DYNAMIC MECHANISTIC MODEL FOR BIOLOGICAL NUTRIENT (NITROGEN AND PHOSPHORUS) REMOVAL ACTIVATED SLUDGE SYSTEMS

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ABSTRACT

The objective of this research was to develop and calibrate a dynamic mechanistic model for biological nutrient (nitrogen and phosphorus) removal activated sludge systems treating municipal wastewater. The IAWPRC (ASM1) model for non-polyP heterotrophic and autotrophic organisms (Henze *et al.*, 1987a,b) and the Wentzel *et al.* (1989b) model for polyP organisms were merged to form a general activated sludge model. After a number of initial modifications the model was tested against literature data from laboratory-scale nitrification denitrification biological excess phosphorus removal (NDBEPR) systems. Based on the preliminary results, a number of specific areas were identified which required further study. These included (1) accounting for sludge production and oxygen utilization in BEPR systems; (2) denitrification behaviour in BEPR systems; and (3) other issues such as hydrolysis under unaerated conditions.

The main body of this thesis is presented as a series of five papers. The first paper (Chapter 4) presents a study of COD and nitrogen balances in activated sludge systems. The results suggest that systems incorporating anaerobic zones exhibit low COD balances compared to aerobic and anoxic-aerobic systems. Possible mechanisms for this "loss" of COD are discussed, including the possibility that the COD loss is related to fermentation processes occurring under anaerobic conditions.

The second paper (Chapter 5) presents a study of denitrification behaviour in BEPR activated sludge systems. Results of a review of microbiological studies and many continuous and batch reactor experimental studies indicate that a significant fraction of the polyP organisms can use nitrate as an electron acceptor in the absence of oxygen for oxidation of stored PHB and simultaneous uptake of phosphorus.

The development of a general activated sludge model for biological nutrient removal activated sludge systems is discussed in the third paper (Chapter 6). Several modifications were made to both the ASM1 and Wentzel *et al.* (1989b) model components, based on the results of literature review and model simulations. A fermentation process has been included for the conversion of readily biodegradable COD to short chain fatty acids

(assuming a loss of COD). Hydrolysis of enmeshed slowly biodegradable COD under anaerobic conditions has been incorporated, as well as anoxic growth of polyP organisms. These modifications and others are discussed in this paper. The matrix representation and a description of the model processes are also presented, as well as a brief outline of influent wastewater characterization.

The application of the general model is demonstrated in the fourth paper (Chapter 7) for aerobic and anoxic-aerobic systems, as well as a number of nutrient removal (NDBEPR) systems for both steady state and dynamic conditions. Results of simulations show the model is capable of predicting sludge production and oxygen utilization for a range of system types and configurations, as well as tracking changes in a number of parameters including soluble phosphorus and nitrate concentrations.

In the final paper (Chapter 8) the consequences of the COD loss assumptions incorporated in the model are demonstrated for a number of experimental anoxic-aerobic and anaerobic-anoxic-aerobic systems. Results of model simulations indicate that without the assumption of COD loss, predictions of oxygen consumption and volatile suspended solids production are significantly over-estimated for NDBEPR systems (and to a lesser extent anoxic-aerobic systems). These systems apparently consume less oxygen and produce less volatile solids than aerobic systems for the same amount of COD removal.

In conclusion, the merits and weaknesses of the general model are discussed. An important feature of the model is that a single set of kinetic and stoichiometric parameters produced quite accurate predictions for the wide range of systems to which the model was applied (with the exception of the nitrifier growth rate - discussed in Chapter 6). This provides a degree of support for the model structure and integrity. Many aspects of NDBEPR modelling require further investigation, including: the COD loss phenomenon, the fermentation processes occurring under anaerobic (and possibly anoxic) conditions, the hydrolysis of slowly biodegradable colloidal and particulate organics (particularly under anoxic and anaerobic conditions), and the impact these aspects have on denitrification behaviour in NDBEPR systems.

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GLOSSARY OF TERMS AND SYMBOLS

a	Nitrified/aerobic mixed liquor recycle ratio
ASM1	IAWPRC (now IAWQ) Activated Sludge Model No.1
ASM2	IAWQ Activated Sludge Model No.2
b_A	Autotrophic organism decay rate
b_H	Non-polyP heterotrophic organism decay rate
b_P	PolyP heterotrophic organism decay rate
BOD	Biochemical oxygen demand
BEPR	Biological excess phosphorus removal
COD	Chemical Oxygen Demand
f_{BS}	Fraction of total influent COD which is readily biodegradable
f_{CV}	COD/VSS ratio
f_N	Nitrogen fraction of waste sludge [mgN/mgVSS]
f_{NA}	Fraction of total influent TKN which is free and saline ammonia
f_{NOP}	Fraction of biodegradable organic TKN which is particulate
f_{NUP}	Fraction of total influent TKN which is unbiodegradable particulate
f_{NUS}	Fraction of total influent TKN which is unbiodegradable soluble
f_{UP}	Fraction of total influent COD which is unbiodegradable particulate
f_{US}	Fraction of total influent COD which is unbiodegradable soluble
IAWPRC	International Association on Water Pollution Research and Control
IAWQ	International Association on Water Quality
K_{NH}	Autotroph half saturation coefficient for growth
$K_{S,H}$	Heterotroph half saturation coefficient for growth
K_{SP1}	PolyP half saturation coefficient for growth (not P limiting)
K_{SP2}	PolyP half saturation coefficient for growth (P limiting)
$M_{COD,aer}$	Mass of COD oxidized under aerobic conditions [mgCOD/d]
$M_{COD,denit}$	Mass of COD oxidized through denitrification [mgCOD/d]
$M_{COD,effl}$	Mass of COD in the system effluent [mgCOD/d]
$M_{COD,oxid}$	Total mass of COD oxidized in the system [mgCOD/d]
$M_{COD,was}$	Mass of COD in the wastage stream [mgCOD/d]

M_{denit}	Mass of nitrate denitrified in the anoxic zone [mgN/d]
$M_{denit,anaer}$	Mass of nitrate denitrified in the anaerobic zone [mgN/d]
$M_{denit,T}$	Total mass of nitrate denitrified in the system [mgN/d]
$M_{N,Ne}$	Mass of nitrate-nitrogen in the system effluent [mgN/d]
$M_{N,Te}$	Mass of TKN in the system effluent [mgN/d]
$M_{N,was}$	Mass of nitrogen in the wastage stream [mgN/d]
MCRT	Mean cell residence time
MO_N	Mass of oxygen consumed for nitrification [mgO/d]
MW	Molecular weight
N	Nitrogen
N_{BP}	Particulate biodegradable organic nitrogen
N_{BS}	Soluble biodegradable organic nitrogen
N_{BPi}	Influent particulate biodegradable organic nitrogen
N_{BSi}	Influent soluble biodegradable organic nitrogen
N_{H3}	Ammonia nitrogen
N_{H3i}	Influent ammonia nitrogen
$N_{N,aer}$	Average aerobic nitrate [mgNO3-N/L]
$N_{N,anaer}$	Average anaerobic nitrate [mgNO3-N/L]
$N_{N,anox}$	Average anoxic nitrate [mgNO3-N/L]
N_{Ne}	Average effluent nitrate [mgNO3-N/L]
N_{OB}	Biodegradable organic nitrogen
N_{OBi}	Influent biodegradable organic nitrogen
N_{03}	Nitrate nitrogen
N_{Te}	Effluent TKN
N_{Ti}	Influent TKN
N_{UP}	Unbiodegradable particulate nitrogen
N_{UPi}	Influent unbiodegradable particulate nitrogen
N_{US}	Unbiodegradable soluble nitrogen
N_{USi}	Influent unbiodegradable soluble nitrogen
ND	Nitrification denitrification
NDBEPR	Nitrification denitrification biological excess phosphorus removal
O_T	Total oxygen utilization rate [mgO/L/hr]
OUR	Oxygen utilization rate
P	Phosphorus

P_{O4}	Soluble phosphate
P_{PP-HI}	Fixed (high molecular weight) stored polyphosphate
P_{PP-LO}	Releasable (low molecular weight) stored polyphosphate
P_{Ti}	Total influent phosphorus
PHA	poly-β-hydroxyalkanoates
PHB	poly-β-hydroxybutyrate
PHV	poly-β-hydroxyvalerate
Q	Influent flowrate
q	Wastage flowrate
r	Anoxic mixed liquor recycle ratio
RAS	Return activated sludge
RBCOD	Readily biodegradable COD
s	Solids recycle ratio
S_{BS}	Readily biodegradable substrate
S_{BSA}	Readily biodegradable SCFA substrate (VFA)
S_{BSC}	Readily biodegradable "complex" substrate
S_{BSi}	Influent readily biodegradable substrate
S_{ENM}	Enmeshed slowly biodegradable substrate
S_{ENMi}	Influent enmeshed slowly biodegradable substrate
S_O	Dissolved oxygen
S_{PHB}	Stored SCFA
S_{Te}	Total effluent COD [mgCOD/L]
S_{Ti}	Total influent COD [mgCOD/L]
S_{UP}	Unbiodegradable particulate substrate
S_{UPi}	Influent unbiodegradable particulate subtrate
S_{US}	Unbiodegradable soluble substrate
S_{USi}	Influent unbiodegradable soluble substrate
SBR	Sequencing batch reactor
SCFA	Short chain fatty acids
SRT	Solids retention time (sludge age)
SUP	Soluble unreactive phosphorus
TCA	Tri-Carboxylic Acid
TKN	Total Kjeldahl nitrogen
TP	Total phosphorus

TOC	Total organic carbon
TSP	Total soluble phosphorus
V_{acr}	Volume of aerobic reactor [L]
VFA	Volatile fatty acids
VSS	Volatile suspended solids
X_A	Active autotrophic biomass (VSS units)
X_E	Endogenous mass (VSS units)
X_H	Active non-polyP heterotrophic biomass (VSS units)
X_P	Active polyP heterotrophic biomass (VSS units)
X_V	Mixed liquor volatile suspended solids of waste stream [mgVSS/L]
Y_A	Autotrophic organism yield constant
Y_H	Non-polyP heterotrophic organism yield constant
Y_P	PolyP heterotrophic organism yield constant
Z_A	Active autotrophic biomass (COD units)
Z_E	Endogenous mass (COD units)
Z_H	Active non-polyP heterotrophic biomass (COD units)
Z_P	Active polyP heterotrophic biomass (COD units)
μ_A	Maximum specific growth rate for autotrophs
μ_H	Maximum specific growth rate for non-polyP heterotrophs
μ_{P1}	Maximum specific growth rate for polyP heterotrophs (not P limiting)
μ_{P2}	Maximum specific growth rate for polyP heterotrophs (P limiting)

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CHAPTER ONE

INTRODUCTION

1.1 INTRODUCTION

The activated sludge system is the most widely applied method for the treatment of domestic wastewater. Originally developed for the purpose of removing organic matter from wastewater, the process has been expanded to include removal of ammonia, nitrogen, and phosphorus. The expanded function principally has evolved out of an increased awareness of eutrophication problems, and the need to reduce the quantity of nutrients (N and P) entering natural ecosystems.

The first treatment objective beyond that of organics removal was biological nitrification. This is the biological oxidation of ammonia to nitrate via the growth of autotrophic organisms. As these organisms have a lower growth rate than heterotrophs, a longer solids retention time (SRT) was required to prevent washout. The function of nitrification is to reduce effluent toxicity through reducing the effluent concentration of free ammonia. However, the conversion of ammonia-nitrogen to nitrate-nitrogen does not reduce the effluent nitrogen load on the receiving water.

The inclusion of unaerated zones in the activated sludge system to achieve biological nitrogen removal (denitrification) marked the first major change in the system configuration. This process relies on the ability of certain heterotrophic organisms to utilize nitrate in the absence of oxygen as a terminal electron acceptor. The nitrate is converted to gaseous nitrogen, thereby removing nitrogen from the wastewater. A number of different system configurations have been developed in order to achieve nitrogen removal (Wuhrmann, 1960; Barnard, 1973).

Phosphorus removal in North America in general has been accomplished to date through chemical precipitation. Chemicals such as alum or ferric chloride are added to the wastewater, causing the precipitation of aluminum or ferric hydroxy-phosphates. The

precipitates then settle out and are removed with the waste sludge. This leads to the production of large quantities of chemical sludge which require disposal. The U.S. EPA estimated that, compared to a system not practicing phosphorus removal, for an effluent total phosphorus (TP) limit of 0.5 g m^{-3}, the increase in sludge production is between 100 and 200%. For an effluent TP limit of 0.2 g m^{-3}, sludge production is expected to increase by more than 200% (Nutt, 1991).

An alternative to chemical phosphorus removal which obviates the problem of chemical sludge production is biological excess phosphorus removal (BEPR). In BEPR activated sludge systems, phosphorus removal is mediated by a group of organisms (termed polyP organisms) that are able to store phosphorus as polyphosphate polymers (Comeau *et al.*,1985; Wentzel *et al.*, 1986). The essential requirements for BEPR are an alternating anaerobic/aerobic sequence, and the provision of short-chain fatty acids (SCFA) during the anaerobic phase. A number of different BEPR system configurations have been developed, including: the Phostrip process (Levin, 1964), the Bardenpho system (Barnard, 1974), the modified 5-stage Bardenpho system (McLaren and Wood, 1976; Davelaar, 1978), the A/O process (Hong *et al.*, 1982), the University of Cape Town (UCT) process (Ekama *et al.*, 1984), the Biodenipho process (Arvin and Kristensen, 1985), and the VIP process (Wable and Randall, 1989).

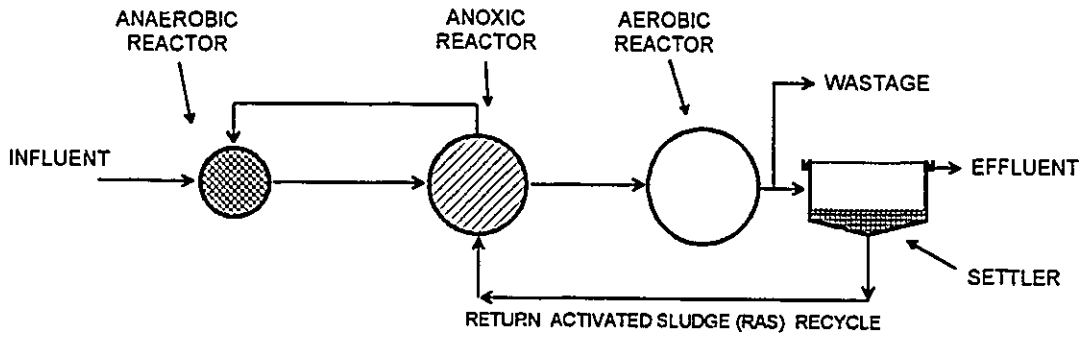

Figure 1.1 The UCT/VIP Nitrification Denitrification Biological Excess Phosphorus Removal (NDBEPR) System Configuration.

Activated sludge systems become more complex as their function is expanded from carbonaceous removal alone to include nitrification, denitrification and biological excess phosphorus removal. Typically, a nutrient removal system involves multiple reactors, some aerated and some not, with inter-reactor recirculation of mixed liquor. The UCT/VIP process configuration is shown as an example in Figure 1.1. The number of biological reactions and the number of compounds involved in the process also increases correspondingly. This is because a nitrification denitrification biological excess phosphorus removal (NDBEPR) system involves at least three separate groups of microorganism (polyP heterotrophs, non-polyP heterotrophs, nitrifying autotrophs) operating on a large number of chemical components in three distinct environmental regimes (aerobic zones, anoxic zones where nitrate but not oxygen is present, and anaerobic zones where nitrate and oxygen are excluded as far as possible). These features make for complex behaviour which has increased the level of difficulty in design, operation and control.

Computer modelling of system behaviour provides the obvious means for predicting the response of a particular system. In recent years modelling has had a significant impact on the development of design and operational procedures for activated sludge systems. In full-scale plant operation it has also found application as a optimization tool in assessing the effects of changes in waste flows and loads, operational modifications (e.g. changes in recycles), and proposed modifications to plant configuration. Also it has proved valuable in operator training; through simulation exercises using the model, the operator acquires "instant" experience in the behaviour to be expected with changes in inputs, system configuration and operational strategies.

Currently the approach to modelling activated sludge systems is to use mechanistic models. These mechanistic models incorporate mathematical expressions which represent the biological interactions, based on hypotheses proposed for the biological processes occurring within the system. The best known model of this kind is the IAWPRC Model No. 1 (ASM1).

Development of the IAWPRC model was initiated in 1982 when the International Association on Water Pollution Research and Control (IAWPRC, now IAWQ) appointed a task group to review modelling of activated sludge systems incorporating *carbonaceous*

energy removal, nitrification and denitrification. The initial deliberations of the group resulted in a preliminary version of the "IAWPRC model" (Grady *et al.*, 1986). Dold and Marais (1986) conducted a comprehensive evaluation of the preliminary model. It was proposed that certain changes should be made, in particular with respect to the way in which the fate of organic nitrogen was modeled. These changes were subsequently adopted in the final version of the IAWPRC Activated Sludge Model No. 1 [ASM1] (Henze *et al.*, 1987a, 1987b).

The task group drew on a wide range of information in formulating the model. One research initiative which had a major influence on the model was the dynamic activated sludge model developed by Marais and co-workers at the University of Cape Town (Dold *et al.*, 1980; van Haandel *et al.*, 1981). This dynamic model evolved out of the steady state model of Marais and Ekama (1976). The steady state model, in turn, constituted a development from a number of previous models for carbonaceous and nitrogenous material conversion and removal (McKinney, 1962; McKinney and Ooten, 1969; Lawrence and McCarty, 1970; Downing *et al.*, 1964).

The ASM1 model, based on a mechanistic interpretation of the behaviour of the organisms mediating the process reactions, has been shown to give a reliable description of the non-BEPR system response over wide ranges of system configuration (single and series reactor systems, aerated and non-aerated reactors, inter-reactor recycles), influent wastewater characteristics (COD, TKN, flow pattern) and operational parameters (sludge age, temperature, dissolved oxygen concentration).

A restriction of ASM1 is that its scope is limited to systems incorporating carbonaceous energy removal, nitrification and denitrification (ND), and the phenomenon of biological excess phosphorus removal is not included. In BEPR activated sludge systems removal of phosphorus (P) is mediated by a group of organisms (polyP organisms) which exhibit the propensity to store P as polyphosphate (polyP) polymers called volutins (Buchan, 1981). Proposed explanations of the biochemical behavioral patterns associated with P release and uptake (and net P removal) have been presented in a number of models; for example, that of Comeau *et al.* (1985), extended and modified by Wentzel *et al.* (1986), and that of Mino *et al.* (1987). The biochemical models are largely in agreement regarding the biochemical control mechanisms and have provided an explanation for the essential

requirements for attaining BEPR; namely, an alternating anaerobic/aerobic sequence with the provision of short-chain fatty acids (SCFA) during the anaerobic phase [also referred to as volatile fatty acids (VFA)]. In "normal" municipal wastewater the SCFA content usually is minimal. In BEPR systems the readily biodegradable COD component is transformed to SCFA by the non-polyP organism mass, thereby making SCFA available to the polyP organisms (Meganck *et al.*, 1985; Brodisch, 1985; Wentzel *et al.*, 1985). Aside from this linkage, the polyP and non-polyP organisms in BEPR systems have been shown to act essentially independently of one another. For this reason Wentzel *et al.* (1988) adopted the approach of developing "enhanced" cultures of polyP organisms as the basis for studying the kinetics and stoichiometry of BEPR without the behaviour being masked by that of the non-polyP organisms.

Enhanced cultures of polyP organisms were developed by Wentzel *et al.* (1988) in continuous flow activated sludge systems (modified Bardenpho and UCT process configurations), with acetate as the only organic substrate. The sludge mass in these systems was shown to comprise the polyP organism *Acinetobacter* spp. in excess of 90 percent. Based on observations of the continuous flow systems and batch experiments using mixed liquor drawn from these systems, Wentzel *et al.* (1989a, 1989b) developed a kinetic model for the enhanced culture BEPR system. The model provided a very reasonable description of the response observed in a number of continuous flow enhanced culture systems and the batch experiments with *a single set of kinetic and stoichiometric parameters*. The authors identified certain minor limitations in the proposed model, and outlined problems which might be encountered when extending the model to mixed organism systems with municipal wastewater as influent. Despite any minor limitations, the enhanced culture model constituted a most significant step towards the development of a general activated sludge model capable of modelling the biological processes of carbonaceous energy removal, nitrification, denitrification *and biological excess phosphorus removal.*

1.2 OBJECTIVE

The objective of this research was to develop and calibrate a dynamic mechanistic model for biological nutrient (nitrogen and phosphorus) removal activated sludge systems treating municipal wastewater.

As the enhanced culture model of Wentzel *et al.* (1989b) is cast in the same framework as the IAWPRC model, the merging of the two models appeared to be a suitable starting point. Similar kinetic and stoichiometric formulations have been used, and concepts such as switching functions are included in the kinetic expressions in both models. Given this similarity in structure, and given the relative independence of the polyP and non-polyP organism masses, a combination of the two models was a logical starting point for developing a general activated sludge model.

Development of the model was an iterative process. Initially a model was formulated, and then tested against an extensive database from experimental systems. Modifications to the model were then proposed, based on deficiencies in model predictions. These modifications sometimes involved extensive review of literature. The predictive ability of the modified model then was re-tested. This iterative procedure was repeated until it was deemed that the model provided accurate predictions for a range of BEPR and non-BEPR systems over a wide range of operating conditions. The main chronological stages in the model development were as follows:

- The IAWPRC (ASM1) model for non-polyP heterotrophic organisms and autotrophic organisms (Henze *et al.*, 1987a, 1987b) and the Wentzel *et al.* (1989b) model for polyP organisms were merged to form a general activated sludge model for biological nutrient (nitrogen and phosphorus) removal activated sludge systems treating municipal wastewater.

- After a number of initial modifications the model was tested against literature data from NDBEPR systems. Based on the preliminary results, a number of specific areas were identified which required further study (refer to Chapter 3).

- A review of the literature pertaining to BEPR was conducted, focusing on the problem areas identified in the initial model application.

- Further modifications were made to the general model. This included incorporating a number of new parameters, as well as making changes to process rate equations.

- The predictive capacity of the model was tested using literature data for a variety of activated sludge system types (i.e. aerobic, anoxic-aerobic, anaerobic- anoxic-aerobic) with differing configurations, operating parameters, and influent wastewater characteristics.

- Model parameters were calibrated to give the best overall predictions for the range of systems to which the model was applied (i.e. a single set of model parameters was identified which can be used for application of the model to any of the system types mentioned above). The calibration exercise also included an evaluation of the sensitivity of the model to various parameters.

The main body of this thesis is presented as a series of five papers (Chapters 4 to 8). As a result, the literature review is divided into a number of sections. Chapter 2 provides a short background on the mechanisms involved in biological excess phosphorus removal. Chapter 3 outlines results of initial model applications, and the identification of specific areas to be investigated. Results of the literature review and data analysis for two of these areas are presented in Chapters 4 and 5 ("COD and Nitrogen Mass Balances in Activated Sludge Systems" and "Denitrification Behaviour in Biological Excess Phosphorus Removal Activated Sludge Systems" respectively). Chapter 6 presents the model in its final form, and includes a process by process description of the model. Chapter 7 demonstrates application of the model to a number of types of activated sludge system, as well as discussing the sensitivity of the model. The final paper "Sludge Production and Oxygen Demand in Nutrient Removal Activated Sludge Systems" is presented in Chapter 8. This paper demonstrates the practical significance of a number of the modifications made to the model. The issue of model sensitivity is addressed in an appendix.

CHAPTER TWO

BACKGROUND ON BIOLOGICAL EXCESS PHOSPHORUS REMOVAL

2.1 INTRODUCTION

The biological excess phosphorus removal process involves complex interactions between different organism types under varying environmental conditions. To understand the complexities of biological excess phosphorus removal it is useful to investigate some of the microbiological and biochemical aspects of the process.

