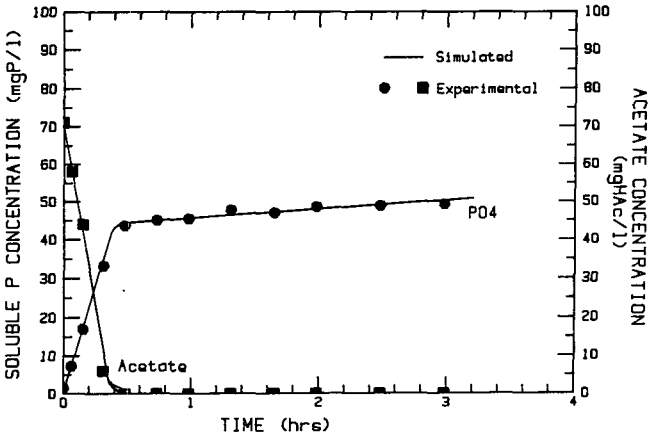

Figure 10
Experimentally observed and simulated total soluble phosphate (PO_4) and acetate concentration-time profiles with anaerobic addition of 0,11 mgCOD acetate/mgVSS to a mixed liquor batch drawn from the Bardenpho enhanced culture system (VSS = 684 mgVSS/ℓ).

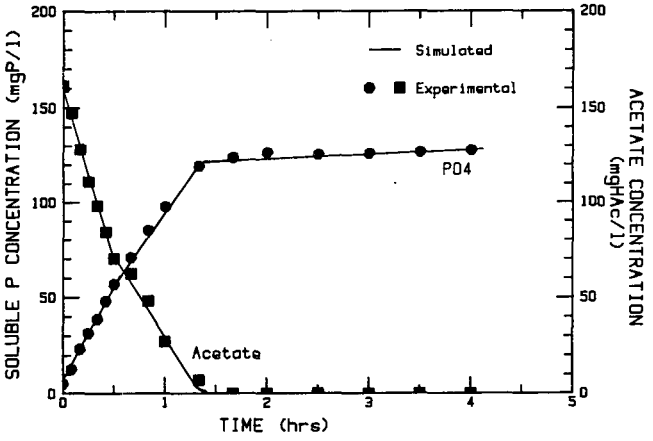

Figure 11
Experimentally observed and simulated total soluble phosphate (PO_4) and acetate concentration-time profiles with anaerobic addition of 0,265 mgCOD acetate/mgVSS to a mixed liquor batch drawn from the Bardenpho enhanced culture system (VSS = 651 mgVSS/ℓ).

TABLE 4
SWITCHING FUNCTIONS USED IN THE MATRIX (Table 1)

Abbreviation	Formulation	Value of half saturation coefficient (K)
Air on	$\frac{O}{K_{OH} + O}$	K_{OH} = 0,002 (mgO/ℓ)
Air off	$\frac{K_{OH}}{K_{OH} + O}$	
NH_3 limit	$\frac{N_{h3}}{K_{NA} + N_{h3}}$	K_{NA} = 0,05 (mgN/ℓ)
NO_3 limit	$\frac{N_{O3}}{K_{NO} + N_{O3}}$	K_{NO} = 1,0 (mgN/ℓ)
P limit	$\frac{P}{K_{LP} + P}$	K_{LP} = 0,1 (mgP/ℓ)
PolyP limit	$\frac{P_{polyP}}{K_{xp} + P_{polyP}}$	K_{XP} = 1,0 (mgP/ℓ)
Ac limit	$\frac{S_{bs,a}}{K_{SSEQ} + S_{bs,a}}$	K_{SSEQ} = 1,0 (mgCOD/ℓ)