2.2 BIOLOGICAL EXCESS PHOSPHORUS REMOVAL - AN OVERVIEW

In BEPR activated sludge systems phosphorus removal is mediated by a particular group of organisms (termed polyP organisms) that are able to store phosphorus as polyphosphate polymers (Comeau *et al.*,1985; Wentzel *et al.*, 1986). Many of the polyP organisms commonly encountered in wastewater treatment have been found to belong to the genus *Acinetobacter* spp. (Fuhs and Chen, 1975; Buchan, 1983). The genus requires oxygen for catabolic metabolism (Juni, 1978); however there are some species which can use nitrate as an electron acceptor in the absence of oxygen (Lotter, 1985). One characteristic of the genus is that they utilize sugars (such as glucose) exclusively via the Entner-Doudoroff pathway. As this pathway is inoperative under anaerobic conditions, *Acinetobacter* spp. are not capable of producing energy through fermentation. In addition, the genus is able to store phosphorus as polyphosphate and carbon as poly-β-hydroxybutyrate (PHB). In the activated sludge system, the polyP organisms release phosphorus during the anaerobic stage, and utilize the energy available from the hydrolysis of the stored polyphosphate polymers to sequester SCFA. These SCFA are then used to form PHB, a storage product which can be used for growth when an external electron acceptor is present. Under aerobic conditions, where the amount of SCFA is minimal, the polyP organisms are able to utilize their stored PHB, and at the same time, synthesize more polyphosphate, for use later when no external electron acceptor is available. Other

organic storage products have also been documented. Comeau *et al.* (1987) conducted a series of batch tests which suggest that if the SCFA substrate contains an even number of carbon atoms (e.g. acetate, butyrate), then the majority of stored carbon will be in the form of PHB (a four carbon compound). However, if the substrate contains an odd number of carbon atoms (e.g. propionate, lactate, valerate), then the majority of stored carbon will be in the form of poly-β-hydroxyvalerate (PHV), a five carbon compound. These compounds have been referred to collectively as poly-β-hydroxyalkanaotes (PHA). Matsuo *et al.* (1992) have also identified two other organic storage polymers: 3-hydroxy-2-methylbutyrate (3H2MB) and 3-hydroxy-2-methylvalerate (3H2MV).

Organisms other than *Acinetobacter* have been reported as being capable of storing phosphorus in excess of metabolic requirements. Brodisch and Joyner (1983) detected polyphosphate granules in *Nocardia* spp. and *Pseudomonas*. Meganck *et al.* (1985) also confirmed the presence of P removing *Pseudomonas* in a pilot plant study.

The main net effects of the biological excess phosphorus removal phenomenon are:

In the Anaerobic Zone:

- A decrease in SCFA concentration in the bulk solution.
- An increase in phosphate concentration in the bulk solution.
- An increase in intracellular PHB (and/or PHV).
- A decrease in intracellular polyphosphate.

In the Aerobic Zone:

- A decrease in phosphate concentration in the bulk solution (generally of much greater magnitude than the release of phosphate which occurred in the anaerobic zone).
- A decrease in intracellular PHB (and/or PHV).
- An increase in intracellular polyphosphate.

Since apparently only a fraction of the polyP organisms can use nitrate as an electron acceptor in place of oxygen (Lotter, 1985), presumably under anoxic conditions those

polyP organisms which can denitrify behave as they would under aerobic conditions, and those which cannot denitrify behave as they would under anaerobic conditions (refer to Chapter 5 for more information on anoxic behaviour of polyP organisms).

2.3 BIOCHEMICAL MODELS

There are two main biochemical models which attempt to describe the phenomenon of BEPR: the Comeau/Wentzel model (Comeau *et al.*, 1985; Wentzel *et al.*, 1986) and the Mino model (Mino *et al.*, 1987). Both present possible biochemical pathways for the release of phosphate and simultaneous conversion of SCFA to PHB under anaerobic conditions, and the uptake of phosphorus and simultaneous oxidation of stored PHB under aerobic conditions. Both models recognize the importance of the anaerobic/aerobic sequencing, as well as the need for the provision of SCFA under anaerobic conditions. However there are a number of differences in the two models. These models are considered briefly below.

2.3.1 The Comeau/Wentzel Model

The Comeau/Wentzel model accepts the genus *Acinetobacter* spp. as being representative of the polyP organism group. With this in mind, the model was developed by considering the biochemical pathways which have been identified in the literature as being operative in this genus, *i.e.* the tricarboxylic acid (TCA) and glyoxylate cycles, and the Entner-Doudoroff pathway (Juni, 1978). Acetate is taken as the typical substrate. The model can be divided into anaerobic and aerobic processes.

Under anaerobic conditions the proposed behaviour is shown schematically in Fig. 2.1. An outline of the proposed model is as follows (from Wentzel *et al.*, 1991):

- Acetate enters the cell by passive diffusion which occurs when the extracellular acetate concentration is sufficiently high.

- The intracellular acetate is activated to acetyl-CoA by coupled ATP hydrolysis.

- ATP hydrolysis also results in the release of cations (denoted by M^+) and the anion $H_2PO_4^-$. Generally the cations released are potassium (K^+) or magnesium (Mg^{2+}).

- Cations are released to the bulk solution by the use of a proton-mediated antiport protein carrier, and the phosphorus (as $H_2PO_4^-$) is released via a hydroxyl-mediated antiport protein carrier.

- ATP is regenerated from ADP by the transfer of an energy-rich phosphoryl group from intracellular polyphosphate ($polyP_n$) to ADP.

- Two acetyl-CoA molecules condense to form acetoacetyl-CoA, which is reduced by $NAD(P)H_2$ to form hydroxybutyryl-CoA. The hydroxybutyryl-CoA is then polymerized to form poly-β-hydroxybutyrate (PHB).

- Reducing equivalents ($NAD(P)H_2$) required for the conversion of acetoacetyl-CoA to hydroxybutyryl-CoA are hypothesized to result from the metabolism of some of the acetate via the TCA cycle. This results in the production of a small amount of CO_2 (not shown).

A schematic diagram of the proposed behaviour under aerobic conditions is given in Fig.2.2. The following is a summary of the proposed model (from Wentzel *et al.*, 1991):

- Stored PHB is broken down and used for both anabolic or catabolic metabolism.

- Anabolic metabolism results in the incorporation of "carbon skeletons" generated directly or indirectly from PHB into the cell mass.

- In catabolic metabolism the PHB is broken down to acetyl-CoA, which enters the TCA and glyoxylate cycles. The reducing equivalents ($NADH_2$) generated in these cycles are then oxidized via the electron transport chain, which operates in the presence of an electron acceptor (*i.e.* oxygen). Simultaneous oxidative phosphorylation results in the formation of ATP.

- The ATP produced is utilized for synthesis (*i.e.* growth) and polyphosphate formation.

- The uptake of phosphorus (as $H_2PO_4^-$) for resynthesis of polyphosphate occurs via the hydroxyl mediated antiport, and concomitant cation uptake occurs via the proton mediated antiport.

For a more detailed description of the model under anaerobic and aerobic conditions the reader is referred to Wentzel *et al.* (1986) and Comeau *et al.* (1985).

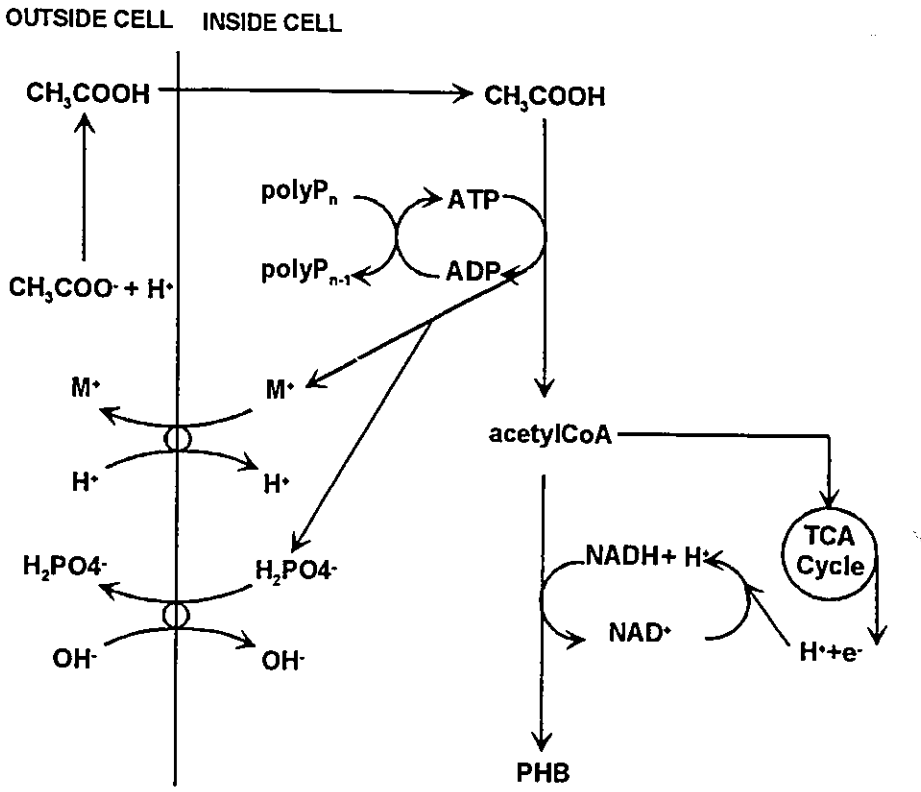

Figure 2.1 Schematic Diagram for the Behaviour Proposed by the Comeau/Wentzel Model For Anaerobic Conditions (from Wentzel *et al.*, 1991).

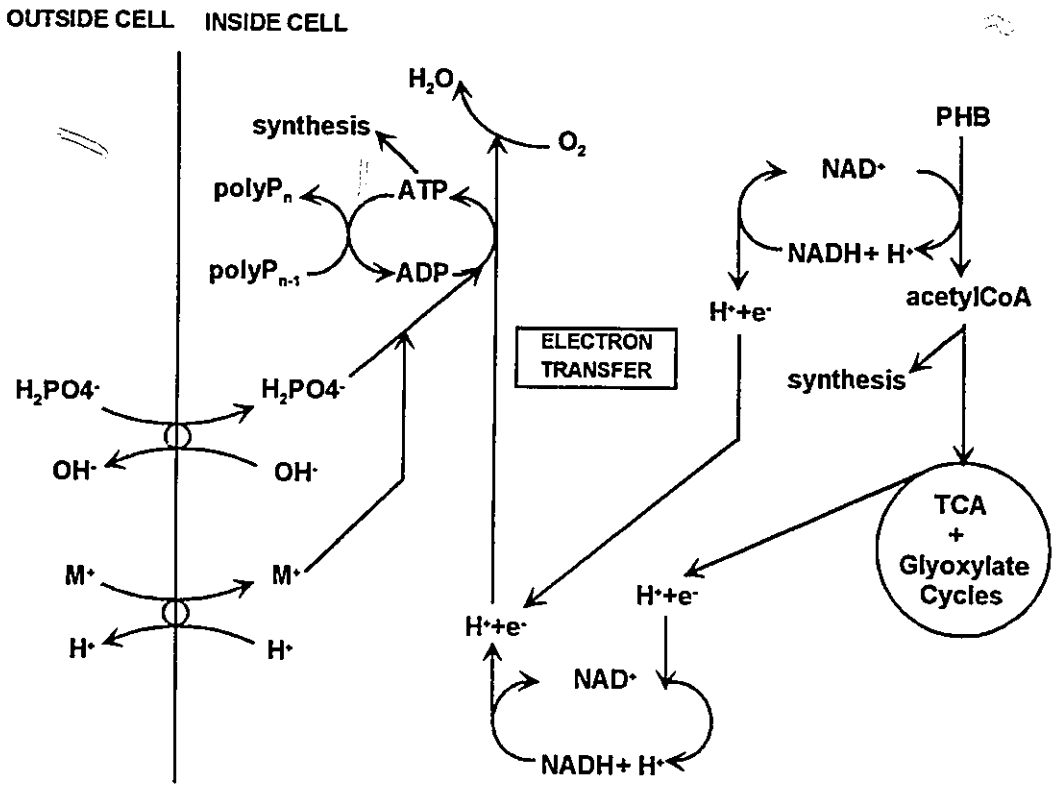

Figure 2.2 Schematic Diagram for the Behaviour Proposed by the Comeau/Wentzel Model For Aerobic Conditions (from Wentzel *et al.*, 1991).

2.3.2 The Mino Model

Schematic diagrams for the behaviour proposed by the Mino model under anaerobic and aerobic conditions are shown in Fig. 2.3 and 2.4 respectively (from Wentzel *et al.*, 1991). Under anaerobic conditions the proposed behaviour is as follows:

- Acetate enters the cell, and is then activated to acetyl-CoA. This is coupled with ATP hydrolysis, and results in the release of phosphorus (denoted Pi) to the bulk solution.

- As in the Comeau/Wentzel model ATP is regenerated from ADP by the transfer of an energy rich phosphoryl group from intracellular polyphosphate ($polyP_n$) to ADP.

- Synthesis of PHB ($(C_4H_6O_2)n$) from acetyl-CoA (AcCoA) is described by the following reaction (also in agreement with the Comeau/Wentzel model):

$$2nAcCoA + nNADH_2 \rightarrow (C_4H_6O_2)_n + nNAD + 2nCoASH$$

- Reducing equivalents for the above PHB synthesis process are hypothesized to derive from the conversion of carbohydrates to pyruvic acid via the Embden-Meyerhof-Panas (EMP) pathway. The pyruvic acid is then converted to acetyl-CoA (with CO_2 production). This method of modelling the production of reducing equivalents differs from the the Comeau/Wentzel model.

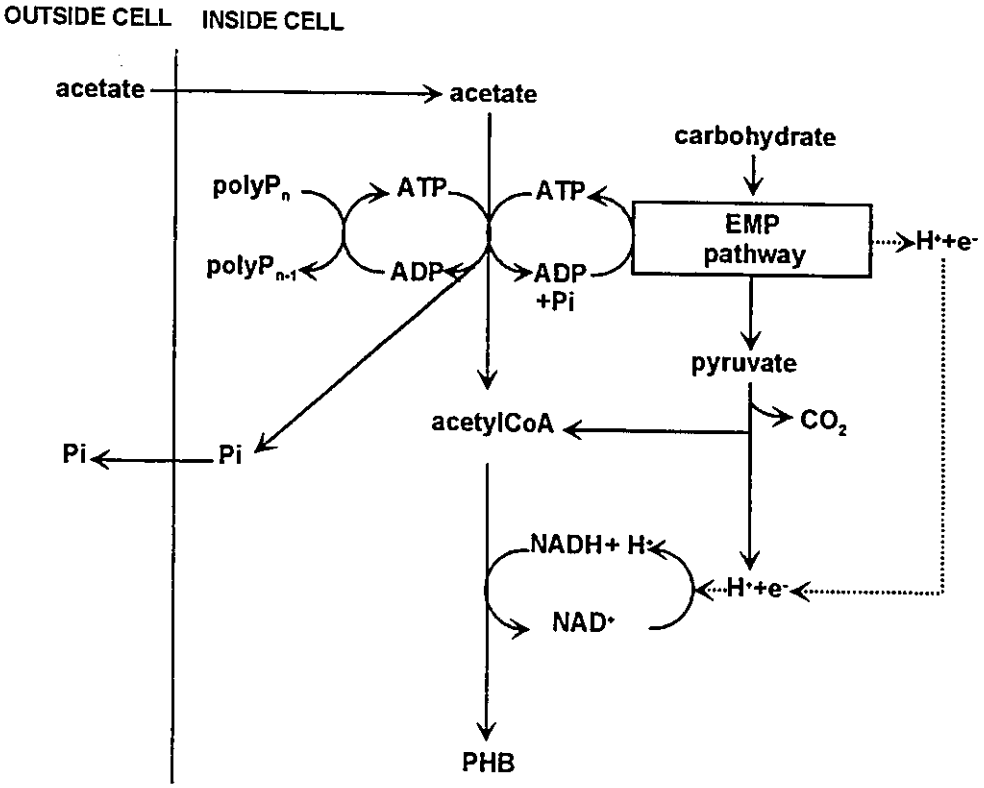

Figure 2.3 Schematic Diagram for the Behaviour Proposed by the Mino Model For Anaerobic Conditions (from Wentzel *et al.*, 1991).

Under aerobic conditions an outline of the behaviour proposed by the Mino model is as follows (shown schematically in Fig. 2.4):

- PHB which is broken down is used for anabolic and catabolic metabolism, as well as carbohydrate synthesis.

- In anabolic metabolism, PHB is used as a carbon source for cell synthesis.
- In catabolism, PHB degradation is coupled to oxidative phosphorylation, resulting in ATP production (as described for the Comeau/Wentzel model). The ATP produced is used to meet cell energy requirements, and for polyphosphate formation.
- The synthesis of carbohydrates from PHB under aerobic conditions is not described explicitly by the model, however this process is crucial to the model in that it supplies the carbohydrates necessary under anaerobic conditions.

For a more detailed description of the Mino model under anaerobic and aerobic conditions the reader is referred to (Mino *et al.*, 1987).

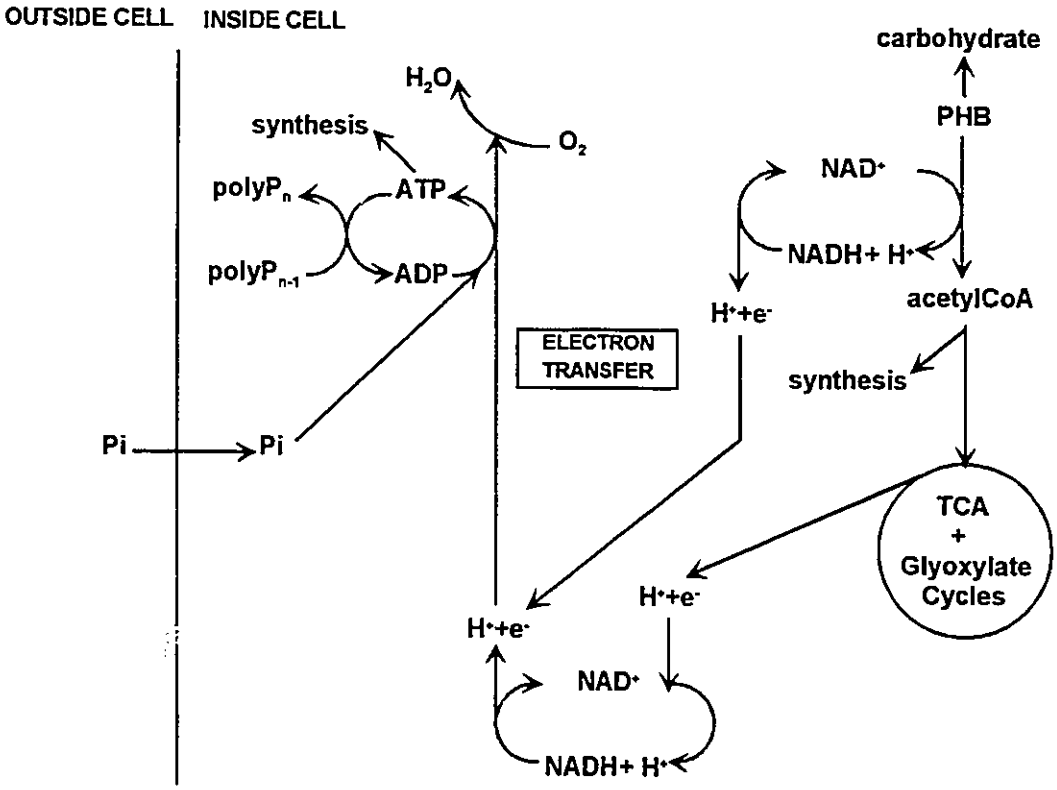

Figure 2.4 Schematic Diagram for the Behaviour Proposed by the Mino Model For Aerobic Conditions(from Wentzel *et al.*, 1991).

2.3.3 Summary of Biochemical Models

The main difference between the Comeau/Wentzel model and the Mino model lies in the assumptions regarding the production of reducing equivalents for PHB synthesis. While the Comeau/Wentzel model assumes that reducing equivalents must be produced by the metabolism of acetate via the TCA cycle, the Mino model does not accept that the polyP organisms do not possess the EMP pathway, and assumes that reducing equivalents are produced by the consumption of carbohydrates via the EMP pathway. As *Acinetobacter* spp. have been shown not to possess this pathway (Bergey, 1984), one might assume that this model is not applicable to these organisms. However Wentzel *et al.* (1991) suggest that the Mino model could be applicable to *Acinetobacter* spp. if the Entner-Doudoroff (ED) pathway were substituted for the EMP pathway. Experimental evidence to support the Comeau/Wentzel model, and the Mino and modified Mino models, is summarized in Wentzel *et al.* (1991).

An important aspect regarding the two biochemical models for explaining BEPR behaviour is that neither considers organism response under anoxic conditions. Apparently the reason for focusing only on anaerobic and aerobic behaviour was because the assumption was made that polyP organisms cannot utilize nitrate as an electron acceptor. However, many experimental studies (several of which pre-date the models) have demonstrated that at least a fraction of polyP organisms in fact can denitrify. This is discussed further in Chapter 5.

2.4 FACTORS AFFECTING PHOSPHORUS REMOVAL

There are numerous factors which play a role in determining the overall performance of a biological excess phosphorus removal system. These factors include:

- Influent wastewater characteristics (e.g. SCFA concentration, TP/COD ratio, TKN/COD ratio, nitrate concentration);
- Environmental factors (e.g. pH, temperature);
- Design and operating parameters (e.g. anaerobic detention time, aerobic detention time, sludge age, waste sludge handling method).

A number of these factors are outlined briefly below.

2.4.1 Influent Wastewater Characteristics

The influent TP/COD ratio has been shown to be an important wastewater characteristic in determining the suitability of implementing a BEPR process. Sedlak (1991) reports that the BOD_5/TP ratio should be greater than 20 if a main stream BEPR process is to be used*. A study by Raymond *et al.* (1991) on the feasibility of implementing BEPR in existing Quebec treatment plants noted that a high BOD_5/TP ratio implies increased anaerobic storage of organics by the polyP organisms, and subsequently implies increased P uptake under aerobic conditions. They concluded that the most favourable plants have BOD_5/TP ratios greater than 35. Pitman (1984) noted that BEPR is generally more suited to strong wastewaters, with an influent COD of at least 300 mg/L, and preferably greater than 400 mg/L.

Perhaps more important than the amount of P per unit total influent COD is the amount of P in relation to the influent readily biodegradable COD (RBCOD) concentration. The RBCOD in the influent wastewater, both as complex and short chain fatty acid RBCOD, plays an important role in determining the extent to which biological excess phosphorus removal occurs in a system. The complex RBCOD which is fermented to SCFA under anaerobic conditions, and the influent SCFA, provide the substrate for the polyP organisms. It has been well documented that P removal can be improved by augmenting the SCFA content of the wastewater by primary sludge fermentation (Sedlak, 1991).

The influent TKN/COD ratio also is of importance to the BEPR process. As the ingress of nitrate to the anaerobic zone has been shown to be detrimental to the BEPR process due to the resulting competition for substrate between polyP and non-polyP organisms, it is generally believed that a low TKN/COD ratio is preferable. Pitman (1984) states that the TKN/COD ratio should be less than 0.10 mgN/mgCOD. In systems where nitrate is present in the influent, steps may have to be taken to ensure that sufficient substrate is available for the polyP organisms (such as increased SCFA addition).

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* Assuming a COD/BOD_5 ratio of 2 for influent wastewater, this would correspond to a TP/COD ratio of 1:40.

2.4.2 Environmental Factors

Pure culture studies suggest that biological excess phosphorus removal is affected by pH. A study by Groenestijn and Deineman (1985) showed that the maximum specific growth rate of *Acinetobacter* was significantly higher at a pH of 8.5 (42% higher than that observed at a pH of 7.0). Tracy and Flammino (1985) observed that pH did not appear to affect the specific uptake rate of phosphorus in the aerobic zone for pH values within the range of 6.5 to 7.0. However, for pH values below 6.5, the rate decreased, until all activity was lost at a pH of 5.2.

Temperature has been shown to affect P removal efficiency in laboratory scale BEPR systems. Sell *et al.* (1981) studied phosphorus removal in systems operated over a temperature range of 5-15°C. The results showed that there was a significant improvement in P removal at lower temperatures (40% more P was removed at 5°C compare to 15°C). These results suggest that a full-scale BEPR plant should be able to operate successfully at low temperatures. However it should be noted that these laboratory scale systems received synthetic wastewater, primarily soluble in nature; therefore the effects of temperature on both fermentation and hydrolysis were not investigated. Conflicting reports on the effect of temperature on BEPR have arisen from more recent studies. Barnard *et al.* (1985) observed excellent P removal in a full-scale plant at an operating temperature of 9°C. While Spatzierer *et al.* (1985) reported a decrease in P removal efficiency at temperatures below 10°C. Results of both pilot plant (McClintock *et al.*, 1991) and lab-scale tests (Mamais and Jenkins, 1992) indicate a decrease in P removal efficiency with decreasing temperature.

2.4.3 Design and Operating Parameters

A given BEPR system has a division into aerated and unaerated sections. [For a continuous flow system this division is in space, *i.e.* different zones in the bioreactor are aerated or unaerated. For sequencing batch reactor (SBR) systems the division is in time rather than space]. In systems with recycle streams the sludge concentration may not be the same in each bioreactor zone, depending on the arrangement of recycles. As a result, the volume fractions of each zone are not necessarily the same as the sludge mass fractions. Also, the detention time in each zone depends on the recycle rates. These

factors have resulted in a certain amount of confusion regarding process design. For example, some references interpret behaviour in terms of detention times, while others are based on mass fractions. This is further complicated when design sludge age or solids retention time (SRT) is considered.

Both the anaerobic and aerobic detention times have been reported as important design parameters. The anaerobic detention time must be sufficient to allow SCFA uptake by the polyP organisms. However, Barnard (1984) noted that if the anaerobic detention time is too long, P release without SCFA uptake may occur (termed "secondary release"). When this occurs less P removal is expected as there is insufficient storage of organics for complete uptake of the released P.

The aerobic detention time must be sufficient to complete biological P uptake. Since generally P removal systems are designed to include nitrification, the aerobic detention time must be sufficient for the growth of nitrifiers, and therefore will generally be long enough to allow maximum P uptake.

The sludge age or SRT also is very important in process design. Selection of the appropriate SRT for a given BEPR system depends on a large number of factors. These include: (1) influent wastewater characteristics, in particular the RBCOD content and TKN/COD ratio; (2) operating temperature, and whether or not year-round nitrification is required; (3) the extent of nitrogen removal required (limits may or may not exist for effluent nitrate concentration); (4) handling of streams from sludge treatment operations.

The waste sludge handling method is also important in the design and operation of a BEPR system. As exposure to anaerobic conditions will result in the re-release of a portion of the P which has been taken up, systems using anaerobic digestion will require treatment of sludge liquors from the digestion process. Generally the quantity of P released will be too great for recycling to the head of the plant (without prior treatment) to be an option (Pitman *et al.*, 1991). However alternatives such as precipitation of struvite, through aeration combined with the addition of lime to the digested sludge, can be used to remove the P from the liquid phase (Pitman *et al.*, 1991). Recycle streams from sludge dewatering and digestion processes must be considered judisciously. Sludge thickening using dissolved air flotation, followed by composting and/or land disposal has been shown to be a viable option for BEPR systems (Oldham, 1984).

CHAPTER THREE

INITIAL MODEL DEVELOPMENT

3.1 INTRODUCTION

The initial stage in the development of a general model incorporating nitrification denitrification and biological phosphorus removal was to combine the IAWPRC model (ASM1) for non-polyP heterotrophic and nitrifying autotrophic organism populations, and the enhanced culture model of Wentzel *et al.* (1989b) for polyP organisms. The combined model describes the behaviour of three separate organism masses (polyP heterotrophs, non-polyP heterotrophs, and nitrifying autotrophs) under three possible environmental conditions (aerobic, anoxic, and anaerobic).

Two initial modifications were made to the IAWPRC component of the model. These are with respect to:

- The nitrogen source for cell synthesis.
- The growth of non-polyP heterotrophs on SCFA.

The first modification was based on a review of the ASM1 model conducted by Dold and Marais (1986). They suggested that under certain conditions nitrate, instead of ammonia, would serve as the nitrogen source for cell synthesis. This suggestion was supported by an analysis of data, particularly that from long sludge age systems with a high degree of nitrification. Wentzel *et al.* (1989a) also reported that nitrate could be used for cell synthesis by polyP organisms when the ammonia level was low, and hence this process was included in the Wentzel model. The inclusion in the model of nitrate as a nitrogen source for cell synthesis for the non-polyP organisms results in two additional processes (aerobic growth of non-polyP heterotrophs with nitrate as the N source, and anoxic growth of non-polyP heterotrophs with nitrate as the N source).

The growth of non-polyP organisms on short chain fatty acids (SCFA) was included due to the necessity of differentiating between "complex" and SCFA readily biodegradable COD in BEPR systems. It was therefore necessary to duplicate the four non-polyP organism growth processes referred to above to account for possible growth on the two components of the readily biodegradable COD for the mixed culture system. With regard to growth on SCFA it is likely that only one of the four processes would be of consequence - anoxic growth with ammonia as the N source. This is because SCFA are removed in the unaerated zones at the "front end" of the continuous flow systems and do not enter the aerobic zones in appreciable concentrations. However, for completeness all four growth processes (for "complex" COD) were duplicated in the general model for growth of non-polyP organisms with SCFA as substrate. The same kinetic formulations and stoichiometry for growth on "complex" readily biodegradable COD and SCFA have been utilized.

3.2 INITIAL MODEL APPLICATION

The initial model was applied to literature data from 30 different laboratory-scale BEPR systems operated over a range of sludge ages (3 to 28 days) with municipal wastewater as influent (data set compiled by Wentzel *et al.*, 1990), as well as data from four different enhanced culture systems with acetate as influent (Wentzel *et al.*, 1989a). The following preliminary conclusions were reached:

- The model consistently over-predicted the volatile sludge production, as well as the oxygen utilization in the mixed culture systems. This suggests that possibly COD "loss" is occurring in the mixed culture systems, perhaps related to a fermentation process occurring in the anaerobic reactor.

- A significant number of mixed culture systems exhibited a net uptake of phosphorus in the anoxic reactor with concomitant denitrification. This lead to the conclusion that at least some of the polyP organisms are able to use nitrate as an electron acceptor in the absence of oxygen to utilize stored PHB and take up phosphorus (contrary to the assumptions made in the Wentzel model component).

- In many of the systems the magnitude of P release in the anaerobic reactor was inconsistent with the amount of readily biodegradable COD (RBCOD) in the influent, suggesting that hydrolysis of slowly degradable COD to form RBCOD is occurring under anaerobic conditions (contrary to the IAWPRC model assumptions).

Despite the deficiencies noted above, experience with application and testing of the initial model was reasonably positive. Perhaps the most important aspect was that the model structure did in fact allow for simulating the balance between the three organism masses in the system.

3.3 SPECIFIC RESEARCH OBJECTIVES

In addressing the main research objective [i.e. to develop and calibrate a dynamic mechanistic model for biological nutrient removal activated sludge systems] in the context of the initial experience, it was decided to concentrate on four specific areas:

(1) Accounting for sludge production and oxygen utilization in BEPR systems (i.e. the COD "loss" phenomenon);

(2) Denitrification behaviour in BEPR systems;

(3) Modifying the general model structure on the basis of (1) and (2), as well as a number of other issues such as hydrolysis under unaerated conditions;

(4) Testing of the predictive capacity of the modified model against existing data sets.

CHAPTER FOUR

COD AND NITROGEN MASS BALANCES IN ACTIVATED SLUDGE SYSTEMS

This chapter contains the complete text of a paper published in *Water Research*. The full reference is:

Barker, P. and Dold, P.L. (1995). COD and Nitrogen Mass Balances in Activated Sludge Systems. *Wat. Res.* **29**, 633-643.

COD AND NITROGEN MASS BALANCES IN ACTIVATED SLUDGE SYSTEMS

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Abstract

COD and nitrogen balances were performed on four different types of laboratory-scale activated sludge system: aerobic, anoxic, anoxic-aerobic, and anaerobic-anoxic-aerobic (biological excess phosphorus removal systems). The systems included a variety of configurations, with differing wastewater characteristics and operating parameters. The results suggest that good COD balances are to be expected in aerobic and anoxic-aerobic systems. Systems incorporating anaerobic zones exhibit low COD balances (less than 80%). Fermentation in the anaerobic zone apparently is implicated in this "loss" of COD. The consequences of the COD "loss" include both a significant decrease in oxygen requirements and in sludge production compared to aerobic or anoxic-aerobic systems. Possible mechanisms for the loss of COD and areas which require further study are discussed.

Key words: Activated sludge, mass balances, COD, TKN, nitrification, denitrification, biological excess phosphorus removal (BEPR), fermentation, anaerobic stabilization.

INTRODUCTION

Current understanding of activated sludge system behaviour has developed from observations on operating systems. These have been full-scale plants, pilot plants and laboratory-scale experimental systems. There is a fundamental requirement if conclusions drawn from analysis of experimental data are defensible; namely, that data gathered from the experimental system are reliable. Mass balances provide one way of checking the reliability of the data. Surprisingly this is seldom done, most likely because gathering the data to conduct these balances may necessitate additional sampling and monitoring on the experimental system, beyond that regarded as necessary for addressing a particular research problem. Also, in certain cases it may not be feasible to gather the required data; for example, on a full-scale plant with dynamic influent loading.

Two balances which often can be applied to experimental data are for chemical oxygen demand (COD) and nitrogen (N). In addition to reflecting the validity of experimental data, results of mass balance calculations can also be used to investigate process behaviour, leading to an improved understanding of the underlying mechanisms.

This paper reviews the results of COD and nitrogen mass balances on laboratory-scale activated sludge systems with a range of configurations, operating parameters, and influent wastewater characteristics. In the discussion of results, emphasis is on nutrient removal systems. In the biological excess phosphorus removal (BEPR) systems investigated in this study, the results of COD balances suggest the possibility of fermentative processes occurring in the anaerobic zone, leading to a "loss" of COD from the system.

DATABASE FOR COD AND NITROGEN MASS BALANCES

Comprehensive data are required to perform COD and N mass balances. The data set includes information on operating parameters (flows, recycle rates, sludge wastage, etc.), influent and effluent concentrations of COD, TKN, and nitrate, as well as the concentration of nitrate in each reactor, the oxygen utilization rate(s), and the volatile suspended solids (VSS) concentration of the waste sludge. In addition, the COD/VSS ratio and the TKN/VSS ratio should also be reported.

The complete data set seldom is available for systems which receive a time-varying (i.e. dynamic) input of flow and/or concentration. Also, for dynamic systems, it is necessary to consider accumulation terms in mass balance calculations; this complicates the procedure considerably. All of the systems considered in this paper were operated under "steady state" conditions as far as is practical. That is, the systems each received a fixed influent volume per day at a constant rate, and the composition of the influent was nearly uniform from day to day. Also, a fixed volume of mixed liquor was removed from the systems each day to maintain a constant sludge age (SRT, MCRT). Where municipal wastewater was used as influent, the influent was prepared by diluting high-strength wastewater to a target COD concentration for the duration of each study. Because the wastewater was drawn from the same source, the composition (TKN/COD ratio, unbiodegradable fractions, etc.) remained reasonably constant.

An important aspect regarding steady state data is that the system necessarily should be operated for an extended period (3 to 4 sludge ages) to ensure attaining a "steady" operating condition. Even under this condition there will be fluctuations in the values of monitored parameters from day to day. Therefore it is essential that data used in mass balances should be averages obtained over an extended period after attaining steady state. This will account for small fluctuations in response. Also, averaging over an extended period avoids the necessity to include accumulation terms in mass balance calculations. In the mass balances reported here the steady state data were gathered in this manner.

Data from five sources for four different types of activated sludge system were used in this investigation:

- Aerobic systems - Schroeter *et al.* (1982);
- Anoxic-only systems - McClintock *et al.* (1988);
- Anoxic-aerobic systems - Arkley & Marais (1981);
- Anaerobic-anoxic-aerobic systems - Wentzel *et al.* (1989, 1990).

COD MASS BALANCES ON EXPERIMENTAL DATA

The premise of a COD balance is that it should be possible to account for the COD entering an activated sludge system via the influent in the following fractions:

- COD (unfiltered) leaving the system in the effluent;
- COD incorporated into the sludge mass through cell synthesis, enmeshment or absorption, leaving the system in the sludge wastage stream;
- COD oxidized (i.e., the electrons which are transferred from the organic material to the electron acceptor). In purely aerobic systems this fraction can be estimated from the oxygen utilization rate (after deducting the oxygen required for nitrification). In systems incorporating anoxic zones (that is, where nitrate is present but oxygen is not), it is also necessary to account for COD oxidized through denitrification.

The assumption here is that any COD loss due to volatilization of organics is negligible. Also, it is assumed that denitrification under aerobic conditions is not significant. These aspects are discussed later.

In systems incorporating denitrification, the mass of COD oxidized through denitrification can be accounted for by estimating the equivalent amount of oxygen which would have been needed if oxygen had been the electron acceptor instead of nitrate. It has been proposed that denitrification is essentially a four step process (Payne, 1981):

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Each step may be represented by a half reaction where e^- denotes electron equivalents (COD) transferred from the organic substrate:

$$2e^- + NO_3^- + 2H^+ \rightarrow NO_2^- + H_2O$$

$$e^- + NO_2^- + 2H^+ \rightarrow NO + H_2O$$

$$2e^- + 2NO + 2H^+ \rightarrow N_2O + H_2O$$

$$2e^- + N_2O + 2H^+ \rightarrow N_2 + H_2O$$

The net reaction is obtained by combining the four equations:

$$10e^- + 2NO_3^- + 12H^+ \rightarrow N_2 + 6H_2O$$

or equivalently,

$$e^- + \frac{1}{5}NO_3^- + \frac{6}{5}H^+ \rightarrow \frac{1}{10}N_2 + \frac{3}{5}H_2O$$

Similarly, the half reaction for the reduction of oxygen is given by:

$$e^- + \frac{1}{4}O_2 + H^+ \rightarrow \frac{1}{2}H_2O$$

The above two equations imply that the transfer of 1 electron equivalent requires the reduction of 1/4 mole of oxygen or 1/5 mole of nitrate, i.e.:

$$\frac{1}{5}\text{ mole nitrate} \equiv \frac{1}{4}\text{ mole oxygen}$$
$$\frac{14}{5}\text{ g } NO_3\text{-N} \equiv \frac{32}{4}\text{ g oxygen}$$
$$1\text{ mg } NO_3\text{-N} \equiv 2.86\text{ mg oxygen}$$

The assumption here is that nitrate denitrified is converted to nitrogen gas (N_2), and that there is no release of intermediates (NO_2^-, NO, N_2O). If intermediates were released the factor of 2.86 would be lower.

A detailed description of the COD mass balance procedure is described in the appendix.

NITROGEN MASS BALANCES ON EXPERIMENTAL DATA

In general, nitrogen enters the system in the form of organic N or ammonia. The influent TKN gives a measure of the amount of these compounds present. If the system is nitrifying, the majority of the influent TKN is converted to nitrate. If the system includes unaerated zones, then denitrification will result in the conversion of a portion of the nitrate to nitrogen gas (or the intermediates discussed above). Nitrogen leaving the system in the gaseous form can be estimated by performing a nitrate balance on the unaerated reactors. A fraction of the influent TKN is also utilized in cell synthesis, leaving the system in the sludge wastage stream. Therefore, it should be possible to account for the mass of nitrogen in the influent in the following fractions

- Effluent TKN (unfiltered);
- Effluent nitrate;
- TKN of the waste sludge;
- Nitrogen converted to gaseous nitrogen through denitrification (if the system includes unaerated zones).

As with the COD balance, aerobic denitrification is not considered here. A significant amount of aerobic denitrification in a system would result in low COD and N balances.

A detailed description of the nitrogen mass balance procedure is described in the appendix.

AEROBIC SYSTEMS

Schroeter *et al.* (1982) operated four pairs of aerobic lab-scale systems at temperatures of 12 and 20°C. The systems were operated at sludge ages of 3, 8, and 20 days; two systems were operated at the 3 day sludge age for reasons discussed later. The influent consisted of domestic wastewater, diluted with tap water to a concentration of 500 mgCOD/L. All systems were single reactor systems as shown in Fig. 4.1.

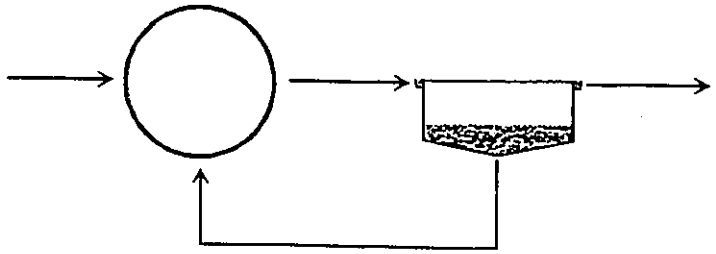

Figure 4.1 Aerobic system configuration utilized by Schroeter *et al.* (1982).

The results of mass balances for COD and N for the Schroeter *et al.* (1982) systems are listed in Table 4.1. The results are very good for all systems, regardless of whether nitrification was occurring (systems at the 3 day sludge age and 12°C were not nitrifying; all other systems nitrified fully). As the nitrogen balances are close to 100%, it is unlikely that aerobic denitrification occurred in these systems to a significant extent.

Initially only one system was operated at a 3 day sludge age; however, the COD balance obtained at 12°C was poor (81.7% *versus* N balance of 97.4%). Examination of the system indicated that inadvertent aeration due to turbulence at the reactor surface was the cause, leading to underestimates of the oxygen utilization rate. When the problem was remedied (by using a smaller stirrer paddle) two systems were operated in parallel and very good COD and N balances were obtained for both. This highlights the need for careful attention to experimental detail, and the utility of mass balances in checking the validity of experimental data.

Table 4.1: COD and nitrogen mass balances for aerobic systems [data from Schroeter *et al.* (1982)].

SYSTEM	SLUDGE AGE (d)	N BALANCE (%)		COD BALANCE (%)	
		12°C	20°C	12°C	20°C
1	3	100.2	100.5	99.6	100.4
2	3	100.2	99.5	99.7	100.2
3	8	100.2	97.5	99.6	99.9
4	20	99.2	99.4	99.4	98.4

ANOXIC-ONLY SYSTEMS

McClintock *et al.* (1988) operated lab-scale single reactor aerobic and anoxic systems in parallel at five different sludge ages. The 3 day sludge age systems were operated as flow through systems; systems at longer sludge ages were operated as single reactor systems with a baffle inserted to separate the mixed liquor zone from the sludge settling zone. Functionally the systems are shown schematically in Fig. 4.2. All systems received a synthetic sewage (primarily bacto-peptone), with nitrate and oxygen supplied in excess to the anoxic and aerobic reactors, respectively. Unfortunately, as oxygen utilization rates were not reported, COD balances cannot be conducted on the aerobic systems.

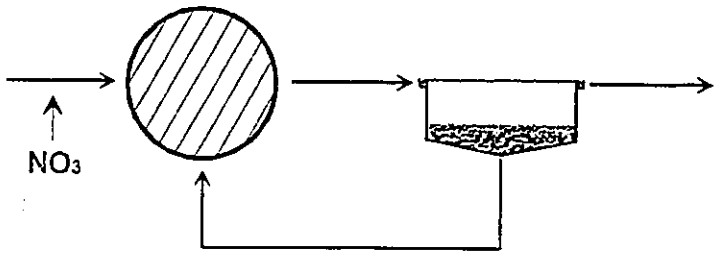

Figure 4.2 Anoxic system configuration utilized by McClintock *et al.* (1988).

Results of mass balances for COD and N for the McClintock *et al.* (1988) systems are listed in Table 4.2. COD balances on the anoxic systems ranged from approximately 95 to 85%, with a decreasing trend with increasing sludge age (except for the 15 day system); nitrogen balances are reasonable for all systems. [It should be noted that the data from the 15 day anoxic system are questionable as solids production in this system was reportedly greater than that for the 15 day aerobic system, while the other anoxic systems were observed to produce approximately 40% less solids than the corresponding aerobic systems]. Comparing these COD balance results with those for the Schroeter *et al.* (1982) aerobic systems, it appears that completely anoxic systems (especially at longer sludge ages) may exhibit poorer balances.

In considering possible explanations for the lower COD balances in anoxic systems, it is useful to consider the assumptions made in performing a COD balance on an anoxic system. The implicit assumption with an oxygen equivalence factor of 2.86 for nitrate

denitrified is that denitrification is complete. If denitrification intermediates such as nitric oxide (NO) or nitrous oxide (N_2O) were released to the atmosphere, fewer electrons would be transferred per unit nitrate denitrified, and the equivalence factor would be lower than 2.86. If this were the case, the actual COD balance would be even lower than that calculated using a factor of 2.86. As these anoxic systems tend to have low COD balances, it seems unlikely that the release of denitrification intermediates is a major factor; therefore other possible causes for the lower COD balances should be considered (these are discussed later).

Table 4.2: COD and nitrogen mass balances for anoxic and aerobic systems [data from McClintock *et al.* (1988)].

SYSTEM	TYPE	SLUDGE AGE (d)	N BALANCE (%)	COD BALANCE (%)
1	Aerobic	1.5	107.9	Not available
2	Aerobic	3.0	99.9	Not available
3	Aerobic	6.0	103.3	Not available
4	Aerobic	10.0	96.0	Not available
5	Aerobic	15.2	98.8	Not available
6	Anoxic	1.5	95.5	94.7
7	Anoxic	3.0	98.3	94.4
8	Anoxic	6.1	95.4	91.0
9	Anoxic	9.6	95.9	85.5
10	Anoxic	15.1	98.0	93.6

ANOXIC-AEROBIC SYSTEMS

Arkley & Marais (1981) operated lab-scale aerobic, pre-denitrification, and post-denitrification systems. All systems were operated at a 20 day sludge age with municipal wastewater as influent. System 1 (operated as a control) was a single reactor aerobic system (Fig. 4.1). Systems 2, 3 and 4 were two-in-series reactor configurations operated in three possible modes: (i) both reactors aerated; or (ii) first reactor unaerated (pre-denitrification); or (iii) second reactor unaerated (post-denitrification). The pre- and post-denitrification system configurations are shown in Fig. 4.3. Data for the experimental study were reported for a number of phases corresponding to different operating modes. For example, System 2 was operated sequentially in a post-denitrification, a pre-

denitrification, and a fully aerobic mode in phases I, II and III, respectively (see Table 4.3). Table 4.3 also lists the unaerated volume (or mass) fractions for phases with unaerated reactors.

An important feature of the data is the nitrate concentration in the unaerated reactor in systems operated in the pre-denitrification mode. For System 2 (phase II, with an unaerated volume fraction of 0.4) the nitrate concentration in the unaerated reactor was approximately 14 mgN/L; that is, the reactor was *anoxic*. For System 4 (phases II and IV, with a larger unaerated volume fraction of 0.7) the nitrate concentration in the unaerated reactor was essentially zero; that is, the reactor was *anaerobic*.

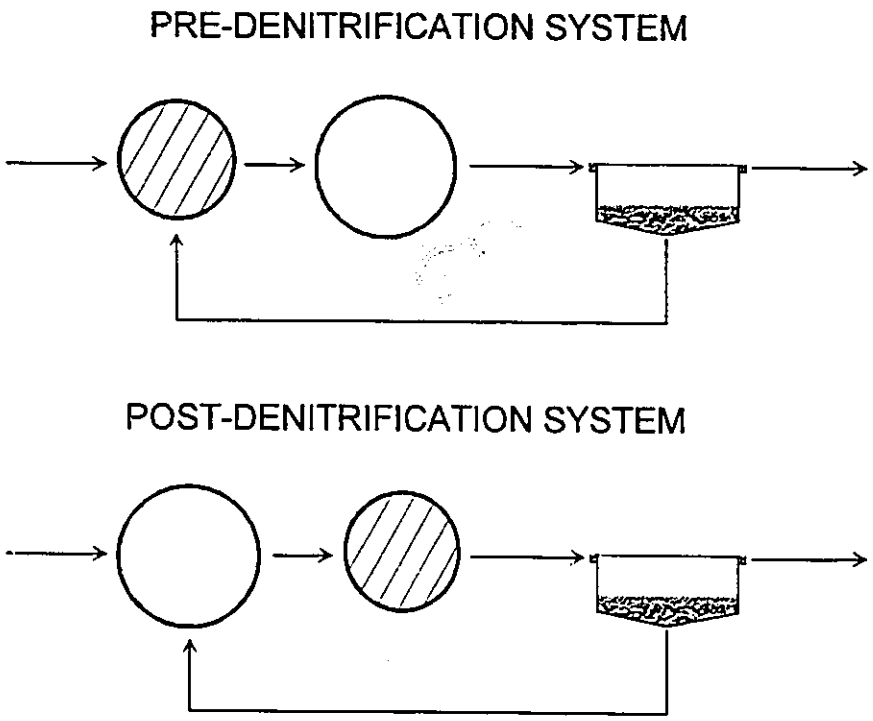

Figure 4.3 **Pre- and post-denitrification system configurations utilized by Arkley & Marais (1981).**

Results of mass balances for COD and N for the Arkley & Marais (1981) systems are listed in Table 4.3. Balances were performed only for those phases where the systems appeared to be at steady state. The following features are evident:

- COD balances on completely aerobic systems average approximately 95 %.