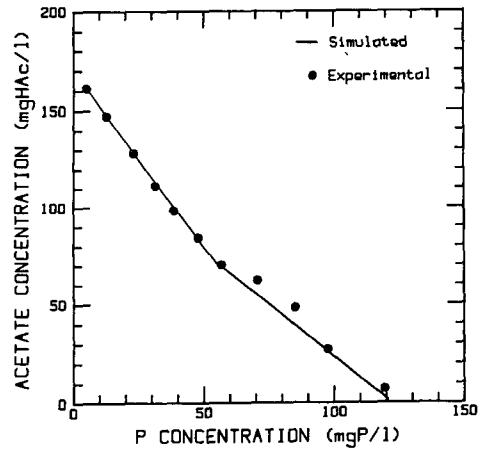

Figure 12
Plot of experimentally observed and simulated acetate concentration versus total soluble phosphate concentration for the time paired data in Fig. 11.

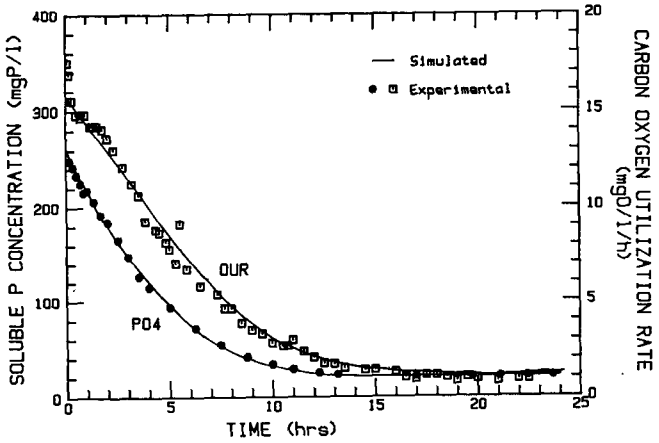

Figure 13
Experimentally observed and simulated total soluble phosphate concentrations (PO_4) and carbonaceous oxygen utilisation rate (OUR) on aeration following anaerobic acetate addition of 0,207 mgCOD acetate/mgVSS to mixed liquor batch drawn from the Bardenpho enhanced culture system (VSS = 1 041 mgVSS/ℓ).

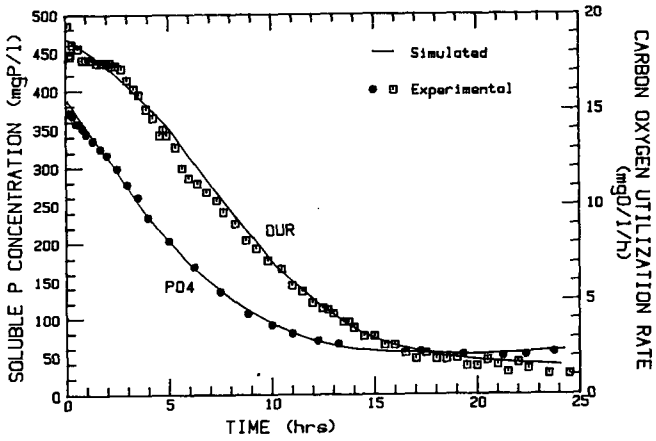

Figure 14
Experimentally observed and simulated total soluble phosphate concentrations (PO_4) and carbonaceous oxygen utilisation rate (OUR) on aeration following anaerobic acetate addition of 0,363 mgCOD acetate/mgVSS to mixed liquor batch drawn from the Bardenpho enhanced culture system (VSS = 1 199 mgVSS/ℓ).

Model verification

The acceptability of the model is promoted if, on applying it to a range of situations, one finds consistency between observation and prediction. In this respect one can distinguish two types of verification, against batch and steady state system response.

Batch verification

In Figs. 9 to 15, the predicted behaviour of various compounds is compared with those observed in the different batch tests described in **Part II**. (It should be noted that these plots are examples selected to represent the various types of batch tests; a number of each type of batch test were conducted, all of which show similar results). Note that the data in Fig. 18 (showing the direct utilisation of acetate for growth under aerobic conditions simultaneous with acetate uptake, PHB storage and utilisation, and P release and uptake) is not modelled for reasons set out in **Part II**.

Even though the same set of tests has been used for evaluating some of the constants, the closeness with which the predictions conform to the observations over the wide range of conditions in the batch tests constitutes evidence for the acceptability of the model.

Steady state system verification

In simulating the steady state systems responses it should noted that:

(1) The model does not incorporate denitrification; accordingly it cannot simulate the denitrification observed experimentally. A method for taking the denitrification effects into account can be developed from the following experimental observations:

- Denitrification was minimal in the anoxic zones of the systems where the acetate concentration was zero, and the stored PHB at a maximum. This would indicate that PHB is not utilised for denitrification. (This also was observed in the batch experiments, see **Part II**).

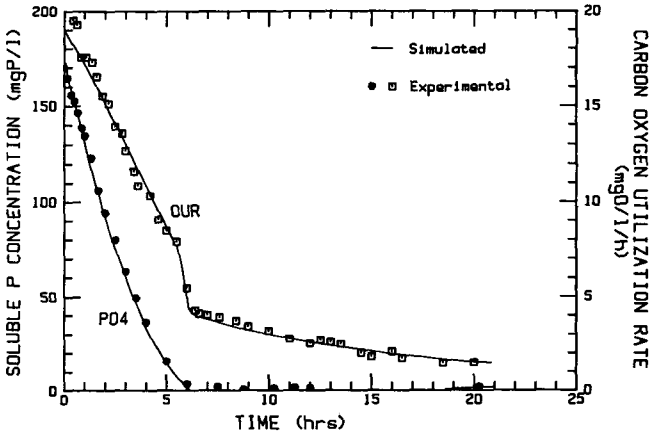

Figure 15
Experimentally observed and simulated total soluble phosphate concentrations (PO_4) and carbonaceous oxygen utilisation rate (OUR) on aeration following anaerobic acetate addition of 0,22 mgCOD acetate/mgVSS to mixed liquor batch drawn from the Bardenpho enhanced culture system. The PO_4 concentration falls to zero during the course of this test (VSS = 1 226 mgVSS/ℓ).

- Denitrification took place almost totally in the anaerobic reactor, in the first anaerobic reactor for two anaerobic reactors in series. This would indicate that denitrification takes place virtually only while "free" acetate is present.

These two observations imply that the major fraction of the denitrification in the system is mediated by the non-polyP organisms in the anaerobic reactor with acetate as electron donor. The mass of these organisms produced by the denitrification action would be relatively small, as indicated by the high specificity of the organism population (see **Part II**) and the relatively small fraction of the total influent COD implicated in denitrification. One can accept, therefore, that the non-polyP organism mass effect on the total volatile mass is minor and can be neglected, which is equivalent to assuming that the COD in the influent available to the polyP organisms is reduced by the COD lost in denitrification. This assumption will give rise to a slightly high prediction of the specific yield constant for the polyP organisms. In a large measure this problem will resolve itself when the polyP organism model is incorporated into the general model.

(2) The yeast extract added to the influent is a complex organic material, and appears to be unbiodegradable with respect to the polyP organism mass, in which event it will pass unaltered to the effluent. This conclusion arises from the simulation studies on the systems, in which it was noted that with higher yeast extract addition the effluent COD also appears to be raised relative to the influent COD. If the COD of the yeast extract is added to the influent substrate as unbiodegradable soluble COD, then the system effluent COD is closely predicted by the sum of the concentration of unbiodegradable soluble COD generated by endogenous mass loss (using the constants derived from the batch tests) and the COD of the yeast extract.