- The pre-denitrification system with an anoxic reactor (as opposed to anaerobic) exhibits a COD balance close to 100% [96.7% - System 2, phase II].

- The post-denitrification system with an anoxic reactor (as opposed to anaerobic) also exhibits a COD balance close to 100% [97.7% - System 2, phase I].

- The pre-denitrification systems which maintained essentially anaerobic conditions in the unaerated reactor both exhibit COD balances below 80 % [System 4, phases II and IV].

- The operating mode for System 4 sequentially was changed from pre-denitrification to fully aerobic and then returned to pre-denitrification.in phases II, III and IV, respectively. The nitrate concentration in the unaerated reactor for phases II and IV achieved a steady state value of zero. The COD balance changed from 77.3 to 98.1 to 74.2% as the operating mode changed.

- Nitrogen balances for all phases average close to 100%.

These observations suggest that COD balances for both aerobic and anoxic-aerobic systems should be close to 100%. However, when an anaerobic condition exists in the system, the calculated COD balance is significantly lower; this phenomenon is discussed later.

Table 4.3: COD and nitrogen mass balances for aerobic and anoxic-aerobic systems [data from Arkley & Marais (1981)].

SYSTEM	PHASE	TYPE	UNAERATED FRACTION	N BALANCE (%)	COD BALANCE (%)
1	I	Aerobic	0	99.0	92.7
1	II	Aerobic	0	93.4	95.8
1	III	Aerobic	0	99.4	94.2
2	I	Postdenitrification	0.40	99.2	97.7
2	II	Predenitrification	0.40	110.4	96.9
2	III	Aerobic	0	102.3	96.5
3	III	Aerobic	0	100.4	95.3
4	II	Predenit.- anaerobic	0.70	105.5	77.3
4	III	Aerobic	0	102.1	98.1
4	IV	Predenit.- anaerobic	0.70	93.5	74.2

ANAEROBIC-ANOXIC-AEROBIC SYSTEMS

Wentzel *et al.* (1990) provide comprehensive data for 30 lab-scale nutrient removal systems treating municipal wastewater. These systems varied in configuration, reactor sizes, recycle ratios, influent flowrates, and were operated over a range of sludge ages from 3 to 21 days. There were five basic configurations as shown in Fig. 4.4: Phoredox, 3-stage Bardenpho, Johannesburg, University of Cape Town (UCT), and the modified UCT (MUCT) configuration. Data were reported for each system for a number of different batches of influent wastewater (denoted by a letter appended to the system number in Table 4.4). In addition, Wentzel *et al.* (1989) reported data for four different lab-scale enhanced culture BEPR systems with acetate as influent. The enhanced cultures (greater than 90% polyP organisms) were developed using modified Bardenpho and UCT systems operated at sludge ages of 7.5, 10 and 20 days.

Mass balances for COD and N were conducted on the data sets for which all the relevant data were reported; in certain instances VSS data was omitted and it was not possible to calculate balances. In certain of the remaining cases for the mixed culture systems treating municipal wastewater, the validity of the data was questionable. This was generally reflected by very poor N balances; for example, balances of 200% output N compared to input N. Those data sets were not considered here. Table 4.4 presents results of COD

and N mass balance calculations for the mixed culture systems with N balances between 90 and 110%, as well as the enhanced culture systems. The following observations are noted:

- COD balances on the BEPR systems treating municipal wastewater are generally substantially lower than those for the non-BEPR systems described earlier (some systems show balances below 70%).

- The average of the COD balances for the mixed culture BEPR systems with municipal wastewater as influent is only 78%.

- COD balances for the enhanced culture systems with acetate as influent are all close to the average of 91% for these systems.

- N balances for both the mixed culture and the enhanced culture BEPR systems are close to 100%.

These results suggest that the presence of an anaerobic zone may lead to an appreciable reduction in the calculated COD balance for systems with a fermentable substrate (such as domestic wastewater).

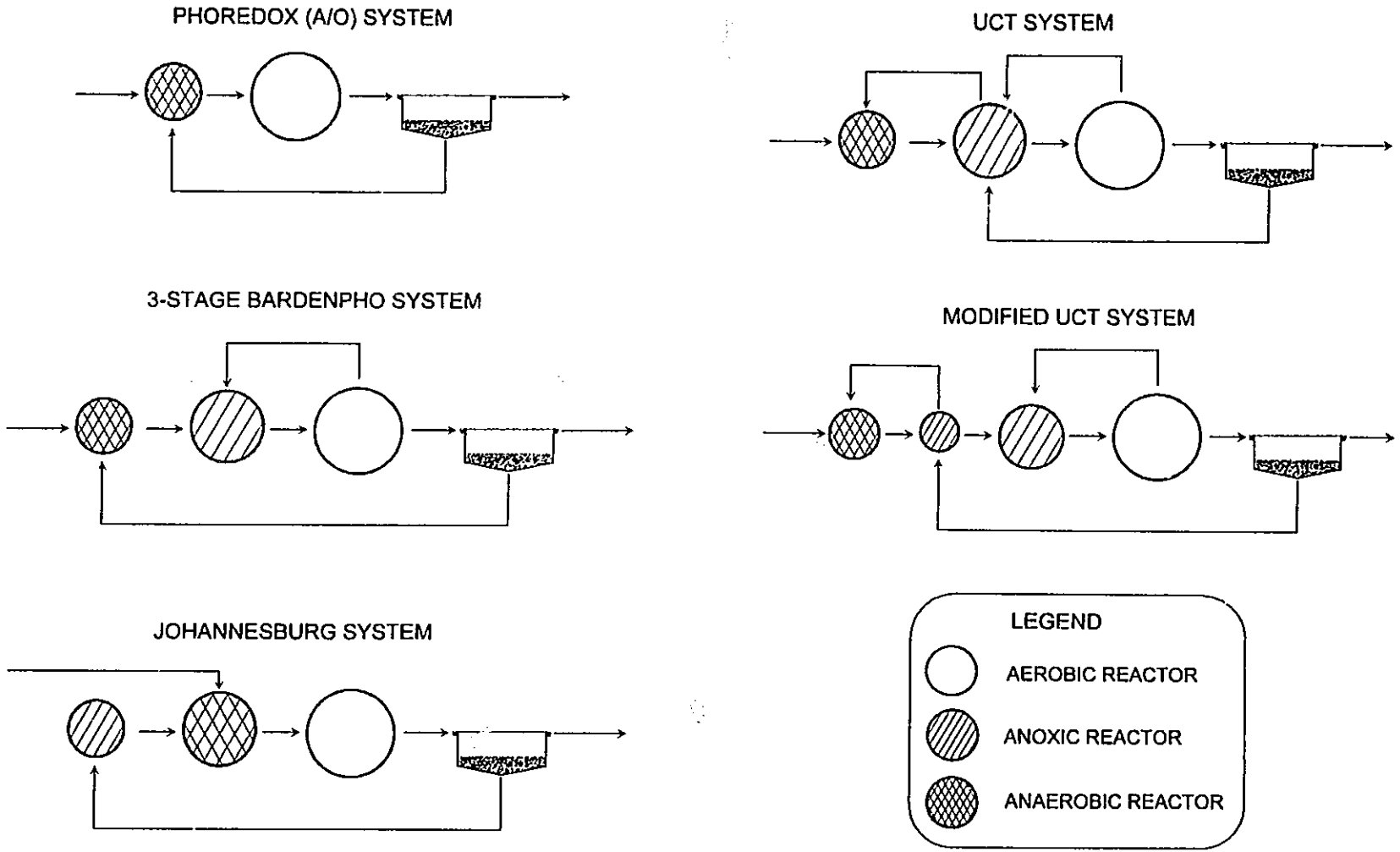

Figure 4.4 NDBEPR system configurations for which Wentzel *et al.* (1989,1990) reported data.

Table 4.4: COD and nitrogen mass balances for BEPR systems [data from Wentzel *et al.* (1989, 1990)].

SYSTEM	TYPE*	SLUDGE AGE (d)	N BALANCE (%)	COD BALANCE (%)
SYSTEMS WITH MUNICIPAL WASTEWATER AS INFLUENT				
1a	Phoredox	3	93.9	79.4
1b	Phoredox	3	109.8	64.6
2a	Phoredox	4	95.7	85.6
5a	Jhb	5	103.3	81.3
6a	UCT	6	97.5	67.0
8a	UCT	8	99.2	89.7
10b	UCT	8	110.0	74.1
11a	UCT	10	98.0	70.0
16a	MUCT	15	95.2	85.5
18a	MUCT	15	98.6	83.2
19b	MUCT	15	96.8	74.2
19c	MUCT	15	94.6	85.4
22a	MUCT	20	103.9	65.3
22b	MUCT	20	97.6	77.8
23a	MUCT	20	95.1	73.2
23b	MUCT	20	92.1	86.9
23c	MUCT	20	100.3	87.6
24a	MUCT	20	100.2	60.7
24c	MUCT	20	92.4	80.0
24d	MUCT	20	93.4	84.3
26a	MUCT	21	102.8	85.2
		Averages	98.6	78.1
ENHANCED CULTURE SYSTEMS WITH ACETATE AS INFLUENT				
1	Bardenpho	20	103.6	88.9
2	UCT	10	103.1	91.1
3	Bardenpho	10	88.6	90.4
4	Bardenpho	7.5	95.9	92.3
		Averages	97.8	90.7

DISCUSSION

The following points summarize the results for COD and N balances conducted on the four types of activated sludge system:

- COD balances on the completely aerobic systems are close to 100%.

- COD balances on the anoxic-only systems range from 95 to 85%, possibly with a decreasing trend as the sludge age increases.

- The anoxic-aerobic systems which did not exhibit anaerobic conditions show COD balances close to 100%, while those in which the unaerated reactor nitrate concentration dropped to zero have balances less than 80%.

- The average of the COD balances for the mixed culture BEPR systems with municipal wastewater as influent is only 78%. The average for the enhanced culture BEPR systems with acetate as influent is 91%.

- Nitrogen balances for all systems are close to 100%. This would indicate that nitrogen loss through denitrification under aerobic conditions was not significant for these systems.

The most significant finding is that for systems incorporating anaerobic zones (i.e. BEPR systems) the COD balances, averaging less than 80%, do not account for a substantial portion of the influent COD.

This apparent "loss" of COD in BEPR systems with anaerobic zones has been reported previously, for example, by Burke *et al.* (1986) in a study on short sludge age BEPR systems. Bordacs and Tracy (1988) observed that the presence of an anaerobic zone leads to as much as a 30% reduction in oxygen requirements compared to a conventional aerobic process. However, the study was based on the assumption that the reduction in oxygen consumption is due to the retention of organic storage products (such as PHB) by the polyP organisms, and COD measurements were not made. Dold (1990) noted that, unless COD loss associated with anaerobic fermentation was taken into account, BEPR activated sludge models over predict both oxygen consumption rates in aerated zones of BEPR systems and volatile suspended solids production.

A requisite for BEPR is the presence of an anaerobic zone which allows the polyP organisms to sequester short chain fatty acids (SCFA) such as acetate. These SCFA are stored by the organisms in the form of PHB until an electron acceptor is available. The stored PHB is then used for growth and P uptake.

Generally the influent waste contains only a very low concentration of SCFA; therefore the SCFA necessary for BEPR must be produced within the system, likely in the anaerobic reactor through a fermentative process. The production of SCFA under anaerobic conditions has been observed by Meganck *et al.* (1985). It was noted that significant numbers of the bacteria *Aeromonas hydrophila*, a facultative organism capable of utilizing some sugars and alcohols under anaerobic conditions, were present in sludge from a lab-scale BEPR system. Production of SCFA in the anaerobic zone of BEPR systems presumably results from the fermentation of the "complex" readily biodegradable COD in the influent (i.e., the SCFA are produced via the oxidation of the influent complex readily biodegradable COD using an internally supplied organic compound as the oxidizing agent). This hypothesis is supported by the work of Bordacs and Chiesa (1989) who used radiolabelled substrates (glucose and acetate) to track the carbon flow in phosphorus accumulating cultures. Results indicated that a greater percentage of the labelled carbon was converted to carbon dioxide under anaerobic conditions when glucose was the labelled substrate compared to acetate (12% and 2%, respectively).

The "loss" of COD in BEPR systems most likely is associated with the fermentation process occurring in the anaerobic zone. However, a full understanding of the fermentation behaviour does not exist. It has been suggested that the COD "loss" is due to release of gaseous fermentation products (excluding carbon dioxide which does not have a COD).

Burke *et al.* (1986) suggested that generation of hydrogen gas occurs during the acidogenesis process in the anaerobic reactor. Many facultative organisms have been documented that are capable of fermenting glucose to produce hydrogen and carbon dioxide gases (Stanier *et al.*, 1976). Among these are some species of the genus *Aeromonas*, mentioned earlier as one of the organisms found to occur in significant numbers in BEPR pilot plants (Meganck *et al.*, 1985, Malnou *et al.*, 1984).

A possible alternative to hydrogen as a gaseous COD loss would be generation of methane during fermentation. For the systems investigated in this study, theoretically methane production should not have been possible due both to the temperature at which these pilot plant systems were operated (20°C), and the fact that methanogenic bacteria are obligate anaerobes (Stanier, 1976) and would not likely survive the anaerobic/aerobic sequencing. However, this possibility should not be ignored as methanogenic bacteria capable of tolerating low oxygen concentrations have been documented (Grady and Lim, 1980).

An alternative theory to explain the significant disappearance of COD in BEPR systems is the hypothesis that fermentation in the anaerobic reactor results in the production of volatile compounds, which are then released from the system under aerobic conditions. The production of volatile compounds (such as ethanol, acetic acid, and other volatile fatty acids) under oxygen limited conditions has been documented for a number of facultative organisms (Stanier *et al.*, 1976, Vollbrecht, 1982). A recent study by Wable and Randall (1992) proposed that this is a more probable mechanism for COD loss than that of hydrogen or methane generation. However, the volatilization mechanism seems unlikely as these readily biodegradable components should be removed from solution prior to the aerated zone.

Aside from the observations on BEPR systems treating municipal wastewater, this study has identified two additional aspects which require further research:

- Results from anoxic-only systems indicate that COD "loss" occurs to a limited extent in these systems; this may also be associated with fermentation. Generally the perception is that fermentation should not occur in anoxic zones of activated sludge systems. However, fermentation has been observed in the presence of nitrate in pure culture studies (Hadjipetrou & Stouthamer, 1965; Stouthamer & Bettenhausen, 1972).

- In the enhanced culture systems with acetate as influent the COD balances do not account for approximately 10% of the input COD. Fermentation in these systems should be minimal. The COD "loss" possibly is associated with the process of PHB formation.

CONCLUSIONS

The results of this study suggest that while good COD balances are to be expected in aerobic and aerobic-anoxic systems, systems incorporating anaerobic zones (i.e. BEPR systems) tend to exhibit low COD balances (less than 80%). This "loss" of COD apparently is associated with the fermentation processes occurring in the anaerobic zone of BEPR systems treating municipal wastewater. Whether this COD loss is a direct result of fermentation (through the generation of gas which evolves during the actual fermentation process), or an indirect result (through the production of volatile compounds which are released from the system under aerated conditions), remains to be determined.

Irrespective of the reason(s) for the COD "loss", this phenomenon has significant implications with regards to reduced aeration costs and sludge production in BEPR *versus* conventional activated sludge systems. If the causes of this loss of COD can be determined, it may be possible to design and/or operate systems so as to maximize COD loss thereby reducing the cost of aeration and sludge treatment/disposal.

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APPENDIX TO CHAPTER FOUR: COD & N BALANCE CALCULATIONS

I List of Symbols

Symbol	Description
Q	Average influent flowrate [L/d]
q	Average wastage flowrate [L/d]
S_{Ti}	Total influent COD [mgCOD/L]
S_{Te}	Total effluent COD [mgCOD/L]
f_{CV}	COD/VSS ratio [mgCOD/mgVSS]
X_V	Mixed liquor volatile suspended solids of waste stream [mgVSS/L]
O_T	Total oxygen utilization rate [mgO/L/hr]
MO_N	Mass of oxygen consumed for nitrification [mgO/d]
V_{aer}	Volume of aerobic reactor [L]
N_{Ti}	Average influent TKN [mgN/L]
N_{Te}	Average effluent TKN [mgN/L]
N_{Ne}	Average effluent nitrate [mgNO3-N/L]
$N_{N,aer}$	Average aerobic nitrate [mgNO3-N/L]
$N_{N,anox}$	Average anoxic nitrate [mgNO3-N/L]
$N_{N,anaer}$	Average anaerobic nitrate [mgNO3-N/L]
f_N	Nitrogen fraction of waste sludge [mgN/mgVSS]
s	Settler underflow recycle ratio with respect to influent flowrate
r	Anoxic mixed liquor recycle ratio
a	Nitrified/aerobic mixed liquor recycle ratio
$M_{denit,anox}$	Mass of nitrate denitrified in the anoxic zone [mgN/d]
$M_{denit,anaer}$	Mass of nitrate denitrified in the anaerobic zone [mgN/d]
$M_{denit,T}$	Total mass of nitrate denitrified in the system [mgN/d]
$M_{COD,effl}$	Mass of COD in the system effluent [mgCOD/d]
$M_{COD,was}$	Mass of COD in the wastage stream [mgCOD/d]
$M_{COD,aer}$	Mass of COD oxidized under aerobic conditions [mgCOD/d]
$M_{COD,denit}$	Mass of COD oxidized through denitrification [mgCOD/d]
$M_{COD,oxid}$	Total mass of COD oxidized in the system [mgCOD/d]
$M_{N,Ne}$	Mass of nitrate-nitrogen in the system effluent [mgN/d]

$M_{N,Te}$ Mass of TKN in the system effluent [mgN/d]
$M_{N,was}$ Mass of nitrogen in the wastage stream [mgN/d]

II Denitrification Calculations

In nitrifying systems with unaerated zones, in order to perform both COD and N balances, the mass of nitrate which is denitrified in each of the unaerated reactors must be determined from a mass balance on nitrate. Referring to Fig. 4.5, for a UCT type system, the mass of nitrate entering the anoxic reactor per day is given by:

$$\text{Input nitrate} = a\,Q\,N_{N,aer} + s\,Q\,N_{Ne} + (1+r)\,Q\,N_{N,anaer}$$

Similarly, the mass of nitrate leaving the anoxic reactor is given by:

$$\begin{aligned}\text{Output nitrate} &= r\,Q\,N_{N,anox} + (1+s+a)\,Q\,N_{N,anox} \\ &= (1+r+s+a)\,Q\,N_{N,anox}\end{aligned}$$

The mass of nitrate denitrified per day ($M_{denit,anox}$) is equal to the difference between the input and output nitrate:

$$M_{denit,anox} = a\,Q\,N_{N,aer} + s\,Q\,N_{Ne} + (1+r)\,Q\,N_{N,anaer} - (1+r+s+a)\,Q\,N_{N,anox} \quad (1)$$

As a small quantity of nitrate will often be inadvertently recycled to the anaerobic reactor, any denitrification occurring in the anaerobic reactor should also be included in mass balance calculations. For a UCT system with one anaerobic reactor (assuming no nitrate in the influent), this is given by:

$$M_{denit,anaer} = r\,Q\,N_{N,anox} - (1+r)\,Q\,N_{N,anaer} \quad (2)$$

The total mass of nitrate denitrified per day in the system is therefore the sum of the mass denitrified in the anaerobic reactor, and the mass denitrified in the anoxic reactor, i.e.:

$$M_{denit,T} = M_{denit,anox} + M_{denit,anaer} \quad (3)$$

III COD Balance Calculations

To perform a COD balance on a system, it is necessary to estimate the mass of COD in the effluent, the COD of the waste sludge, and the amount of COD oxidized. If the effluent COD is known, the mass of COD in the effluent is simply:

$$M_{COD,effl} = Q S_{Te} \quad (4)$$

Similarly, if the volatile suspended solids concentration of the waste sludge (X_V) is known, then by assuming a value of 1.48 mgCOD/mgVSS for f_{CV}, the mass of COD wasted is given by:

$$M_{COD,was} = q X_V f_{CV} \quad (5)$$

Ideally, the COD/VSS ratio f_{CV} should be determined experimentally for a particular sludge; however, the value of 1.48 mgCOD/mgVSS has been shown to be a good approximation over a range of sludge ages and wastewater characteristics (Schroeter *et al.*, 1982).

In a purely aerobic system, the amount of COD oxidized is determined from the oxygen utilization rate, after deducting the oxygen required for nitrification. This can be done by assuming the somewhat simplified relationship:

$$NH_4^+ + 2\,O_2 \rightarrow NO_3^- + 2\,H^+ + H_2O \quad (6)$$

Equation (6) implies that 1 mole of ammonia requires 2 moles of oxygen to form one mole of nitrate. Taking molecular weights into account, this implies that 14 mgNH_4-N require 64 mg oxygen, or equivalently, if x mg/L of NO_3-N are formed, then 4.57*x mgO/L are consumed. In a purely aerobic system, the mass of nitrate formed is given by the product of the influent flowrate and the effluent nitrate concentration (N_{Ne}). For systems incorporating denitrification, the mass of nitrate formed is given by:

$$\text{Mass nitrate formed} = M_{denit,T} + Q\,N_{Ne}$$

Thus the mass of oxygen consumed due to nitrification (MO_N) is given by:

$$MO_N = (M_{denit,T} + Q\,N_{Ne})\,4.57 \qquad (7)$$

Therefore the total mass of COD oxidized per day under aerobic conditions ($M_{COD,aer}$), is given by:

$$\begin{aligned} M_{COD,aer} &= O_T\,V_{aer}\,24 - MO_N \\ &= O_T\,V_{aer}\,24 - (M_{denit,T} + Q\,N_{Ne})\,4.57 \end{aligned} \qquad (8)$$

Although Eq. (6) represents a simplification of the actual reactions mediated by the nitrifying organisms *Nitrosomonas* and *Nitrobacter*, the error introduced by this simplification should be minimal (Grady & Lim, 1980).

In systems incorporating unaerated zones, such as the UCT design, the mass of COD oxidized through denitrification must also be taken into account in the COD balance. This is done by using the equivalence factor of 2.86 outlined earlier.

Thus if $M_{denit,T}$ is the total mass of nitrate denitrified per day, then the total COD consumed through denitrification is given by:

$$M_{COD,denit} = 2.86\,M_{denit,T} \qquad (9)$$

Therefore the total amount of COD oxidized in a system incorporating both nitrification and denitrification, is given by:

$$\begin{aligned} M_{COD,oxid} &= M_{COD,denit} + M_{COD,aer} \\ &= 2.86\,M_{denit,T} + O_T\,V_{aer}\,24 - (M_{denit,T} + QN_{Ne})\,4.57 \end{aligned} \qquad (10)$$

The total amount of "output" COD can therefore be determined from the sum of $M_{COD,effl}$, $M_{COD,was}$, and $M_{COD,oxid}$, using Eqs. (4), (5), and (10), as well as the estimate for $M_{denit,T}$

obtained from mass balances on nitrate around the unaerated reactors (as described earlier for the UCT system), i.e.:

$$\text{Output COD} = M_{COD,effl} + M_{COD,was} + M_{COD,oxid} \quad (11)$$

The total mass per day of "input" COD is given by the product of the influent flowrate and the influent COD, i.e.:

$$\text{Input COD} = Q\,S_{Ti} \quad (12)$$

Thus the % COD balance is given as:

$$\%\ \text{COD balance} = \left(\frac{\text{Output COD}}{\text{Input COD}}\right)100$$

IV Nitrogen Balance Calculations

To perform a nitrogen balance on a system, it is necessary to estimate the mass of nitrate in the effluent, the mass of effluent TKN (unfiltered), the mass of TKN in the waste sludge, and the nitrogen loss through denitrification.