Taking the above two factors into account, the influent concentration *available* for polyP organism metabolism is given by:

$$\begin{aligned}\text{COD (available)} = {} & \text{COD (measured in influent)} \\ & - \text{COD (associated with denitrification)} \\ & - \text{COD (yeast extract)}.\end{aligned}$$

In the simulation, the "predicted" influent COD is given by:

$$\begin{aligned}\text{COD ("predicted" influent)} = {} & \text{COD (measured in influent)} \\ & - \text{COD (denitrification)}.\end{aligned}$$

The COD (yeast extract) is retained in the "predicted" influent value because the model makes provision for this COD fraction and passes it through the system as unbiodegradable soluble material.

Using the method above for determining the influent COD, in simulating the systems responses it was found that all the constant values derived from the batch tests could be kept the same, except for two – the maximum specific growth rate, $\hat{\mu}_{G_1}$ (increased from 1 to 1,2/d) and the ratio P uptake per mgCOD (as PHB) utilised, $f_{P,upt}$ (reduced from 1,0 to 0,75 mgP/mgCOD). Although it is not possible to give a determinative explanation for these changes, the following may be of significance:

In the batch tests, in which responses under aerobic conditions following anaerobic acetate addition were used to determine values for $\hat{\mu}_{G_1}$ and $f_{P,upt}$ (see **Part II**, Figs. 12 and 13) the mixed liquor first was aerated for 24 h before commencing the anaerobic acetate addition. The initial 24 h aeration period may have affected the estimation of both $\hat{\mu}_{G_1}$ and $f_{P,upt}$. The long aeration period was applied because in the aerobic digestion tests (see **Part II**, Fig. 2) it was observed (and correctly simulated) that endogenous mass loss did not become dominant until after about 18 hours. It is possible that, by inducing a completely endogenous condition in the batch test for determining $\hat{\mu}_{G_1}$ and $f_{P,upt}$, the organism's response thereafter with substrate addition, may deviate, for a period, from the "normal".

Taking due account of the remarks above, the responses of the following enhanced culture systems were simulated; modified Bardenpho systems at sludge ages of 20, 10 and 7,5 d (see **Part II**, Figs. 1(a) and 1(c) for systems set-ups and **Part II**, Tables 2 and 3 for systems responses); UCT system at a sludge age of 10 d (see **Part II**, Fig. 1(b) for system set-up and **Part II**, Table 2 for system response). In Tables 5 to 8 the observed and predicted responses for the respective systems are listed. Comparing the observed and predicted responses it is evident that:

- Over the range of sludge ages, from 7,5 to 20 d, using *one* set of constants the model appears to predict the behaviour closely.
- Except for one reactor, no discernable inconsistency is apparent, nor any deviatory tendency with sludge age. The exception is the underflow aeration reactor in the 20 d sludge age modified Bardenpho system (Table 5) where there is an observed P concentration of 22 mgP/ℓ as against the simulated 0,2 mgP/ℓ.

TABLE 5
MEASURED AND PREDICTED RESPONSES FOR 20 DAY SLUDGE AGE MODIFIED BARDENPHO ENHANCED CULTURE SYSTEM

		Value	
Parameter	**Sample point**	**Measured**	**Predicted**
COD (mgCOD/ℓ)	Influent	544,0	462,3*
	Effluent	62,0	62,6
TKN (mgN/ℓ)	Influent	35,2	35,2
	Effluent	2,5	1,8
VSS (mgVSS/ℓ)	Reactor 5	2998	3075
Carbonaceous OUR (mgO/ℓ.h)	Reactor 3	19,9	20,0
	Reactor 4	15,3	14,8
	Reactor 5	10,3	8,2
	Underflow aeration	14,5	12,7
P(mgP/ℓ)	Influent	53,6	53,6
	Anaerobic 1	145,8	147,8
	Anoxic 2	76,8	80,1
	Aerobic 3	49,1	58,7
	Aerobic 4	23,4	31,6
	Aerobic 5	5,6	6,2
	Underflow aeration	22,2	0,2
P removal (mgP/ℓ)		49,7	47,6

* "Predicted" influent COD = (COD measured – COD denitrified).
"Predicted" influent COD includes unbiodegradable soluble COD due to the yeast extract, equal to 25 mgCOD/ℓ.