In terms of the variables defined earlier, the mass of nitrate in the effluent ($M_{N,Ne}$) is given by:

$$M_{N,Ne} = Q\,N_{Ne} \quad (13)$$

Similarly, the mass of TKN in the effluent ($M_{N,Te}$) is given by:

$$M_{N,Te} = Q\,N_{Te} \quad (14)$$

To estimate the mass of N in the waste sludge, a value for f_N, the nitrogen fraction of the sludge, must be assumed. Experimental evidence suggests a value of 0.1 mgN/mgVSS is reasonable over a range of sludge ages (WRC, 1984); however, ideally f_N should be

determined experimentally for a particular system and set of operating parameters. Given a value for f_N, the mass of N in the waste sludge ($M_{N,was}$) is calculated from:

$$M_{N,was} = q X_V f_N \quad (15)$$

In section II the method was outlined for estimating the mass of NO_3-N which is denitrified in the unaerated reactors. For a UCT system, $M_{denit,T}$ is calculated using Eqs. (1), (2), and (3).

The total output N is therefore the sum of $M_{N,Ne}$, $M_{N,Te}$, $M_{N,was}$, and $M_{denit,T}$, which can be calculated using Eqs. (13), (14), and (15), as well as the estimate for $M_{denit,T}$ obtained from a mass balance on nitrate, i.e.:

$$\text{Output N} = M_{N,Ne} + M_{N,Te} + M_{N,was} + M_{denit,T} \quad (16)$$

The total mass per day of input N is given by the product of the influent flowrate and the influent TKN (assuming zero nitrate in the influent), i.e.:

$$\text{Input N} = Q N_{Ti} \quad (17)$$

Therefore the % N balance is given as:

$$\% \text{ N balance} = \left(\frac{\text{Output N}}{\text{Input N}}\right) 100$$

Using System 6a from Wentzel *et al.* (1990) as an example, the following section outlines the mass balance procedure.

V COD and N Balances - *Example Calculations*

The data necessary for performing N and COD balances for System 6a are listed in Table 4.5 below. System 6a is a UCT configuration with two aerobic reactors, one anoxic, and one anaerobic reactor as shown below.

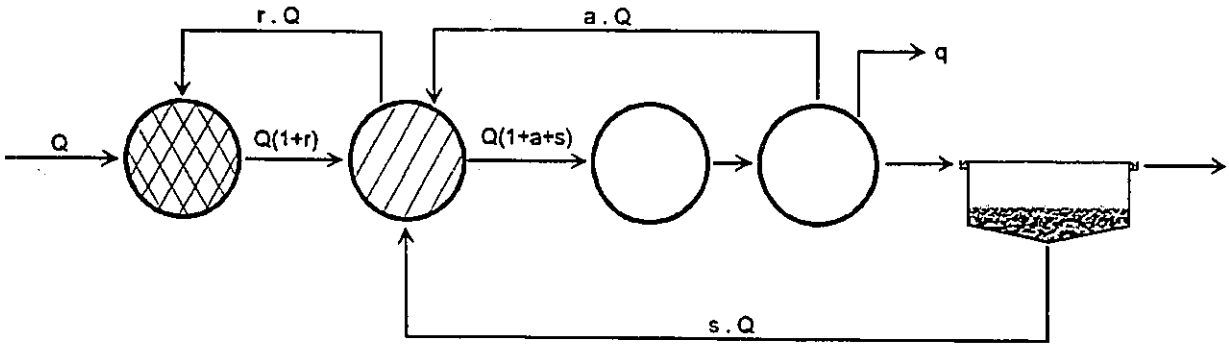

Figure 4.5 UCT system 6A configuration [from Wentzel *et al.* (1990)].

Table 4.5: Steady state data for the four-reactor UCT System 6a [data from Wentzel *et al.* (1990)].

Reactor volumes (L)	Anaerobic	2.0	Influent flowrate (L/d)	25
	Anoxic	2.0	r recycle ratio	1
	Aerobic	2.0	s recycle ratio	1
	Aerobic	2.0	a recycle ratio	1
			Wastage rate (L/d)	1.174

Parameter	Influent	Anaerobic	Anoxic	Aerobic	Aerobic	Effluent
COD (mg/L)	510	-	-	-	-	40
TKN (mgN/L)	42	-	-	-	-	4
NO_3 (mgN/L)	0.0	0.5	1.5	9.4	10.6	10.5
OUR (mg/L/h)	-	-	-	78	43	-
VSS (mg/L)	-	-	-	-	2100	-

Denitrification Calculations

The mass of NO_3-N denitrified in the anoxic reactor is given by Eq. (1):

$$M_{denit,anox} = 402.5 \text{ mgN/d}$$

The mass of NO_3-N denitrified in the anaerobic reactor is obtained from Eq. (2):

$$M_{denit,anaer} = 12.5 \text{ mgN/d}$$

The total mass of NO_3-N denitrified in the system is the sum of $M_{denit,anox}$ and $M_{denit,anaer}$ [Eq. (3)]:

$$M_{denit,T} = 415 \text{ mgN/d}$$

COD Balance Calculations

From Eq. (4), the mass of COD in the effluent is:

$$M_{COD,effl} = 1000 \text{ mgCOD/d}$$

The mass of COD in the waste sludge is calculated using Eq. (5):

$$M_{COD,was} = 3649 \text{ mgCOD/d}$$

Using Eq. (10), and the value for $M_{denit,T}$ calculated above, the mass of COD oxidized is:

$$M_{COD,oxid} = 3899 \text{ mgCOD/d}$$

The total output COD is the sum of the above three terms [or Eq. (11)]:

$$\text{Output COD} = 8548 \text{ mgCOD/d}$$

Applying Eq. (12) gives:

$$\text{Input COD} = 12750 \text{ mgCOD/d}$$

Therefore, the % COD balance is given by:

$$\begin{aligned} \%\ \text{COD balance} &= (\text{Output COD} / \text{Input COD}) * 100 \\ &= (8548/12750) * 100 \\ &= 67.0\ \% \end{aligned}$$

The results of the COD balance for System 6a are shown in Table 6 below.

Table 4.6: COD balance calculations for System 6a [data from Wentzel *et al.* (1990)].

INPUT COD (mg COD / d)			OUTPUT COD (mg COD / d)	
$Q\,S_{Ti}$		12750	$M_{COD,\,effl}$	1000
			$M_{COD,\,was}$	3649
			$M_{COD,\,oxid}$	3899
	Total	12750	*Total*	8548
% COD Balance = 67.0 %				

Nitrogen Balance Calculations

Referring to Eq. (13), the mass of NO_3-N in the effluent is:

$$M_{N,Ne} = 263 \text{ mgN/d}$$

From Eq. (14), the mass of TKN in the effluent is:

$$M_{N,Te} = 100 \text{ mgN/d}$$

The mass of N leaving with the waste sludge is given by Eq. (15):

$$M_{N,was} = 247 \text{ mgN/d}$$

The total output N is then calculated by summing the above values, together with $M_{denit,T}$ calculated earlier [i.e. Eq. (16)], giving:

$$\text{Output N} = 1024 \text{ mgN/d}$$

Equation (17) is used to calculate the total input N:

$$\text{Input N} = 1050 \text{ mgN/d}$$

Therefore, the % N balance is given by:

$$\begin{aligned} \%\text{ N balance} &= (\text{Output N} / \text{Input N}) * 100 \\ &= (1024 / 1050) * 100 \\ &= 97.5\ \% \end{aligned}$$

The results of the nitrogen balance for System 6a are shown in Table 4.7 below.

Table 4.7: Nitrogen balance calculations for System 6a [data from Wentzel *et al.* (1990)].

INPUT N (mg N / d)			OUTPUT N (mg N / d)		
$Q\,N_{Ti}$		1050	$M_{N,ne}$		263
			$M_{N,Te}$		100
			$M_{N,was}$		247
			$M_{denit,T}$		415
	Total	1050		*Total*	1024
% N Balance = 97.5 %					

CHAPTER FIVE

DENITRIFICATION BEHAVIOUR IN BIOLOGICAL EXCESS PHOSPHORUS REMOVAL ACTIVATED SLUDGE SYSTEMS

This chapter contains the complete text of a paper to be published in *Water Research* (accepted in September, 1994). The full reference is unknown at this time.

DENITRIFICATION BEHAVIOUR IN BIOLOGICAL EXCESS PHOSPHORUS REMOVAL ACTIVATED SLUDGE SYSTEMS

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Abstract

A literature review of denitrification behaviour in biological excess phosphorus removal (BEPR) activated sludge systems was performed. Wentzel *et al.* (1989a,b) excluded denitrification by polyP organisms in modelling the BEPR process as observations indicated that minimal denitrification ocurred in laboratory systems comprised mainly of polyP organisms. In contrast, results of microbiological studies and many continuous and batch reactor experimental studies reviewed here indicate that a significant fraction of the polyP organisms can use nitrate as an electron acceptor in the absence of oxygen for oxidation of stored PHB and simultaneous uptake of phosphorus. Quantifying the extent of denitrification by polyP organisms in a particular system requires further information on factors determining the fraction of organisms capable of denitrification and the stoichiometry of the process.

Key words: Activated sludge, biological excess phosphorus removal (BEPR), denitrification.

INTRODUCTION

Conflicting evidence exists in the literature concerning the fate of nitrate in biological excess phosphorus removal (BEPR) systems. It is accepted widely that the introduction of nitrate to the anaerobic zone is detrimental to the phosphorus (P) removal process, and a number of BEPR systems have been designed with this in mind. The current interpretation of this phenomenon is that nitrate entering the anaerobic zone will be utilized as an electron acceptor in the growth of non-polyP heterotrophs. This reduces the amount of substrate available for sequestration by the polyP organisms, and hence reduces the amount of P removal that can be achieved. This interpretation does not consider the behaviour of the polyP organisms directly. The implied assumption has been that the polyP organisms are unable to utilize nitrate as an electron acceptor, and hence there is no competition for substrate between the polyP and non-polyP organisms under anoxic conditions. Observations by Wentzel *et al.* (1989a) have provided support for this conclusion:

- Continuous flow enhanced culture systems comprised mainly of polyP organisms (Bardenpho and UCT configurations) showed low nitrate removal.

- Generally a net release of P rather than uptake was observed in the anoxic zones of the enhanced culture systems.

- Batch tests simulating the conditions in an anoxic enhanced culture reactor indicated the rate of denitrification was low compared to the rate for heterotrophic organisms from mixed culture systems treating municipal wastewater under similar conditions.

Wentzel *et al.* (1989a,b) concluded that only a small fraction of the polyP organisms have the capacity for denitrification; hence denitrification was excluded from their polyP model. However, a number of factors regarding the Wentzel *et al.* enhanced culture systems suggest this decision should be re-examined:

- Denitrification accounted for the removal of a significant fraction of the influent COD (between 15 and 20 %) in the enhanced culture continuous flow systems. If

it is assumed that all the denitrification was due to the small number of non-polyP heterotrophs present, then the rate of denitrification calculated based on the mass of these organisms would seem excessively high.

- The nitrate removal rates per mg of VSS [mass of NO_3-N removed per day per unit reactor volume divided by the reactor VSS concentration, *i.e.* units of $mgNO_3$-N $(mgVSS)^{-1}$ d^{-1}] in the anoxic reactors of the enhanced culture systems do not differ substantially from corresponding rates in mixed culture systems (BEPR and non-BEPR) treating municipal wastewater and operated at similar sludge ages. For example, the enhanced culture system operated at a 20 day sludge age exhibited nitrate removal rates of 0.028 and 0.005 $mgNO_3$-$N(mgVSS)^{-1}$ d^{-1} in the two unaerated reactors, and the mixed culture system operated at a 20 day sludge age by Arkley and Marais (1981) exhibited nitrate removal rates of 0.027 and 0.015 $mgNO_3$-N $(mgVSS)^{-1}$ d^{-1} depending on the system configuration (pre- or post-denitrification, respectively). Nitrate removal rates for a range of systems are listed in Table 5.1. For all these systems, the nitrate concentration in the anoxic reactor was 1 mg/L or greater. Rates are reported for the first anoxic reactor only for the case of multiple anoxic reactor systems. [It should be recognized that the anoxic reactors in the different system configurations received different soluble substrate loadings; this also causes variations in nitrate removal rates].

- The influent TKN/COD ratio for the enhanced culture systems was relatively low (approximately 0.06 mgN/mgCOD). Consequently the nitrate load on the unaerated reactors was very low. The limited exposure of organisms to nitrate in the unaerated zones possibly resulted in the selective growth of a polyP organism population not having the capability for denitrification

Table 5.1: Nitrate removal rates for laboratory scale nutrient removal systems [data from Wentzel *et al.* (1989a, 1990), Arkley & Marais (1981)].

System*	Type	Sludge age (d)	Nitrate removal rate ($mgNO_3$-N $(mgVSS)^{-1}$ d^{-1})
Systems with municipal wastewater as influent			
5a	Jhb	5	0.045
6a	UCT	6	0.096
8a	UCT	8	0.041
10b	UCT	8	0.119
11a	UCT	10	0.068
16a	MUCT	15	0.015
18a	MUCT	15	0.025
19b	MUCT	15	0.017
19c	MUCT	15	0.021
22a	MUCT	20	0.118
23a	MUCT	20	0.085
23b	MUCT	20	0.020
23c	MUCT	20	0.024
24a	MUCT	20	0.161
24c	MUCT	20	0.044
24d	MUCT	20	0.038
26a	MUCT	21	0.021
2	Post-denit.	20	0.015
2	Pre-denit.	20	0.027
Enhanced culture systems with acetate as influent			
1	Bardenpho	20	0.028
2	UCT	10	0.044
3	Bardenpho	10	0.004
4	Bardenpho	7.5	0.003

* Data for systems 5a to 26a were obtained from the data set compiled by Wentzel *et al.* (1990); data for system 2 (post- and pre-denitrification systems) were obtained from Arkley & Marais (1981); data for the enhanced culture systems were taken from Wentzel *et al.* (1989a).

In addition, other observations reported over recent years suggest the need for re-evaluation of the role of nitrate in BEPR systems; for example:

- A number of researchers (Hascoet and Florentz, 1985; Malnou *et al.*, 1984; Comeau *et al.*, 1986; and others) have reported a net uptake of P under anoxic conditions in both batch and continuous tests, indicating that polyP organisms can denitrify.

- Microbiological tests indicate the propensity for denitrification exists in a significant fraction of polyP organisms (Lotter, 1985).

- Batch tests with different substrates suggest that it is substrate type that determines whether or not a net P uptake or P release is observed in the presence of nitrate (Gerber, 1986).

In reviewing the literature regarding the role of nitrate in BEPR systems, the following questions should be considered:

- Can nitrate serve as an electron acceptor for the oxidation of stored PHB by polyP organisms?

If so then:

- What fraction of the polyP organisms have the capacity for denitrification?

- With denitrification is there concomitant P uptake as with aerobic growth?

- What is the stoichiometry of P taken up per unit of PHB oxidized when nitrate is the electron acceptor?

- Does P uptake/PHB oxidation occur simultaneously with P release/PHB storage when short chain fatty acids (SCFAs) are available under anoxic conditions?

- Can nitrate serve as an electron acceptor for direct utilization of SCFAs (*i.e.*, without intermediate PHB storage)? If so, will P uptake occur?

- Does the presence of nitrate in the anaerobic zone (even at low concentrations) inhibit the fermentation of "complex" soluble COD to SCFAs through increasing the redox potential?

The object of this study was to review the literature concerning denitrification in BEPR systems in order to investigate answers to the above questions. In the first section microbiological studies on phosphorus removing organisms are examined, the second section discusses continuous flow BEPR studies, and batch studies on anoxic growth of phosphorus removing organisms are investigated in the third section.

MICROBIOLOGICAL STUDIES

Juni (1972)

Juni (1972) found that many species previously considered members of various other genera, actually belong to the ubiquitous genus, *Acinetobacter*. Juni used the discovery that one strain of *Acinetobacter* is competent for genetic transformation to identify other members of this genus. It was found that all 265 strains of *Acinetobacter* investigated were able to transform auxotrophs of the competent strain to prototrophy. Juni was then able to identify six strains known to be capable of reducing nitrate to nitrite, previously believed to belong to other genera, as members of the genus *Acinetobacter*. However, bacteriological tests for nitrate reduction showed no evidence of growth occurring in the nitrate broth, and therefore it was concluded that there is no proof that any strains of *Acinetobacter* are able to use nitrate as an alternative electron acceptor in the absence of molecular oxygen.

Lotter (1985)

Lotter (1985) studied bacterial isolates from activated sludge plants in an effort to understand phosphate metabolism in relation to BEPR. The results of bacterial population studies of three mixed liquor samples from the aerobic zone of a 5-stage Bardenpho system at different levels of P removal (19-43%) indicated between 56 and 66% of the organisms to be of the genus *Acinetobacter* (species *calcoaceticus var lwoffi*). In

addition, the presence of other organisms capable of phosphate accumulation was noted, including more than half the *Aeromonas hydrophila, Pseudomonas paucimobilis* and Gram positive organisms tested. Of the one hundred isolates of *Acinetobacter* spp. tested for nitrate reduction on Bacto nitrate agar, 52 were shown to be capable of reducing nitrate to nitrogen gas; suggesting the possibility of oxidative metabolism (with P uptake) in the anoxic zone. Lotter concluded that while *Acinetobacter* are the predominant P accumulating organisms, other organisms may also play a major role in phosphorus removal.

Lotter *et al.* (1986)

In another study Lotter *et al.* (1986) operated three laboratory scale activated sludge systems:

- a single completely mixed aerobic reactor with municipal wastewater as influent;
- two aerobic reactors in series; the first acting as a selector, receiving municipal wastewater;
- a modified Bardenpho system receiving a mixture of acetate and municipal wastewater.

All systems were operated at a 20 day sludge age. Only the Bardenpho system exhibited excess P removal, although each system showed an appreciable fraction of *Acinetobacter* spp. (40% of the total viable bacterial colonies in the sludge from the single aerobic reactor were estimated to be *Acinetobacter*, 60% in the system with a selector, and 90% in the Bardenpho system). [However, a study by Venter *et al.* (1989) suggests the API 20E system used in the identification of bacterial isolates overestimates the *Acinetobacter* spp. count]. Mixed liquor samples were taken from the aerobic zone of each system and 25 *Acinetobacter* isolates from each system were examined. The nitrate reducing ability of each isolate was tested by growth in nitrate agar (in the absence of oxygen). The results showed no significant difference between the isolates from the different systems in their capacity for nitrate reduction. Lotter *et al.* therefore concluded that the ability to denitrify did not appear to be linked to environmental conditions as the *Acinetobacter* spp. from systems with anoxic zones did not appear to have an increased capacity for nitrate

reduction. The majority of isolates capable of nitrate reduction, only reduced the nitrate as far as nitrite, with only a small percentage reducing the nitrate completely to nitrogen gas (between 32% and 43% of *Acinetobacter* isolates reduced nitrate to nitrite, and between 6% and 12% reduced the nitrate to nitrogen gas).

EXPERIENCE WITH CONTINUOUS FLOW SYSTEMS

Malnou *et al.* (1984)

Malnou *et al.* (1984) operated a laboratory scale system with anaerobic, anoxic and aerobic zones in order to study biological phosphorus removal. The plant was seeded with sludge from a conventional (low-loaded) sewage treatment plant and feed consisted of a mixture of domestic sewage, meat extract, skimmed milk powder, and peptone. The sludge age was maintained at 9.6 days, and the average influent COD at 656 mg/L. It was observed that P uptake occurred in the anoxic zone. Also, when the nitrogen content of the raw wastewater was high, nitrate was recycled with the settled sludge to the anaerobic zone, and a reduction in phosphorus removal was observed.

Malnou *et al.* (1984) postulated that nitrate served as the electron acceptor for phosphorus uptake in the anoxic zone. The reduction in phosphorus removal efficiency with the recycling of nitrate to the anaerobic zone was explained in terms of the Fuhs and Chen (1975) theory; that is, the nitrate caused the cessation of acidogenesis, which deprived the phosphorus removing bacteria of volatile fatty acids, and prevented PHB accumulation.

Hascoet and Florentz (1985)

Hascoet and Florentz (1985) operated two continuous laboratory scale systems, one receiving nitrate in the influent, the other not. The plants were of the same design, with a single tank which was alternately aerated for 5.5 hours, and unaerated for 2.5 hours. Both units were operated at a sludge age between 10 and 15 days. The unit without nitrate was first inoculated with activated sludge from a wastewater treatment plant treating domestic waste, and then acclimatized to a synthetic substrate (meat extract diluted with tap water). Once this system reached steady state, the second system was initiated using the waste sludge from the first. Both systems exhibited a net P uptake, however the unit with nitrate achieved only 70% removal of influent phosphate, compared to 88% for the unit without

nitrate. It should be noted that although the system with nitrate was reported to operate stably, it did not exhibit a net P release during the unaerated stage; rather P uptake was observed. Hascoet and Florentz surmised that the decreased P removal in the reactor receiving nitrate may have been due to the lack of fermentation products available for the polyP organisms, as the feed to this reactor was not exposed to anaerobic conditions. However, another possibility is that the stored PHB was used less efficiently with nitrate as the electron acceptor, than with oxygen, resulting in less P uptake.

Vlekke *et al.* (1988)

Vlekke *et al.* (1988) used sequencing batch reactors (SBRs) to investigate the possibility of using nitrate as the sole electron acceptor for biological phosphate removal. The reactors were seeded from a nitrifying UCT type pilot plant achieving excess P removal. Two reactors were operated in parallel on an 8 hour cycle. For the first 3 hours of each cycle both reactors were unaerated. At time zero each reactor received an input of domestic wastewater, and an input of acetate solution 1.5 hours into the cycle. At 3 hours one reactor (SBR-O_2) was aerated, until 7 hours. The other reactor (SBR-NO_3) was not aerated; rather, a solution of nitrate was added continuously from 3 to 7 hours. At 7 hours aeration or nitrate addition was terminated, allowing a settle/draw/idle period up to the end of the cycle at 8 hours. A sludge age of 14.2 days was maintained for SBR-O_2, and 12.9 days for SBR-NO_3. Both systems achieved excess P removal (0.1 mgP/L in the effluent for each system). This would indicate that there was a significant number of polyP organisms capable of using nitrate as an electron acceptor in SBR-NO_3. PHV and PHB profiles for the two systems indicated that storage of both PHV and PHB occurred after the acetate was added, and depletion of both PHV and PHB occurred during the aerated/anoxic stage. However, Vlekke *et al.* (1988) noted that when the P uptake in both systems was approximately the same, the total amount of PHB and PHV consumed was about 50% larger in the nitrate system than in the system supplied with oxygen. Based on the change in PO_4-P, PHB and PHV concentrations over the anoxic/aerobic period, the ratio of PO_4-P taken up/PHA consumed can be calculated on a molar basis as 1.5 and 2.2 moles PO_4-P/molePHA, respectively (PHA represents the total number of moles of PHB and PHV). This difference lead Vlekke *et al.* (1988) to surmise that nitrate possibly is not as efficient as oxygen for P uptake since more stored carbon was utilized for a given amount of P taken up. [However, it should be noted that the effluent phosphate concentration was essentially reduced to zero for both systems. It is possible that each

system could have removed additional phosphorus. Therefore a definitive conclusion is not possible]. Nevertheless, it was demonstrated that with an acclimated biomass it is possible to use nitrate as the sole electron acceptor for biological excess P removal. It is interesting to note that the system using nitrate showed a significantly higher filtered effluent COD (65 mg/L compared with 21 mg/L for the aerobic system). This may indicate that a portion of the products from hydrolysis of the slowly degradable wastewater component were not utilized when NO_3 was the electron acceptor.

It is also interesting to consider the observed nitrate responses for the two systems, noting that the reported nitrate values actually were the sum of nitrate plus nitrite. System SBR-O_2 nitrified during the aerobic period, with accumulation of nitrate at the end of the cycle. Over the first portion of the following cycle (unaerated) before acetate addition, the nitrate (NO_2 + NO_3) concentration decreased to zero, and there was a small amount of P uptake. In SBR-NO_3 there also was a reported accumulation of nitrate (NO_2 + NO_3) when nitrate solution was added from 3 to 7 hours. Over the first portion of the following cycle (without nitrate addition) the reported nitrate concentration decreased to zero as in SBR-O_2. However, net P release occurred over this period in SBR-NO_3 *versus* net P uptake in SBR-O_2. In explaining this behaviour in terms of observations in other literature discussed in this review, it is possible that nitrite played an important role which was masked through reporting data as nitrate concentrations which however may have contained appreciable levels of nitrite. For example, in SBR-NO_3 during the period of nitrate addition (3 to 7 hours) it is possible that the reported accumulation of nitrate was in fact mainly nitrite. That is, possibly most of the polyP organisms only converted nitrate to nitrite, with net uptake of P. This would explain the net P release in the first part of the subsequent cycle (without nitrate addition).