When account is taken of the complexity of the biological excess P removal phenomenon, the behaviour predicted by the model conforms surprisingly well to the behaviour observed in the experimental batch and steady state system studies. The closeness with which the predictions conform to the observations over the wide range of conditions constitutes evidence for the acceptability of the model.

TABLE 6
MEASURED AND PREDICTED RESPONSES FOR 10 DAY SLUDGE AGE MODIFIED BARDENPHO ENHANCED CULTURE SYSTEM

Parameter	Sample point	Value	
		Measured	Predicted
COD (mgCOD/ℓ)	Influent	417	350*
	Effluent	62,0	62,5
TKN (mgN/ℓ)	Influent	26,9	26,9
	Effluent	2,5	1,9
VSS (mgVSS/ℓ)	Reactor 5	1167	1276
Carbonaceous OUR (mgO/ℓ.h)	Reactor 4	16,6	15,5
	Reactor 5	9,4	9,6
P(mgP/ℓ)	Influent	43,8	43,8
	Anaerobic 1	115,0	120,0
	Anaerobic 2	134,0	124,4
	Anoxic 3	72,9	82,3
	Aerobic 4	38,5	49,1
	Aerobic 5	7,6	4,1
	Effluent	5,2	4,1
P removal (mgP/ℓ)		38,6	39,7

* "Predicted" influent COD = (COD measured – COD denitrified).
"Predicted" influent COD includes unbiodegradable soluble COD due to the yeast extract, equal to 35 mgCOD/ℓ.

TABLE 7
MEASURED AND PREDICTED RESPONSES FOR 7,5 DAY SLUDGE AGE MODIFIED BARDENPHO ENHANCED CULTURE SYSTEM

Parameter	Sample point	Value	
		Measured	Predicted
COD (mgCOD/ℓ)	Influent	410	350*
	Effluent	53,0	56,3
TKN (mgN/ℓ)	Influent	26,3	26,3
	Effluent	2,5	3,8
VSS (mgVSS/ℓ)	Reactor 5	1036	996
Carbonaceous OUR (mgO/ℓ.h)	Reactor 4	15,2	14,7
	Reactor 5	7,8	9,6
P(mgP/ℓ)	Influent	46,0	46,0
	Anaerobic 1	102,12	119,0
	Anaerobic 2	132,14	122,6
	Anoxic 3	72,6	80,8
	Aerobic 4	38,16	49,5
	Aerobic 5	8,2	2,0
	Effluent	3,4	2,0
P removal (mgP/ℓ)		42,64	44,0

* "Predicted" influent COD = (COD measured – COD denitrified).
"Predicted" influent COD includes unbiodegradable soluble COD due to the yeast extract, equal to 35 mgCOD/ℓ.

TABLE 8
MEASURED AND PREDICTED RESPONSES FOR 10 DAY SLUDGE AGE UCT ENHANCED CULTURE SYSTEM

Parameter	Sample point	Value	
		Measured	Predicted
COD (mgCOD/ℓ)	Influent	543	450*
	Effluent	65	48,5
TKN (mgN/ℓ)	Influent	36,0	36,0
	Effluent	2,5	1,3
VSS (mgVSS/ℓ)	Reactor 5	2397	2260
Carbonaceous OUR (mgO/ℓ.h)	Reactor 3	15,4	20,7
	Reactor 4	14,1	15,9
	Reactor 5	10,9	8,9
P(mgP/ℓ)	Influent	63,7	63,7
	Anaerobic 1	157,5	157,2
	Anoxic 2	86,3	90,0
	Aerobic 3	48,2	60,5
	Aerobic 4	12,7	28,7
	Aerobic 5	4,8	1,5
	Effluent	2,9	1,5
P removal (mgP/ℓ)		60,94	62,2

* "Predicted" influent COD = (COD measured – COD denitrified).
"Predicted" influent COD includes unbiodegradable soluble COD due to the yeast extract, equal to 25 mgCOD/ℓ.

Conclusions

The mathematical model presented in this paper deals specifically with enhanced cultures of polyP organisms receiving acetate only as a substrate. However, the process for conversion of readily biodegradable substrate to 'acetate-like' substrates is included in anticipation of the model being developed further to be applied to situations where sewage serves as substrate. The mathematical model deals only with the anaerobic and aerobic states; anoxic states are not dealt with because the experimental enhanced cultures developed only induce minimal growth of polyP organisms that utilise nitrate as electron acceptor. However, this aspect requires further investigation, because in systems receiving municipal sewages, on occasion denitrification and P uptake have been observed at laboratory and full-scale.

Despite the restrictions discussed above, the model constitutes a major step towards incorporating biological excess P removal in the general activated sludge model. This incorporation may yet turn out to be less difficult than our subjective assessment has led us to presume, for the following reasons: From the experimental investigation it would appear that the polyP and the non-polyP populations act relatively independently. Independence of action arises principally from the apparent non-predation of polyP organisms, whereas non-polyP ones suffer heavy predation. The principal sources of interaction appear to be in the anaerobic phase where the short chain fatty acids generated by the non-polyP organisms are sequestered by the polyP organisms, and in the endogenous mass loss of the polyP organisms where soluble endogenous COD generated can be utilised by the non-polyP organisms. Competition between the population groups for the same substrate does not influence the structure of the joint model, because this will be governed by kinetics not by interaction, although it influences the solution.

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Appendix I

To fully understand the mathematical model it is useful to gain an insight into the representation and workings of the matrix as described below.

Representation

The matrix is represented by a number of columns and rows; one column for each compound and one row for each process. The symbols for the compounds are listed at the head of the appropriate column and the compounds are defined at the bottom of the corresponding column. The index "i" is assigned to identify a compound in the totality of compounds; in this case "i" can take values between 1 and 14, there being 14 compounds.

The processes are itemised one below the other down the left-hand side of the matrix. The index "j" is assigned to identify the process; it can take on values from 1 to 15, there being 15 processes. The process rates are formulated mathematically and listed down the right-hand side of the matrix, in line with the respective process row. These process rates are given the symbol "ρ_j", where j identifies the process.

Along each process row the stoichiometric coefficient for conversion from one compound to another is inserted so that each column lists the processes that influence that compound. The stoichiometric coefficients are given the symbol "ν_{ij}" where i denotes the index of the compound and j the index of the process. The stoichiometric coefficients ν_{ij} are greatly simplified by working in consistent units; in this case concentrations are expressed in COD, phosphorus (P) or nitrogen (N) units. Sign convention in the matrix for the stoichiometric coefficients is "negative for consumption" and "positive for production".

This matrix forms a succinct summary of the complex interactions between compounds and processes. The matrix in effect constitutes a fingerprint uniquely characterising the phenomenon. It allows alterations in processes, compounds, stoichiometry and kinetics to be readily incorporated.

The matrix representation method has two main benefits:

- It allows the effect of a particular process on the compounds to be easily determined, as follows: The reader moves along a particular row, i.e. process, and multiplies the stoichiometric coefficient (ν_{ij}) by the process rate (ρ_j). This gives the reaction rate (r_{ij}) for the particular compound being affected by the single process, i.e.

$$r = \nu_{ij}\rho_j.$$

  In representing the matrix, by adding up the reaction rates for a particular process, a mass balance must be obtained.
- It allows rapid and easy recognition of the fate of each compound, as follows: The reader moves down the column representing the compound of interest, and multiplies the stoichiometric coefficient (ν_{ij}) by the process rate (ρ_j). The summation of these multiplications gives the overall reaction rate (r_i) for the compound, i.e.

$$r_i = \sum_j \nu_{ij}\rho_j$$

Switching function

Under certain conditions the process rate equations are not operative, e.g. aerobic processes are not operative under anaerobic conditions. Mathematically, switching the process rate "on" and "off" can be achieved by multiplying the appropriate rate by a "switching" factor, which is zero when the process rate is inoperative, or unity when the process rate is operative. The general expression used for the switching function is:

$$\frac{C}{K + C}$$

where C = concentration of compound effecting the switch
K = constant.