Wentzel *et al.* (1989a)

Wentzel *et al.* (1989a) developed enhanced cultures of phosphate removing organisms which analysis using the Analytical Profile Index (API) procedure showed to be greater than 90 percent *Acinetobacter*. The organisms were developed in modified Bardenpho and UCT systems fed primarily sodium acetate. The first test series used a modified Bardenpho system operated at a 20 day sludge age, and a UCT system operated at a 10 day sludge age. The results from the two tests were similar; considerable P removal was achieved (49.7 mgP/L and 60.9 mgP/L influent, respectively). However, little nitrate

removal occurred and both systems were observed to have a net P release in the anoxic reactor. These observations lead the researchers to conclude that only a small number of the *Acinetobacter* spp. could use nitrate as an electron acceptor. It should be noted, however, that the influent TKN/COD ratio for both these systems was low (approximately .064 mgN/mgCOD), and hence very little nitrate was recycled to the unaerated reactors. This may have resulted in the growth of fewer organisms capable of denitrification.

The second test series used only the modified Bardenpho configuration, but with the addition of a second anaerobic reactor (and one less aerobic reactor) to ensure all the acetate was taken up in the anaerobic zone at the shorter sludge ages. The systems were operated at sludge ages of 10 and 7.5 days, with reduced influent CODs (410 mg/L instead of the 544 mg/L used in the first test series). The results obtained were similar to those from the first test series. However, a net uptake of P was observed in the anoxic zones of both systems (18.9 mgP/L influent and 15.8 mg/L influent, respectively) despite low nitrate removals (1.06 mg N/L influent and 0.6 mg N/L influent, respectively) in the anoxic reactors.

Pokethitiyook *et al.* (1992)

Pokethitiyook *et al.* (1992) investigated the role of nitrate in BEPR based on the performance of two continuous flow laboratory scale systems. Influent to each two-reactor system entered an anaerobic reactor. In one system (anaerobic/aerobic) the anaerobic reactor was followed by an aerobic reactor. In the other system (anaerobic/anoxic) the second reactor was unaerated, but nitrate was introduced to the reactor to maintain a nitrate concentration of approximately 3mgN/L. Underflow from each settling tank was recycled to the anaerobic reactor, and each system was operated at a sludge age of 5 days. The feed consisted of domestic wastewater supplemented with sodium acetate and potassium dihydrogen phosphate (total influent COD approximately 350 mg/L, 200 mg/L of which was acetate, and the average total soluble P concentration was 14 mg/L). Both systems were observed to remove phosphorus; the anaerobic/anoxic system with nitrate addition actually removed slightly more P on average (4.4 mg/L influent compared with 3.8 mg/L influent removed in the anaerobic/aerobic system). The P content of the sludge was reported to be 6.5 and 5.6 % on a basis of VSS, respectively (compared with 2-3% for sludge from conventional activated sludge systems).

Pokethitiyook *et al.* (1992) thus concluded that excess P removal can be accomplished using nitrate as the only terminal electron acceptor.

Kuba *et al.* (1993)

Kuba *et al.* (1993) studied biological phosphorus removal in anaerobic-aerobic and anaerobic-anoxic SBR systems. The anaerobic-aerobic (A/O) SBR was seeded from a sewage treatment plant in Leiden, The Netherlands; the anaerobic-anoxic (A_2) system was seeded from a Renpho-process treating municipal wastewater at Wageningen Agricultural University. The A/O SBR had a 3.5L volume and the A_2 SBR had a 1.9L volume. A sludge age of 15 days was maintained for the A/O SBR, and 20 days for the A_2 SBR. The A/O SBR was operated on a 6 hour cycle consisting of a 2.25 hour anaerobic period, a 2.25 hour aerobic period, and a 1.5 hour settling period. The A_2 SBR was operated on a cycle between 6 and 8 hours (depending on the phase of operation). In the final phase (when phosphorus removal was virtually complete) the cycle consisted of a 2.5 hour anaerobic period, a 3.0 hour anoxic period, and a 0.5 hour settling period. In this phase, nitrate was added continuously throughout the first 2.75 hours of the anoxic period (in the earlier phases nitrate addition occurred in the first 1.67 hours of the anoxic period only, resulting in anaerobic conditions before the end of the 3 hour period). Nitrogen gas was pumped into the reactor head space to prevent oxygen ingression. The feed to both systems was a synthetic wastewater which was added in the first 10 minutes of the anaerobic period. The feed consisted of 400 mgCOD/L (as acetic acid) and 15 mgP/L (as K_2HPO_4 and KH_2PO_4) as well as additional nutrients. Both systems achieved virtually complete phosphorus removal. However the authors noted that when nitrate was the electron acceptor the amount of phosphorus taken up per mole of electrons transferred was 20-30% lower than with oxygen as the electron acceptor (approximately 0.19 mol-P/mol-e^-, and 0.23 mol-P/mol-e^- respectively). These values are within the range of phosphorus uptake ratios obtained from Comeau *et al.*(1987) and Vlekke *et al.* (1988).

EXPERIENCE WITH BATCH TESTS

Osborn and Nicolls (1978)

Osborn and Nicolls (1978) studied the effect of nitrate addition on mixed liquor from the anaerobic zone of a BEPR pilot plant. The plant received primarily domestic sewage and was operated at a sludge age of 25 days. In batch tests, after the addition of substrate

(domestic wastewater supplemented with acetate) and phosphate, the mixed liquor sample was divided in two; with one portion being aerated, and with nitrate addition (90 mgNO_3-N/L) to the other. Both samples showed an initial rapid uptake of phosphate. For the aerated sample this was followed by a period of slower uptake. In the sample supplied with nitrate, uptake of phosphorus occurred while nitrate was present, and release when denitrification was complete. The results showed a slower rate of phosphate uptake under anoxic conditions compared to aerobic conditions. The authors accepted the claim of Fuhs and Chen (1975) that *Acinetobacter* are obligate aerobes, but rejected the idea that phosphorus removal from activated sludge is exclusively associated with these species, concluding that facultative denitrifying bacteria also make a significant contribution to phosphorus removal.

Malnou *et al.* (1984)

Malnou *et al.* (1984) used sludge from a laboratory scale BEPR system (described earlier) to study the effect of nitrate on P uptake. The following was observed:

- Batch tests on sludge taken from the anoxic zone, aerated for one hour, and supplemented with methanol after stopping aeration, indicated that no (net) phophorus release occurred until denitrification was complete. However, it should be noted that the majority of the phosphorus present was taken up in the aerated stage, hence no significant uptake was possible.

- When the nitrate concentration dropped below the detection limit, phosphorus release was initiated, along with a simultaneous drop in redox potential.

- Microbiological studies of bacteria from the aerobic zone of the BEPR system revealed the presence of a significant number of *Pseudomonas, Acinetobacter* and *Aeromonas*.

Hascoet and Florentz (1985)

In a series of unaerated/aerated batch tests on sludge from a continuous flow laboratory scale BEPR system, Hascoet and Florentz (1985) studied the effect of various COD and nitrate levels on P release and uptake behaviour. The substrate, containing an appreciable amount of SCFAs, was the same synthetic substrate used for the continuous reactors

(described earlier). The tests were conducted in two phases; 2.5 hours without aeration, 5.5 hours with aeration. Figures 1 and 2 show an example of the phosphate and nitrate concentration profiles, respectively, for an initial COD of 250 mg/L and initial nitrate additions of 0 to 50 mgN/L. Prior to nitrate addition the nitrate concentration was approximately 5 mgN/L. During the unaerated phase of the tests:

- An initial release of phosphorus occurred for all nitrate levels tested.
- The rate of rapid P release decreased for increasing initial nitrate concentration.
- With increasing initial nitrate concentration, the magnitude of net phosphorus release during the initial rapid phase (0 to 0.5 hours) decreased.
- For tests with higher initial nitrate concentrations (≥15 mgN/L) there was a change from net P release to net P uptake during the unaerated phase.
- With increasing initial nitrate concentration, the net phosphorus uptake during the second phase increased.
- For other tests with different initial substrate concentrations, the nitrate concentration required to cause a switch from P release to P uptake under anoxic conditions was dependent on the initial substrate concentration. The higher the initial COD, the later the switch occurred for a given level of nitrate.

The results appear to indicate that when nitrate is present together with substrate, release of phosphate (presumably with PHB storage), and uptake of phosphate (with denitrification) occur simultaneously.

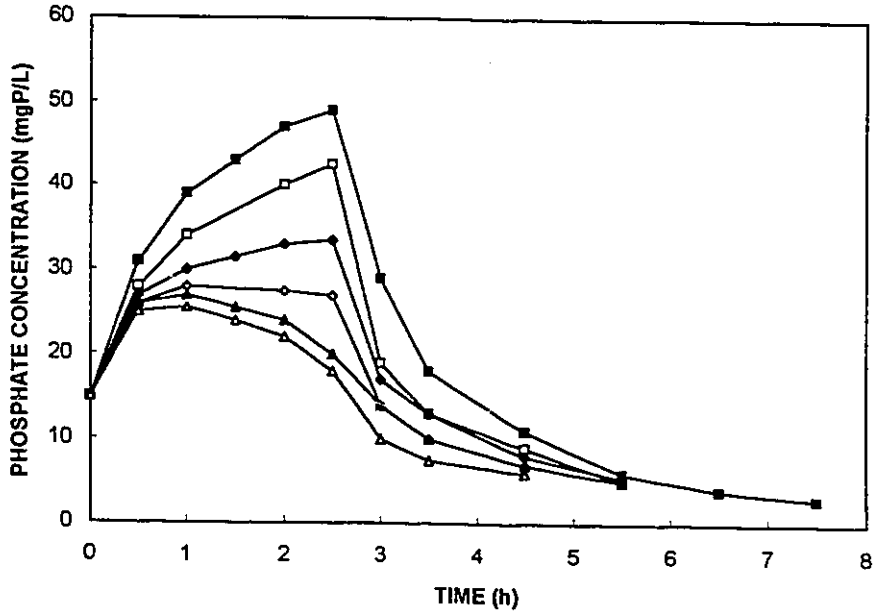

Figure 5.1 Phosphate profiles from batch tests of Hascoet & Florentz (1985). Nitrate was added at time zero; aeration started at 2.5 hours. [■ 0 mg/L nitrate added, □ 5 mg/L nitrate added, ◆ 10 mg/L nitrate added, ◊ 15 mg/L nitrate added, ▲ 25 mg/L nitrate added, △ 50 mg/L nitrate added].

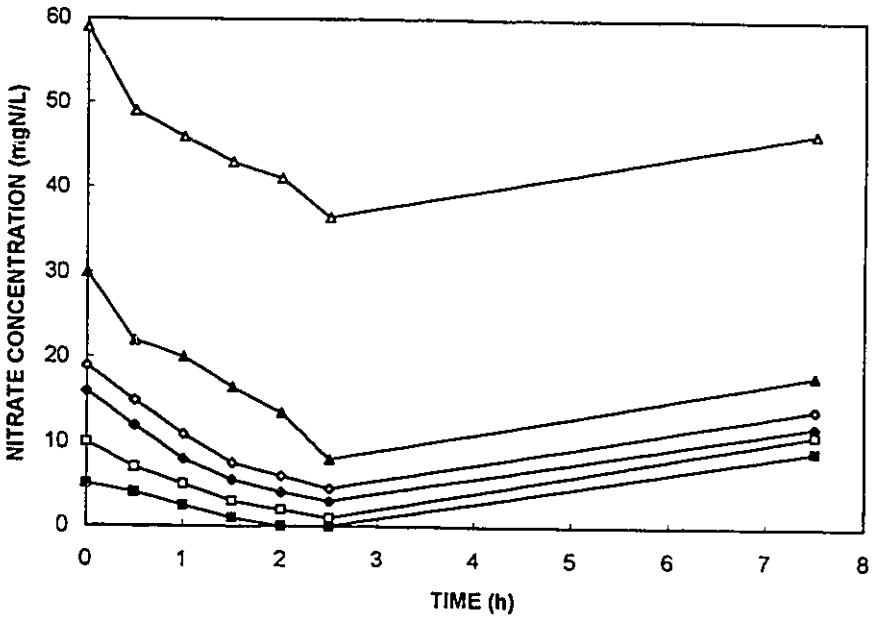

Figure 5.2 Nitrate profiles from batch tests of Hascoet & Florentz (1985). [■ 0 mg/L nitrate added, □ 5 mg/L nitrate added, ◆ 10 mg/L nitrate added, ◊ 15 mg/L nitrate added, ▲ 25 mg/L nitrate added, △ 50 mg/L nitrate added].

Iwema and Meunier (1985)

Iwema and Meunier (1985) performed batch tests on sludge from the aerobic zone of a BEPR pilot plant. The aim of the study was to determine whether a competition exists between denitrifying and P removing bacteria. [The implicit assumption here was that P removing bacteria are not able to denitrify]. The pilot plant was seeded with activated sludge from an extended aeration plant and operated at a sludge age of 5 days. The influent consisted of a synthetic solution of 1000 mg COD/L, including 100 mg/L acetic acid, and 25 mgP/L. The batch tests were run with various levels of substrate (acetic acid) and nitrate. In addition, two different initial phosphorus concentrations were tested (60 and 35 mgP/gMLSS). The following observations were reported:

- In the absence of both acetic acid and nitrate, a slow ("endogenous") release of phosphorus was observed (3.4 mgP/gMLSS/hr for the first 1.5 hours, which decreased slightly for the remaining 1.5 hours)

- When nitrate was present, but no substrate was added, the P profile indicated a constant level of P until all nitrate was consumed, followed by a release equivalent to the endogenous rate reported earlier.

- When nitrate was absent, and acetic acid (100 mg/L) was added, the rate of P release was rapid (9.6 mgP/gMLSS/hr) until the substrate was exhausted, after which time the release was reported to have stopped.

- In the presence of both acetic acid and nitrate, P release occurred until all substrate was consumed, following which P uptake took place if nitrate was still remaining.

- Increasing the initial nitrate concentration (for a constant initial substrate level) resulted in an increase in the rate of acetic acid consumption, and a decrease (slight) in the rate of P release.

- Increasing the initial substrate concentration, with a constant initial nitrate concentration of 40 mg NO_3-N, lead to an increase in P released per mass of sludge.

Iwema and Meunier (1985) concluded that the reason for the decreasing P release with increasing initial nitrate concentration was that an increasing portion of the substrate was consumed by the denitrifiers, and "was not available for P release". It was also proposed that the polyP organisms successfully compete with denitrifying bacteria for acetic acid; however, no conclusions were drawn regarding the ability of the polyP organisms to denitrify.

Gerber *et al.* (1986, 1987)

Gerber *et al.* (1986) studied the effect of substrate type on biological nutrient removal through a series of batch tests on sludge from the aerobic zone of a full scale BEPR plant. The tests were comprised of two phases; an anoxic-anaerobic phase of 22-23 hours with substrate addition at the start, followed by an aerobic phase of 25-30 hours. Twelve different substrates were tested: glucose, methanol, settled sewage, TCA cycle intermediates (citrate and succinate), and a number of glucose fermentation products: acetate, propionate, butyrate, lactate, formate, ethanol, and 2,3 butanediol. The substrates were added in concentrations equivalent to a theoretical COD of 200 mg/L to unaerated batch reactors which contained nitrate, phosphate, and ammonia each at concentrations of approximately 10 mg/L. During the two phases, nitrate, orthophosphate, ammonia and substrate levels were monitored. A number of interesting observations were noted in the first (unaerated) stage of the test:

- P release in the presence of nitrate occurred upon addition of three of the twelve substrates tested: formate, acetate, and propionate. The addition of acetate and propionate both resulted in a rapid release of P and a simultaneous rapid consumption of nitrate and substrate; the rate of release dropped abruptly once the substrate was consumed. Alternatively, the formate was consumed at a much slower rate, showing no initial rapid P release. This response was also found to occur in sludge from six other BEPR plants not presented in the study.

- All other substrates tested failed to induce P release until the nitrate was consumed, with various rates of P release after denitrification was complete. However, it was reported that butyric and lactic acid induced release in sludges from two plants not presented in this study.

Figure 5.3 is an example of the unaerated phase of a test with nitrate present initially (acetate added at time zero). The following observations can be noted:

- As the acetate concentration decreases, an almost linear rapid increase in the phosphate concentration is observed.

- Once the acetate concentration reaches zero, a slow uptake of P is observed while nitrate is present. P uptake stops when the nitrate concentration reaches zero. This is followed by a slow release of P for the remainder of the test. These results again indicate that at least a fraction of the polyP organisms can denitrify with simultaneous P uptake.

- Two rates of denitrification are exhibited in this test (demonstrated by a change in the slope of the nitrate *versus* time plot). When acetate is present a higher rate is observed; once the acetate is depleted, the rate of denitrification decreases. This is possibly due to the presence of non-polyP organisms, *i.e.* while acetate is present in solution the overall rate of denitrification is the sum of the denitrification rate of the non-polyP organisms and denitrification rate of the polyP organisms. Once the external substrate is depleted, the rate of denitrification presumably reflects the oxidation of stored PHB by the polyP organisms.

Gerber *et al.* (1986) concluded that the initial rapid release of phosphate primarily is dependent on the nature of substrate used, rather than the presence of an anaerobic state, which simply provides the environment for conversion of complex substrates into products which initiate P release. This has been reported elsewhere; for example, Wentzel *et al.* (1989a) demonstrated P release on addition of acetate under aerobic conditions. [For systems where the influent does not contain a substrate such as acetate, the anaerobic zone/period is necessary]. It was inferred that the rate of P release/uptake under anoxic conditions is a function of a number of variables, including the maximum amount of phosphate that is available for release and the relative amounts of short-chain fatty acids and nitrate present. Gerber *et al.* (1986) also postulated that acetate-induced P release occurs simultaneously with uptake of phosphate within the sludge mass under anoxic conditions. The result is that the more predominant reaction (P uptake or release) masks the less predominant reaction.

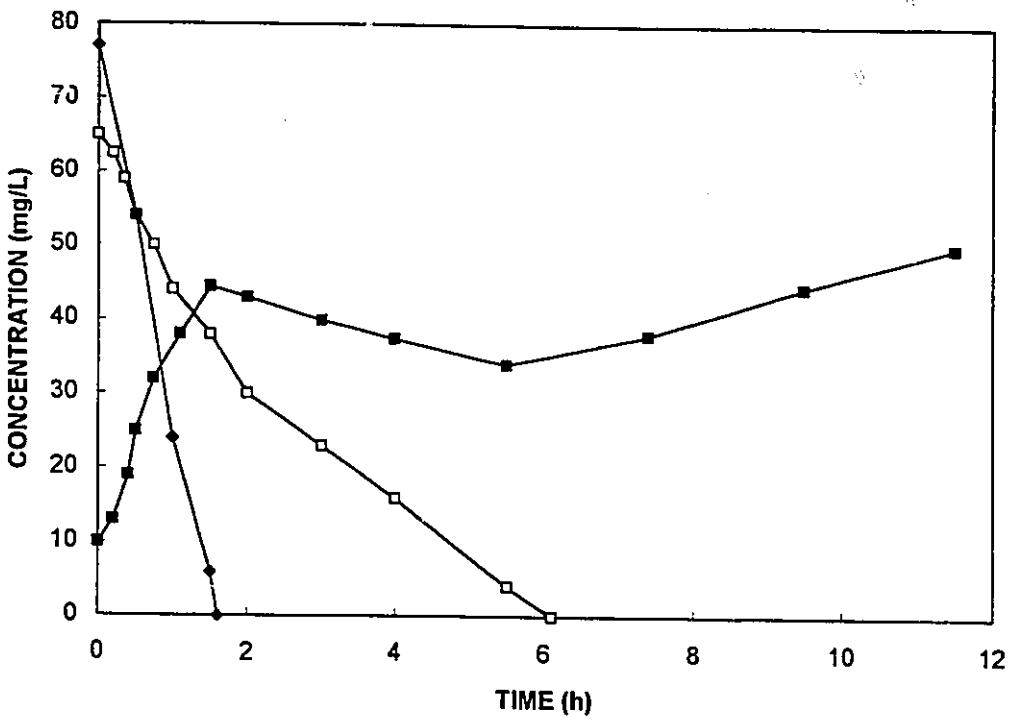

Figure 5.3 Concentration profiles from batch tests of Gerber *et al.* (1986). [■ soluble phosphate, □ nitrate (as N*2), ◆ acetate (as COD/2)].

In another study, Gerber *et al.* (1987) compared phosphate uptake/release patterns in aerobic and anoxic batches which received acetate at varying times. The mixed liquor used for this study was taken from the anaerobic zone of a full-scale BEPR plant. The results indicated that:

- Addition of acetate leads to P release (while acetate is present) regardless of whether oxygen or nitrate is available.

- The rate of P uptake under anoxic conditions is significantly lower than that under aerobic conditions. Under anoxic conditions the rate was approximately constant at 0.9 mgP/gVSS/h; under aerobic conditions the rate of uptake was highest at the start of the test, then decreased with time (approximately 14 mgP/gVSS/h initially).

In a second part of the study, mixed liquor from the aerobic zone of a full-scale BEPR plant was used to investigate the phosphate response when an electron acceptor (oxygen or nitrate) was added after varying anaerobic periods (acetate added at time zero). The results indicate that that the observed magnitude of phosphate release is lessened in the presence of an electron acceptor. This concurs with the previous conclusions of Gerber *et al.* (1986), *i.e.* that P release and uptake occur simultaneously. Rapid P release is initiated by the presence of acetate (or other similar substrates such as propionate). When nitrate was added before the acetate had been removed from solution, release of P continued, but at a reduced rate.

Comeau *et al.* (1986, 1987)

In an attempt to formulate a biochemical model which describes enhanced biological P removal under anoxic conditions as well as aerobic and anaerobic conditions, Comeau *et al.* (1986) examined the effect of nitrate on sludge from a BEPR pilot plant. Batch tests were performed in which mixed liquor from the pilot plant aerobic zone was placed in an unaerated container, injected with sodium acetate (30 or 60 mg/L) , and 4 hours later, injected with sodium nitrate (10 mgN/L). The soluble P, oxidized N, and PHB profiles were recorded. A release of phosphate proportional to the amount of acetate added was observed by the end of the anaerobic period, as well as an accumulation of PHB. With the addition of nitrate, uptake of P was observed until denitrification was complete, as well as a concomitant decrease in PHB concentration. Comeau *et al.* (1986) concluded that a fraction of the polyP organisms are able to utilize oxidized nitrogen (nitrate or nitrite) as an electron acceptor in the absence of oxygen.

In another study, Comeau *et al.* (1987) performed batch tests on sludge from a BEPR pilot plant in order to compare the effects of different electron acceptors on phosphate uptake/release and PHB and PHV storage/consumption. The batch reactors were unaerated for nine hours prior to the addition of an electron acceptor (either nitrate, nitrite, or oxygen). The results show P uptake with concomitant PHB and PHV consumption in reactors which received oxygen or nitrate. However, the reactor which received nitrite did not show any P uptake after nitrite addition, and in fact showed a continued release of P and PHB accumulation. Based on the change in PO_4, PHB, and PHV concentrations over the anoxic/aerobic period, the ratio of PO_4-P taken up/mole PHA consumed can be calculated on a molar basis as 2.3 and 2.6 moles PO_4-P/mole PHA

respectively. These calculations show a difference of 11% between the anoxic and aerobic ratios, which is significantly lower than the difference shown in SBR tests of Vlekke *et al.* (1988).

Wentzel *et al.* (1989a)

Wentzel *et al.* (1989a) also performed batch tests in order to further study the effect of nitrate addition on polyP organisms. Mixed liquor from the anaerobic zone of a continuous enhanced culture system was placed in a sealed batch reactor sparged with nitrogen gas to prevent the ingress of oxygen. No acetate was present at the start of the test. After the addition of nitrate (20 mgN/L as KNO_3), the soluble P, nitrate, nitrite, COD and PHB profiles were recorded for the subsequent four hours. The following observations were reported:

- A linear decrease in nitrate concentration occurred at a rate of 0.043 mgN/mgVSS/d (a rate much lower than that recorded for mixed culture activated sludge systems).

- A linear increase in nitrite concentration was observed over the duration of the test (amounting to approximately 2mgN/L over the four hours), suggesting that approximately 40% of the nitrate removed was reduced only to nitrite.

- The soluble P concentration increased slightly over the duration of the test, from approximately 90 mgP/L initially, to approximately 110 mgP/L at the end of the four hour period.

- The intracellular PHB concentration showed little change; leading Wentzel *et al.* to include this as evidence that PHB was not being used as a substrate source for denitrification. However the PHB data were erratic and it is therefore difficult to draw conclusions.

Wentzel *et al.* (1989a) concluded, based on the results of both the continuous and batch tests, that few of the polyP organisms present in the enhanced cultures had the ability to denitrify, and therefore very little uptake of P is likely to occur with nitrate as the electron acceptor.

Kerrn-Jespersen and Henze (1993)

Kerrn-Jespersen and Henze (1993) conducted a series of batch tests using mixed liquor from the aerobic zones of two different BEPR pilot plants. Prior to most of the tests the mixed liquor was first aerated, then centrifuged to separate the sludge from the supernatant. This provided sludge from the aerobic zone, but without nitrate and other components in the liquid phase. After the supernatant was decanted, the sludge was resuspended with tap water and divided into a number of batches. Substrate (either municipal wastewater or acetate) was added to each reactor at time zero, and varying amounts of nitrate were added following an anaerobic period of between zero and four hours. In the third set of tests, the reactors were aerated following the anoxic period and additional phosphorus was supplied in the form of K_2HPO_4 to three of the six reactors.

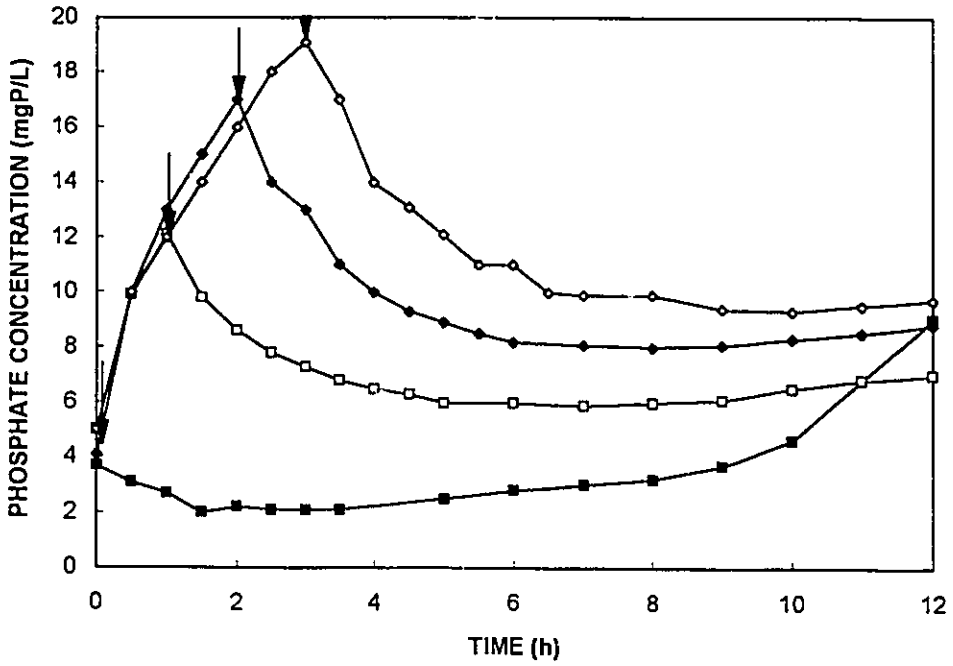

Figure 5.4 Soluble phosphate profiles from batch tests of Kerrn-Jespersen & Henze (1993) using municipal wastewater as substrate (added at time zero). Arrows indicate time of nitrate addition [▲ batch 2.0, □ batch 2.1, ◆ batch 2.2, ◊ batch 2.3].

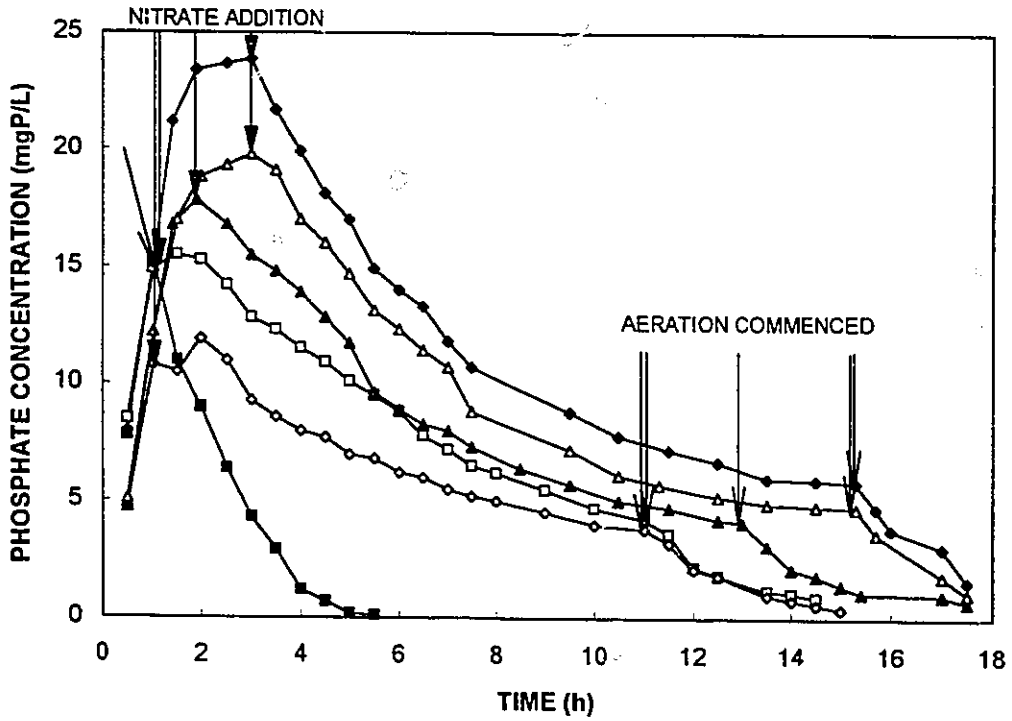

Figure 5.5 Soluble phosphate profiles from batch tests of Kerrn-Jespersen & Henze (1993) using acetate as substrate (added at time zero). Solid arrows indicate nitrate addition, open arrows oxygen addition [■ batch 3.0, □ batch 3.1, ◆ batch 3.2, ◊ batch 3.3, ▲ batch 3.4, △ batch 3.5].

Figure 5.4 shows the soluble phosphate profiles for batches subjected to varying anaerobic times, followed by an anoxic period (municipal wastewater added at time zero). Figure 5.5 shows soluble phosphate concentrations in batches which underwent anaerobic, anoxic, and aerobic conditions (acetate added at time zero). The results were interpreted as follows:

- In all the tests P uptake was observed following nitrate addition.

- The rate of P uptake, and the associated denitrification rate under anoxic conditions, increased for increased amounts of acetate added. It was hypothesized that the rates are directly related to the stored PHB concentration. With increased acetate added, and PHB stored, higher rates of P uptake and denitrification would be anticipated.

- Anoxic P uptake appeared to occur at a slower rate than that under aerobic conditions. This was indicated in Fig. 5.5 by the change in slope of the phosphorus *versus* time curve when aeration was commenced.

- Based on the two stages of P uptake shown in Fig. 5.5, it was concluded that the polyP organism mass comprises two groups: a portion which can utilize either oxygen or nitrate as an electron acceptor, and a portion only able to use oxygen. Based on this hypothesis it would be anticipated that aerobic P uptake would be more rapid than anoxic uptake, where only a fraction of the organisms are implicated. However, it should be noted that factors such as PHB concentration which influence the P uptake rate differed for the different batch tests. Therefore a definitive conclusion on anoxic *versus* aerobic rate perhaps is not possible from this data.

CONCLUSIONS

From the review of experimental studies, it is evident that phosphorus uptake by polyP organisms does occur in anoxic zones of nutrient removal systems; that is, concomitant denitrification and phosphorus uptake. Specific conclusions from the review are as follows:

- As stated above, polyP organisms are capable of denitrification. However, indications are that not all polyP organisms have this ability.

- Nitrate can serve as an electron acceptor for the oxidation of stored PHB; however, not all polyP organisms capable of reducing nitrate appear able to use nitrite as an electron acceptor.

- Nitrate may not be as efficient as oxygen for P uptake. Batch tests indicate that more stored carbon (PHB, PHV) is utilized for a given amount of P taken up when nitrate is the electron acceptor in place of oxygen.

- P uptake/PHB oxidation appear to occur simultaneously with P release/PHB storage when SCFAs are available under anoxic conditions.

- As for aerobic P uptake, the occurrence of phosphorus release/uptake under anoxic conditions is strongly influenced by the amount and type of readily biodegradable material in the feed.

Further study still is required to resolve a number of issues concerning denitrification behaviour of polyP organisms. Issues to be addressed include:

- Quantifying the extent of denitrification by polyP organisms in a particular system is difficult as laboratory studies show considerable variability, possibly due to variations in wastewater characteristics, process operation, and seed organisms.

- The factors which determine what fraction of the polyP organism mass is capable of denitrification have yet to be established. Related to this is the question of partial denitrification to nitrite.

- The stoichiometry of P taken up per unit of PHB oxidized under anoxic conditions must be determined.

- The question of whether nitrate can serve as an electron acceptor for direct utilization of SCFAs (rather than via PHB) still remains unanswered.

- Whether the presence of nitrate in the anaerobic zone (even at low concentrations) inhibits fermentation of complex soluble COD to SCFAs through increasing the redox potential must also be established.

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CHAPTER SIX

GENERAL MODEL FOR BIOLOGICAL NUTRIENT REMOVAL ACTIVATED SLUDGE SYSTEMS

PART I: MODEL PRESENTATION

P. S. Barker and P. L. Dold

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GENERAL MODEL FOR BIOLOGICAL NUTRIENT REMOVAL ACTIVATED SLUDGE SYSTEMS

PART I: MODEL PRESENTATION

P. S. Barker and P. L. Dold

Abstract

The development of a general model for biological nutrient removal activated sludge systems is discussed. The general model is a mechanistic model based on the IAWPRC (now IAWQ) model for carbonaceous energy removal, nitrification and denitrification (ASM1), and the Wentzel *et al.* (1989a,b) model for biological phosphorus removal, with a number of modifications. A fermentation process has been included for the conversion of readily biodegradable COD to short chain fatty acids [assuming a loss of COD from the system]. Hydrolysis of enmeshed slowly biodegradable COD under anoxic and anaerobic conditions has been incorporated, as well as anoxic growth of polyP organisms. These modifications and others are discussed in this paper. The matrix representation and a description of the model processes are also presented, as well as a brief outline of influent wastewater characterization (Appendix). A subsequent paper demonstrates application of the model to a number of nutrient removal systems for both steady state and dynamic conditions.

Key words: Activated sludge, biological excess phosphorus removal, biological nutrient removal, modelling, nitrogen, phosphorus.

INTRODUCTION

Activated sludge systems become more complex as their function is expanded from carbonaceous removal alone to include nitrification, denitrification and biological excess phosphorus removal (BEPR). The number of biological reactions and the number of compounds involved in the process also increases correspondingly. This is because a nitrification, denitrification, biological excess phosphorus removal (NDBEPR) system involves three separate groups of microorganism (polyP heterotrophs, non-polyP heterotrophs, nitrifying autotrophs) operating on a large number of chemical components in three distinct environmental regimes (aerobic zones, anoxic zones where nitrate but not oxygen is present, and anaerobic zones where both nitrate and oxygen are excluded as far as possible). These features make for complex behaviour which has increased the level of difficulty in design, operation and control.

Computer modelling of system behaviour provides the obvious means for predicting the response of a particular system. In recent years modelling has had a significant impact on the development of design and operational procedures for activated sludge systems. In full-scale plant operation it has also found application as a optimization tool in assessing the effects of changes in waste flows and loads, operational modifications (e.g. changes in recycles), and proposed modifications to plant configuration. It has also proved valuable in operator training; through simulation exercises using the model, the operator acquires "instant" experience in the behaviour to be expected with changes in inputs, system configuration and operational strategies.

Currently the approach to modelling activated sludge systems is to use mechanistic models. These mechanistic models incorporate mathematical expressions which represent the biological interactions, based on hypotheses proposed for the biological processes occurring within the system. The best known model of this kind is the IAWPRC Model No. 1 (ASM1). A restriction of ASM1 is that its scope is limited to systems incorporating carbonaceous energy removal, nitrification and denitrification (ND), and the phenomenon of biological excess phosphorus removal (BEPR) is not included.

This paper presents a general model for biological nutrient removal activated sludge systems. The following section outlines the development of activated sludge models. The

basis of this NDBEPR model is discussed in the subsequent section, following which a description of the model processes is given and the model matrix is presented. Areas which require further study also are discussed.

BACKGROUND ON MODEL DEVELOPMENT

In 1982 the International Association on Water Pollution Research and Control (IAWPRC, now IAWQ) appointed a task group to review modelling of activated sludge systems incorporating *carbonaceous energy removal, nitrification and denitrification.* The initial deliberations of the group resulted in a preliminary version of the "IAWPRC model" (Grady *et al.*, 1986). Dold and Marais (1986) conducted a comprehensive evaluation of the preliminary model. It was proposed that certain changes should be made, in particular with respect to the way in which the fate of organic nitrogen was modelled. These changes were subsequently adopted in the final version of the IAWPRC Activated Sludge Model No. 1 [ASM1] (Henze *et al.*, 1987a, 1987b).

The task group drew on a wide range of information in formulating the model. One research initiative which had a major influence on the model was the dynamic activated sludge model developed by Marais and co-workers at the University of Cape Town (Dold *et al.*, 1980; van Haandel *et al.*, 1981). This dynamic model evolved out of the steady state model of Marais and Ekama (1976). The steady state model, in turn, constituted a development from a number of previous models for carbonaceous and nitrogenous material conversion and removal (McKinney, 1962; McKinney and Ooten, 1969; Lawrence and McCarty, 1970; Downing *et al.*, 1964).

The ASM1 model, based on a mechanistic interpretation of the behaviour of the organisms mediating the process reactions, has been shown to give a reliable description of the system response over wide ranges of system configuration (single and series reactor systems, aerated and non-aerated reactors, inter-reactor recycles), influent wastewater characteristics (COD, TKN, flow pattern) and operational parameters (sludge age, temperature, dissolved oxygen concentration).

A restriction of ASM1 is that the phenomenon of biological excess phosphorus removal (BEPR) is not included. In BEPR activated sludge systems removal of phosphorus (P) is mediated by a group of organisms (polyP organisms) which exhibit the propensity to store P as polyphosphate (polyP) polymers called volutins (Buchan, 1981). Proposed explanations of the biochemical behavioural patterns associated with P release and uptake (and net P removal) have been presented in a number of models; for example, that of Comeau *et al.* (1985), extended and modified by Wentzel *et al.* (1986), and that of Mino *et al.* (1987). The biochemical models are largely in agreement regarding the biochemical control mechanisms and have provided an explanation for the essential requirements for attaining BEPR; namely, an alternating anaerobic/aerobic sequence with the provision of short-chain fatty acids (SCFA) during the anaerobic phase [also referred to as volatile fatty acids (VFA)]. These SCFA are taken up by the polyP organisms and stored as organic polymers, generally as either poly-β-hydroxybutyrate (PHB) or poly-β-hydroxyvalerate (PHV) [referred to collectively as poly-β-hydroxyalkanaotes (PHA).] In "normal" municipal wastewater the SCFA content usually is minimal. In BEPR systems the readily biodegradable COD component is transformed to SCFA by the non-polyP organism mass, thereby making SCFA available to the polyP organisms (Meganck *et al.*, 1985; Brodisch, 1985; Wentzel *et al.*, 1985). Aside from this linkage, the polyP and non-polyP organisms in BEPR systems have been shown to act essentially independently of one another. For this reason Wentzel *et al.* (1988) adopted the approach of developing "enhanced" cultures of polyP organisms as the basis for studying the kinetics and stoichiometry of BEPR without the behaviour being masked by that of the non-polyP organisms.

Enhanced cultures of polyP organisms were developed by Wentzel *et al.* (1988) in continuous flow activated sludge systems (modified Bardenpho and UCT process configurations), with acetate as the only organic substrate. The sludge mass in these systems was shown to comprise the polyP organism *Acinetobacter* spp. in excess of 90 percent. Based on observations of the continuous flow systems and batch experiments using mixed liquor drawn from these systems, Wentzel *et al.* (1989a, 1989b) developed a kinetic model for the enhanced culture BEPR system. The model provided a very reasonable description of the response observed in a number of continuous flow enhanced culture systems and the batch experiments with *a single set of kinetic and stoichiometric parameters*. The authors identified certain minor limitations in the proposed model, and outlined problems which might be encountered when extending the model to mixed

organism systems with municipal wastewater as influent. Despite any minor limitations, the enhanced culture model constituted a most significant step towards the development of a general activated sludge model capable of modelling the biological processes of carbonaceous energy removal, nitrification, denitrification *and biological excess phosphorus removal.*

Dold (1990, 1991) merged the ASM1 model for non-polyP heterotrophic organisms and autotrophic organisms (Henze *et al.*, 1987a, 1987b) and the Wentzel *et al.* (1989b) model for polyP organisms. In combining the models, certain extensions and modifications were incorporated in both the ASM1 and the Wentzel model components. Since the initial development this NDBEPR model has been evaluated extensively against experimental data from laboratory-scale and full-scale treatment plants. This has lead to further model refinement. The model is termed general in that it can be applied directly for the simulation of aerobic, anoxic-aerobic (ND) or anaerobic-anoxic-aerobic (NDBEPR) systems, predicting an appropriate balance between the three organism masses - the polyP and non-polyP heterotrophs and the autotrophs.

The IAWQ task group also has extended ASM1 to include simulation of combined NDBEPR processes. The ASM2 model "is a compromise between complexity and simplicity, and between the many viewpoints on how the correct model should look like. It should be used as a conceptual platform for further model development." (Henze *et al.*, 1994a).

ASPECTS OF NDBEPR MODEL DEVELOPMENT

A mechanistic model for NDBEPR systems necessarily must account for a large number of biological processes in order to mimic the complex interactions which may impact the performance of a given treatment plant. Certain key features of process behaviour are discussed briefly before presenting the model in detail.

Anoxic Growth of PolyP Organisms

A simplified representation of the behavioural patterns associated with phosphorus release and uptake in a BEPR system is shown in Fig. 6.1. It is readily apparent that nitrate plays

an important role in the performance of these systems. The current consensus interpretation is that nitrate entering the anaerobic zone will be utilized as an electron acceptor in the growth of non-polyP heterotrophs. As a result less substrate will be available for sequestration by the polyP organisms, with the net effect that the amount of phosphorus removal will be reduced. The amount of substrate available to the polyP organisms may be reduced to such an extent that these organisms are unable to sustain themselves in the system and the capacity for BEPR is lost.

This interpretation of the role of nitrate has proved valuable in the design and operation of BEPR systems. A basic principle for maximizing P removal is to "protect" the anaerobic reactor from ingress of nitrate as far as possible. Hence the arrangement of recycles in the UCT system configuration shown in Fig. 6.1; the underflow recycle (nitrate rich) is directed to the anoxic reactor rather than directly to the anaerobic zone, and a recycle from the anoxic reactor (low in nitrate) transfers sludge to the anaerobic zone. However, implicit in this interpretation is the assumption that nitrate does not influence the behaviour of the polyP organisms directly. Denitrification by polyP organisms was excluded from the Wentzel *et al.* (1989b) model as observations showed minimal denitrification occurred in laboratory systems comprised mainly of polyP organisms. However, a recent review of experimental studies concerning denitrification behaviour in BEPR activated sludge systems (Barker and Dold, 1995b) indicates that phosphorus uptake by polyP organisms does occur in anoxic zones of nutrient removal systems. Based on the results of microbiological studies, as well as many continuous and batch reactor experimental studies, a number of conclusions were drawn:

- PolyP organisms are capable of concomitant denitrification and phosphorus uptake; however, indications are that not all polyP organisms have this ability.

- Nitrate can serve as an electron acceptor for the oxidation of stored PHB; however, not all polyP organisms capable of reducing nitrate appear able to use nitrite as an electron acceptor.

- Nitrate may not be as efficient as oxygen for P uptake. Batch tests indicate that more stored carbon (PHB, PHV) is utilized for a given amount of P taken up when nitrate is the electron acceptor in place of oxygen.

- P uptake/PHB oxidation appear to occur simultaneously with P release/PHB storage when SCFA are available under anoxic conditions. The relative rates of these processes, and the endogenous lysis of P, will determine whether or not a net release or uptake of P is observed in an anoxic reactor.

For modelling denitrification by polyP organisms it is assumed that a fraction (η_P) of the polyP organisms can use nitrate as an electron acceptor in the absence of oxygen for oxidation of stored PHB and uptake of phosphorus. In the model of Wentzel *et al.* (1989b) there are four aerobic growth processes; the four permutations reflect switches between ammonia and nitrate as the nitrogen source for synthesis and at high and low soluble phosphorus concentration. Strictly all four growth processes should be duplicated in the model for anoxic conditions. However, in an anoxic reactor of a continuous flow system growth is likely to occur in the presence of sufficient ammonia and soluble phosphorus. Therefore, in evaluating the possibility of anoxic growth only the one aerobic growth process was duplicated for anoxic conditions, i.e. growth with ammonia as the N source for synthesis and with no phosphorus limitation on the growth rate. The stoichiometric coefficient for phosphorus uptake ($f_{P,UPT}$), defined as the ratio of P taken up to PHB oxidized, was determined from batch experiments to be approximately 0.9 - 1.1 gP(gCOD)$^{-1}$ (Wentzel *et al.*, 1989b). With the inclusion of anoxic growth there are now two stoichiometric parameters for P uptake, ($f_{P,UPT1}$) and ($f_{P,UPT2}$). Results of simulations indicate that the value for anoxic growth ($f_{P,UPT2}$) should be reduced to approximately 0.55 gP (gCOD)$^{-1}$; the value for aerobic conditions ($f_{P,UPT1}$) remains unchanged at 0.95 gP (gCOD)$^{-1}$. These values are close to values determined experimentally (Comeau et al., 1987, Vlekke *et al.*, 1988, Kuba *et al.*, 1993).