This is a Monod-type expression. By selecting very small values for K, the function is close to unity when C is present. The function decreases to zero only at very low concentrations of C. A Monod-type expression is utilised as it provides continuity between the "off" and the "on" situation which helps to eliminate problems of numerical instability in computer calculations. Sometimes numerous switching functions are required, for example, anaerobic processes must be inoperative when oxygen or when nitrate is present.

Matrix solution

Solution of the matrix can be fixed in time (e.g. batch test), space (e.g. steady state multiple reactor system), or time and space (e.g. multiple reactor system with time varying flow).

(i) *Solution in time:*

This solution requires that the initial concentration be known whereafter changes in concentration are determined by integrating forward in time. Integration forward follows the basic Euler equation or equivalent:

$$C(t + \Delta t) = C(t) + (\frac{dC}{dt})_t \Delta t$$

where C = compound concentration
t = time
Δt = step size in integration

$(\frac{dC}{dt})_t$ = reaction rate

The reaction rate is obtained from the summation down the particular compound's column of the multiplication terms $\nu_{ij}\rho_j$, as described previously.

(ii) *Solution in space:*

Solution of the matrix in space requires that the transport terms be included. Inclusion of the transport terms and the rate equations is facilitated by use of the mass balance equation:

$$\left[\begin{array}{c}\text{Mass rate}\\ \text{of}\\ \text{accumulation}\end{array}\right] = \left[\begin{array}{c}\text{Mass rate}\\ \text{of}\\ \text{input}\end{array}\right] - \left[\begin{array}{c}\text{Mass rate}\\ \text{of}\\ \text{output}\end{array}\right] + \left[\begin{array}{c}\text{Mass rate of}\\ \text{production}\\ \text{by reaction}\end{array}\right]$$

The mass of input and output are the transport terms and depend on the physical characteristics of the system being modelled. The mass of production for a particular compound is obtained from the matrix. Taking an example, in symbols, for completely mixed reactor:

$$\frac{V dC_{out}}{dt} = Q_{in}C_{in} - Q_{out}C_{out} - r_i V$$

where V = Volume
Q_{in} = Flow rate in
Q_{out} = Flow rate out
C_{in} = Concentration of compound in influent flow
C_{out} = Concentration of compound in outflow (i.e. reactor concentration for completely mixed reactor)

$\frac{dC_{out}}{dt}$ = rate of change of reactor concentration of compound C

$r_i = \sum_j \nu_{ij}\rho_j$, obtain from the matrix (see earlier)

Dividing by V and recognising that at steady state $\frac{dC_{out}}{dt} = 0$

$$\frac{Q_{in}}{V}C_{in} - \frac{Q_{out}}{V}C_{out} - r_i = 0$$

Mass balance equations are derived for each compound in every reactor (including the settler). This yields a set of simultaneous non-linear equations for each reactor which then may be solved to give values for all the compounds. As the equations are non-linear, repetitive techniques must be employed in the solution (Billing, 1987).

(iii) ***Solution in time and space:*** This solution is confined to the situation of single or multiple reactors under repetitive diurnal flows. Again mass balances are set up but, unlike the steady state system, $(\frac{dC_{out}}{dt})$ no longer equal zero. Initial concentration values are selected and the mass balance equations are integrated forward until the solution is reached; this is achieved when the concentration of all compounds in each reactor at the start and at the end of the diurnal cycle are equal (Billing, 1987).