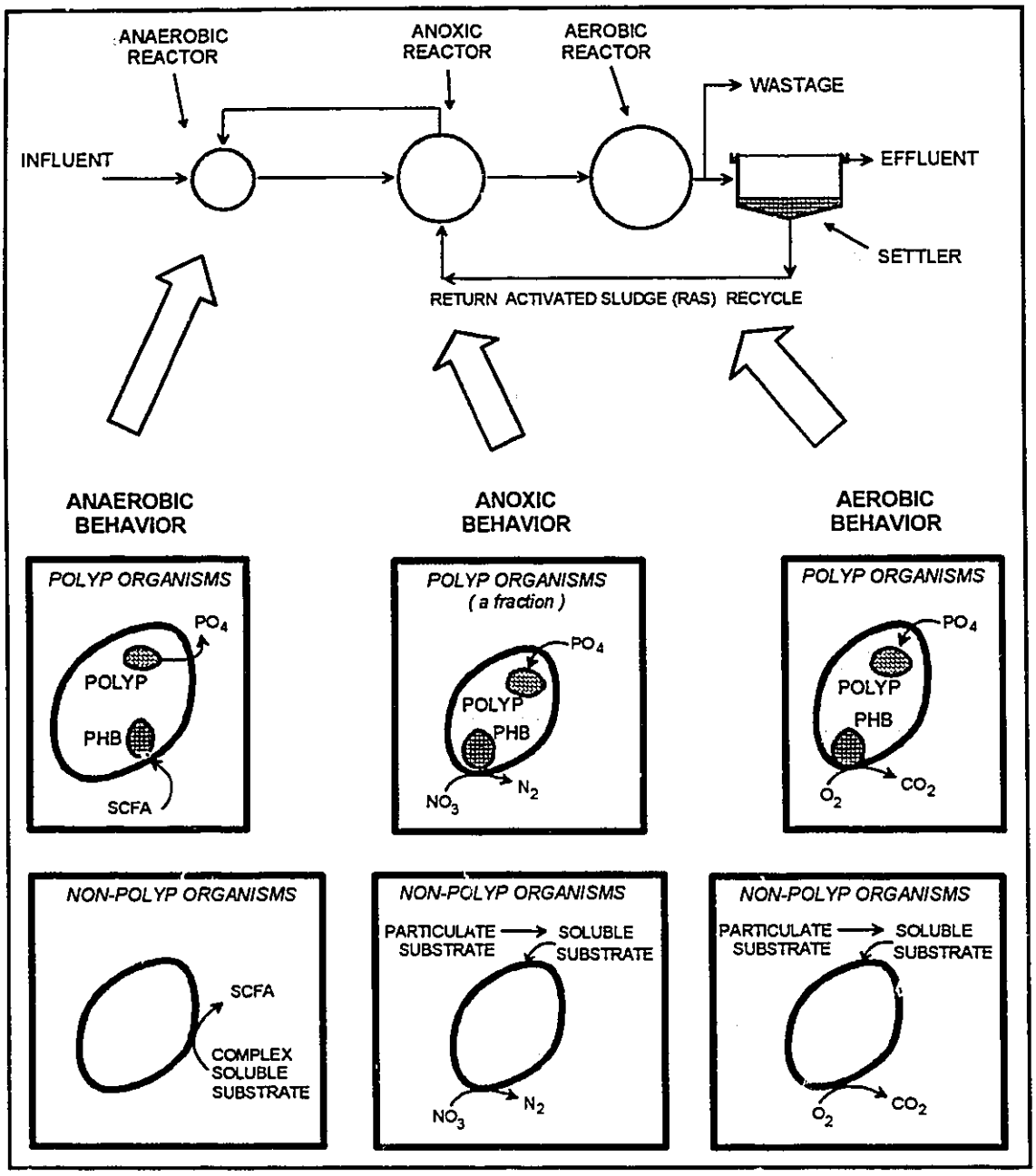

Figure 6.1 **Schematic diagram outlining the roles of polyP and non-polyP heterotrophic organisms in a UCT/VIP process NDBEPR system.**

Conversion of Soluble Readily Biodegradable COD to SCFA

The principal linkage between the polyP and non-polyP heterotrophic organism masses in BEPR systems treating municipal wastewater is the conversion, by non-polyP organisms, of "complex" readily biodegradable soluble COD (S_{BSC}) to short chain fatty acids (S_{BSA}) under anaerobic conditions. This process is the source of SCFA to sustain polyP organism growth in the mixed culture system as the influent SCFA content usually is minimal. Wentzel *et al.* (1985) established the kinetics of this phenomenon and incorporated the process in the enhanced culture model for completeness even though all of the influent COD to the enhanced cultures was in the form of SCFA (acetate). The process was modelled as being first order with respect to the concentrations of S_{BSC} and non-polyP heterotrophs. In terms of stoichiometry the process was assumed to yield one unit of S_{BSA} for each unit of S_{BSC} converted.

A study on COD and nitrogen mass balances in activated sludge systems (Barker and Dold, 1995a) suggests that there is a significant "loss" of COD in activated sludge systems incorporating anaerobic zones. Four different types of laboratory scale system were studied: aerobic, anoxic, anoxic-aerobic, and anaerobic-anoxic-aerobic. The systems included a variety of configurations, with differing wastewater characteristics and operating parameters. The results suggest that while good COD balances are to be expected in aerobic and perhaps in anoxic-aerobic systems, systems incorporating anaerobic zones (i.e. BEPR systems) tend to exhibit low COD balances (less than 80%). [Anoxic-only systems also appear to exhibit a loss of COD, but to a lesser extent]. It would appear that this "loss" of COD apparently is associated with the fermentation processes occurring in the anaerobic zone of BEPR systems treating municipal wastewater. Whether this COD loss is a direct result of fermentation (e.g. through the generation of gas which evolves during the actual fermentation process), or an indirect result (e.g. through the production of volatile compounds which are released from the system under aerated conditions), remains to be determined. Regardless, this "disappearance" of some 20% of the influent COD in BEPR systems translates into reduced sludge production and oxygen demand compared to non-BEPR systems. This feature alone strengthens the case for biological nutrient removal.

The following approach has been adopted for modelling of the readily biodegradable COD conversion process, and includes an empirical factor for modelling loss of COD due to fermentation:

- The process is assumed to be a fermentation; that is, a growth process under anaerobic conditions. This is modelled using a Monod growth expression, with a yield of non-polyP heterotrophic organisms ($Y_{H,ANA}$); correspondingly, the yield of fermentation products is (1 - $Y_{H,ANA}$).

- Further, it is assumed that only a portion (Y_{AC}) of the fermentation products is S_{BSA}. The remainder is assumed to be COD lost from the system.

Initially it was surmised by Barker and Dold (1995a) that COD loss was induced by the inclusion of an anaerobic zone, and that all COD loss was related to the fermentation process in the anaerobic zone. However, analysis of data from a number of anoxic-only and anoxic-aerobic systems indicates that COD loss also occurs under anoxic conditions. For example, Power *et al.* (1992) observed COD balances of approximately 70-85% in a two reactor anoxic-aerobic system with a 70% unaerated mass fraction. In this system nitrate was added to the large pre-denitrification reactor to ensure that the reactor remained anoxic, and did not become anaerobic.

Sequestration of SCFA by PolyP Organisms

In the anaerobic sequestration of SCFA by polyP organisms (for PHB storage, with associated phosphate release) it is assumed that the yield of PHB is Y_{PHB} units of PHB (as COD) per unit SCFA COD taken up. A value of 0.89 gCOD.(gCOD)$^{-1}$ is suggested for Y_{PHB} based on the assumption that for an initial amount of 2.25 moles acetate, 2 moles enter the PHB formation pathway directly and 0.25 moles are directed to the TCA cycle [see biochemical model of Wentzel *et al.* (1986)]. That is, the model also incorporates COD loss in the sequestration reaction. This provides a second mechanism for "losing" COD, and allows the general model to mimic the COD balances (approximately 90%) observed in the enhanced cultures. It should be noted, however, that this COD loss is not suggested in the biochemical model because it is assumed that the available electrons from the 0.25 moles acetate are returned to the PHB formation pathway from the TCA cycle.

Nitrogen Source for Cell Synthesis

In reviewing the ASM1 model, Dold and Marais (1986) postulated that under certain circumstances nitrate, instead of ammonia nitrogen, may serve as the nitrogen source for cell synthesis purposes. This postulate was confirmed from analysis of data collected over an extensive period, particularly in multiple series reactor configurations operated at long sludge ages and which exhibited high nitrification rates. The use of nitrate as a nitrogen source for polyP organism synthesis when the ammonia concentration dropped to low levels also was observed by Wentzel *et al.* (1989a). On the basis of this information, two additional processes have been incorporated to give four growth processes: aerobic and anoxic growth of non-polyP heterotrophs with either ammonia or nitrate as the N source for synthesis.

Growth of Non-polyP Heterotrophs on SCFA

For BEPR systems it is necessary to distinguish between "complex" and SCFA readily biodegradable COD. Therefore it is necessary to duplicate the four growth processes referred to above to account for possible growth on the two components of the readily biodegradable COD for the mixed culture system. With regard to growth on SCFA it is likely that only one of the four processes would be of consequence - anoxic growth with ammonia as the N source. This is because SCFA are removed in the unaerated zones at the "front end" of the continuous flow systems and do not enter the aerobic zones in appreciable concentrations. However, for completeness all four growth processes (for "complex" COD) were duplicated in the general model for growth of non-polyP organisms with SCFA as substrate. The same kinetic formulations and stoichiometry for growth on "complex" readily biodegradable COD and SCFA have been utilized.

Hydrolysis/Solubilization of Slowly Biodegradable COD

In the ASM1 model the biodegradable material is divided into a readily biodegradable fraction (S_{BS}) and a slowly biodegradable fraction (S_{ENM}). The readily biodegradable fraction is hypothesized to consist of material that can be absorbed readily by the organism and metabolized for energy and synthesis, whereas the slowly biodegradable fraction is assumed to be made up of particulate/colloidal material and complex organic molecules that require extracellular enzymatic breakdown prior to absorption and utilization. In the ASM1 model the rate of solubilization under *anoxic* conditions is assumed to be reduced by a factor η_{SOL} compared to the rate under aerobic conditions. Under anaerobic

conditions the rate is assumed zero. Recent research on enzymatic hydrolysis (Dold *et al.*, 1991, San Pedro *et al.*, 1994) indicates that hydrolysis does in fact occur under anaerobic conditions, and under anoxic conditions the rate of hydrolysis appears similar to that under aerobic conditions. This behaviour requires further research. To provide flexibility in the model two η_{SOL} factors are incorporated: $\eta_{S,ANOX}$ and $\eta_{S,ANA}$. In addition, two 'hydrolysis efficiency factors' E_{ANOX} and E_{ANA} have been included to allow for the possibility of COD loss during the breakdown of the enmeshed slowly biodegradable material to readily biodegradable ("soluble") material. That is, in hydrolysis of one COD unit of slowly biodegradable COD there is a production of E units of S_{BSC} and a "loss" of (1-E) units of COD. This third mechanism for COD loss allows the model to simulate the COD loss observed in anoxic-aerobic and anoxic-only systems.

Decay of PolyP Organisms Under Anoxic Conditions

The Wentzel (1989b) enhanced culture model did not consider anoxic behaviour of polyP organisms, and decay processes for these organisms were considered only for aerobic and anaerobic conditions. Processes for anoxic decay of polyP organisms, stored polyphosphate lysis from anoxic decay, and PHB lysis from anoxic decay have been included here [three additional processes]. Simulation results indicate that polyP organisms under anoxic conditions exhibit similar decay processes to those under aerobic conditions. This would seem reasonable since a significant number of the polyP organisms can use nitrate as an electron acceptor.

Yield of Heterotrophs in Anoxic Growth

The ASM1 model assumes a single yield coefficient (Y_H) for non-polyP heterotrophs irrespective of whether oxygen or nitrate serves as the electron acceptor. It has long been surmised that the yield of organisms under anoxic conditions with nitrate as electron acceptor is lower than for aerobic growth. This does not have a very significant impact on ASM1 model predictions of sludge production for ND systems treating municipal wastewater. For this situation the influent TKN/COD ratio usually is relatively low [< 0.12 gN $(gCOD)^{-1}$], so the amount of nitrate generated is limited, and hence the organism mass generated by denitrification is smaller than the mass generated in aerobic growth. However, this is not the case in certain synthetic situations; for example, anoxic-only systems with addition of sufficient quantities of nitrate to maintain the system organic substrate limited. McClintock *et al.* (1988) conducted side-by-side studies on five parallel

sets of single reactor system operated over a range of sludge ages (1.5 to 15 days); in each set one system was aerated while the other not. The unaerated system was mixed, and the soluble influent supplemented with an excess of nitrate (i.e. anoxic). In four of the systems sludge production in the anoxic unit was significantly lower than in the corresponding aerobic one. [Sludge production in the 15 day sludge age systems essentially was the same.] It was concluded that the yield coefficient for anoxic growth was approximately 40% less than for aerobic growth. Smyth (1994) analyzed the results of McClintock *et al.* (1988) and showed that there was a substantial COD "loss" in the anoxic-only systems. [COD balances could not be performed for the aerobic systems as no data on oxygen uptake were reported.] In further analysis, deducting the COD loss from the influent COD, the yield coefficient and the electron acceptor consumption per unit substrate utilized [influent COD - COD loss - effluent COD] essentially were the same as for aerobic systems. Also, it should be noted that the expected decrease in sludge production has not been observed significantly in laboratory scale anoxic-aerobic and anoxic-only systems treating municipal wastewater (Arkley and Marais, 1981; Smyth,1994). To account for the possibility of a lower anoxic yield, yield factors ($Y_{H,AER}$ and $Y_{H,ANOX}$) have been incorporated in the general model for both aerobic and anoxic growth of non-polyP heterotrophs, respectively.

Switching Functions for Phosphorus Limitation

Under aerobic (and anoxic) conditions soluble phosphate serves as a P source for synthesis of the different organism masses in growth processes. Also P is being taken up for BEPR. The Wentzel *et al.* (1989a) model incorporates a switching function which causes the P uptake processes to switch off when soluble P becomes limiting. The same switching function threshold concentration is used to switch off the growth processes when soluble P becomes limiting. Evidence from simulation of full-scale systems indicates that these processes have different threshold values for switching on and off at low P concentrations. For example, the model was applied to simulation of a multi-reactor (almost plug flow) NDBEPR system which had the capacity to remove some 25 gPm^{-3}, but where the influent P concentration was only 4-5 gPm^{-3}. In the system P uptake was rapid and the P concentration was reduced to less than 0.1 gm^{-3} approximately one third along the length of the aerobic zone. This was correctly predicted by the model. However, in the model the low P concentration also caused the growth processes to become P-limited and switch off. This resulted in a predicted substantial increase in soluble biodegradable COD along

the remainder of the aerobic zone. This was not observed in practice, indicating that even though the P concentration was reduced to a very low level, there was still sufficient P available to satisfy the P synthesis requirements. To accommodate this, an additional switching function for P limitation of growth has been employed, and the parameter (K_{LP}) has now been replaced by two parameters, ($K_{LP,GRO}$, $K_{LP,UPT}$). $K_{LP,GRO}$ is used in the switching functions for growth, and has a value of approximately 0.005 gP m^{-3}. $K_{LP,UPT}$ represents the soluble phosphate limit for P uptake by polyP organisms, and has a value of approximately 0.25 gP m^{-3}.

Releasable/Fixed Polyphosphate Components

Experimental observations indicate that stored polyphosphate is portioned between a low and a high molecular weight (MW) fraction (i.e. $P_{PP\text{-}LO}$ and $P_{PP\text{-}HI}$), and that only the low MW fraction can be released after being taken up. In modelling the P uptake/release processes it is assumed that only a fraction (f_{PP}) of the phosphate stored as poly-phosphate can be released in a subsequent anaerobic condition. The value for f_{PP} of 0.94 suggested here was selected on the basis of simulating behaviour in a range of BEPR systems, and is in accordance with values reported in the literature (Mino *et al.*, 1984). The remainder of the stored polyphosphate is termed "fixed".

GENERAL DYNAMIC MODEL FOR NUTRIENT REMOVAL SYSTEMS

The general mechanistic model for biological nutrient removal activated sludge systems is presented in the following sections. The model is presented in two parts: a part for the non-polyP and autotrophic organisms (relating principally to ND systems) and a part for the polyP organisms (relating to BEPR behaviour). The model component (compound) symbols are defined in Table 6.1.

The model is presented in matrix format (two parts). To simplify presentation of the process rate equations, a number of switching functions are incorporated in the kinetic expressions; these are defined in Table 6.2. [The role of switching functions in activated sludge modelling has been described by Billing and Dold (1988)]. Briefly, switching functions serve a mathematical purpose to turn process rates on or off when concentrations of selected components are respectively above (*SwitchYes*) or below

(*SwitchNo*) some low threshold magnitude. The switching functions also facilitate interpretation of the process model in the matrix format.

Table 6.1: Definition of component symbols in the general model.

Component	Symbol	Definition	Units
1	Z_H	Active non-polyP heterotrophic biomass	g cell COD m^{-3}
2	Z_A	Active autotrophic biomass	g cell COD m^{-3}
3	Z_P	Active polyP heterotrophic biomass	g cell COD m^{-3}
4	Z_E	Endogenous mass	g COD m^{-3}
5	S_{ENM}	Enmeshed slowly biodegradable substrate	g COD m^{-3}
6	S_{BSC}	Readily biodegradable "complex" substrate	g COD m^{-3}
7	S_{BSA}	Readily biodegradable SCFA substrate	g COD m^{-3}
8	S_{PHB}	Stored SCFA	g COD m^{-3}
9	S_{UP}	Particulate unbiodegradable matter	g COD m^{-3}
10	S_{US}	Unbiodegradable soluble substrate	g COD m^{-3}
11	$P_{PP\text{-}LO}$	Releasable stored polyP	g P m^{-3}
12	$P_{PP\text{-}HI}$	Fixed stored polyP	g P m^{-3}
13	P_{O4}	Soluble phosphate	g P m^{-3}
14	N_{BP}	Particulate biodegradable organic nitrogen	g N m^{-3}
15	N_{BS}	Soluble biodegradable organic nitrogen	g N m^{-3}
16	N_{03}	Nitrate nitrogen	g N m^{-3}
17	N_{H3}	Ammonia nitrogen	g N m^{-3}
18	N_{US}	Unbiodegradable soluble nitrogen	g N m^{-3}
19	S_O	Oxygen	g (-COD) m^{-3}

Table 6.2: Definition of switching functions in the general model.

Switching function	Equivalent	Definition
AirYesHet	1 - AirNoHet	$\frac{S_O}{K_{O\,HET} + S_O}$
AirNoHet	1 - AirYesHet	$\frac{K_{O\,HET}}{K_{O\,HET} + S_O}$
AirYesAut	1 - AirNoAut	$\frac{S_O}{K_{O\,AUT} + S_O}$
AirNoAut	1 - AirYesAut	$\frac{K_{O\,AUT}}{K_{O\,AUT} + S_O}$
NH_3Yes	1 - NH_3No	$\frac{N_{H3}}{K_{NA} + N_{H3}}$
NH_3No	1 - NH_3Yes	$\frac{K_{NA}}{K_{NA} + N_{H3}}$
NO_3Yes	1 - NO_3No	$\frac{N_{O3}}{K_{NO} + N_{O3}}$
NO_3No	1 - NO_3Yes	$\frac{K_{NO}}{K_{NO} + N_{O3}}$
PO_4GroYes	1 - PO_4GroNo	$\frac{P_{O4}}{K_{LP\text{-}GRO} + P_{O4}}$
PO_4GroNo	1 - PO_4GroYes	$\frac{K_{LP\text{-}GRO}}{K_{LP\text{-}GRO} + P_{O4}}$
PO_4UptYes	1 - PO_4UptNo	$\frac{P_{O4}}{K_{LP\text{-}UPT} + P_{O4}}$
PO_4UptNo	1 - PO_4UptYes	$\frac{K_{LP\text{-}UPT}}{K_{LP\text{-}UPT} + P_{O4}}$
S_{BSA}Yes	1 - S_{BSA}No	$\frac{S_{BSA}}{K_{SSEQ} + S_{BSA}}$
S_{BSA}No	1 - S_{BSA}Yes	$\frac{K_{SSEQ}}{K_{SSEQ} + S_{BSA}}$
PolyPYes	1 - PolyPNo	$\frac{P_{PP\text{-}LO}}{K_{XP} + P_{PP\text{-}LO}}$
PolyPNo	1 - PolyPYes	$\frac{K_{XP}}{K_{XP} + P_{PP\text{-}LO}}$

MODEL COMPONENT FOR THE NON-POLYP HETEROTROPHIC AND NITRIFYING AUTOTROPHIC ORGANISMS

The general model component proposed for describing the kinetic response of the non-polyP heterotrophic and autotrophic organism masses is based on ASM1 (Henze *et al.*, 1987a, 1987b), with a number of modifications/extensions described above. This extended ASM1 model component of the general model is presented in matrix format in Table 6.3. Suggested values for the stoichiometric, kinetic, and switching function parameters are listed in Tables 6.5, 6.6 and 6.7.

Space limitations do not allow for a detailed discussion of the model. The reader is referred to the literature cited above, the publications of the IAWQ task group (Henze *et al.*, 1987a, 1987b, 1994a, 1994b) and the review by Grady (1989). The following paragraphs briefly summarize the essence of this part of the model.

- *Growth of non-polyP heterotrophs on "complex" readily biodegradable COD (processes 1 to 4):* Growth of these organisms is modelled by the Monod relationship. There are four process equations to describe this, depending on whether growth occurs under aerobic or anoxic conditions, and whether nitrate or ammonia is the nitrogen source for cell synthesis. In the absence of dissolved oxygen, only a portion of the non-polyP heterotrophic organism population is capable of using nitrate, if available, as a terminal electron acceptor for the oxidation of organic matter. [Alternatively, all these organisms can utilize nitrate as electron acceptor, but at a reduced rate compared to aerobic conditions]. The process rate is adjusted by a factor (η_{GRO}) to account for the reduced rate of substrate removal under anoxic conditions. Different yield factors ($Y_{H,AER}$ and $Y_{H,ANOX}$) are incorporated for aerobic and anoxic growth, respectively. Switching functions enable the model to simulate the change from one electron acceptor to another, or one nitrogen source to another. For the treatment of domestic wastewater, the growth of non-polyP heterotrophs on complex readily biodegradable COD is responsible for a large portion of the removal of organic matter (and its oxygen requirement) and production of the bulk of the MLVSS.

- *Growth of non-polyP heterotrophs on SCFA COD (processes 5 to 8):* As above, there are four process equations to describe this behaviour, depending on whether growth occurs under aerobic or anoxic conditions, and whether ammonia or nitrate serves as the nitrogen source. For normal conditions these growth processes seldom will be active as the SCFA concentration entering anoxic and aerobic zones usually will be very low.

- *Decay of heterotrophs (process 9):* This process is modelled according to the death-regeneration theory. The organisms are assumed to die at a certain rate, with a portion of the dead cells adding to the endogenous cell residue (non-degradable), and the rest becoming part of the pool of particulate biodegradable COD (S_{ENM}). The cellular nitrogen and phosphorus associated with the particulate biodegradable COD from decay become available as particulate organic nitrogen and soluble phosphate. Decay is assumed to occur under aerobic, anoxic, and anaerobic conditions.

- *Hydrolysis of slowly biodegradable (enmeshed) COD (processes 10 to 12):* The slowly biodegradable COD is assumed to be enmeshed in the sludge mass, and as it is broken down extracellularly, the products of breakdown add to the pool of readily biodegradable (complex) COD. This process is modelled on the basis of Levenspiel's surface reaction kinetics, and is assumed to occur under aerobic, anoxic, and anaerobic conditions. The rate of hydrolysis under anoxic and anaerobic conditions is assumed to be a fraction of that under aerobic conditions ($\eta_{S,ANOX}$ and $\eta_{S,ANA}$, respectively). In addition, the efficiency of hydrolysis is assumed to decrease under anoxic and anaerobic conditions to a fraction of that under aerobic conditions (E_{ANOX} and E_{ANA}, respectively). That is, under anoxic and anaerobic conditions a fraction (1-E) of the hydrolysis products is lost from the system.

- *Hydrolysis of particulate organic nitrogen (process 13):* The breakdown of biodegradable particulate organic nitrogen to soluble organic nitrogen is assumed to occur at the same rate as that for carbonaceous slowly degradable matter described above.

- *Ammonification of soluble organic nitrogen (process 14):* Soluble organic nitrogen is converted to free and saline ammonia, a process mediated by the active non-polyP and polyP heterotrophs. The rate is assumed to be first order with respect to the total concentration of heterotrophs and the concentration of soluble biodegradable organic nitrogen.

- *Fermentation of complex RBCOD to SCFA (process 15):* Non-polyP facultative heterotrophs are responsible for the fermentation of complex RBCOD to SCFA under anaerobic conditions. This is modelled using a Monod growth expression, with a cell yield of $Y_{H,ANA}$, and a corresponding yield of fermentation products of $(1-Y_{H,ANA})$. It is assumed that only a portion (Y_{AC}) of the fermentation products is SCFA; the remainder is assumed to be COD lost from the system. This process represents the principal linkage between the polyP and non-polyP heterotrophic organism masses in BEPR systems treating municipal wastewater.

- *Growth of autotrophs (process 16):* The autotrophic population is responsible for the oxidation of ammonia nitrogen to nitrate (nitrification). It is modelled as a single-step process, occurring under aerobic conditions only, with a cell yield of Y_A [g cell COD (g NH_3-N)$^{-1}$]. This process has a substantial effect on the prediction of oxygen demand; the effect on the total MLVSS is small as the yield of autotrophic nitrifiers is low. As with the growth of heterotrophs, ammonia nitrogen and soluble P are incorporated in the new cells.

- *Decay of autotrophs (process 17):* This process parallels that for the heterotrophs, except that decay is assumed to occur at a much lower rate.

Table 6.3: Model matrix for the non-polyP organism and autotroph component of the general model.

	COMPONENT →	1	2	3	4	5	6	7	8	9	10	11	12	13
	PROCESS ↓	Z_H	Z_A	Z_P	Z_E	S_{ENM}	S_{BSC}	S_{BSA}	S_{PHB}	S_{UP}	S_{US}	$P_{PP\text{-}LO}$	$P_{PP\text{-}HI}$	P_{O4}
1	Aerobic growth of heterotrophs on S_{BSC} with N_{H3}	1					$\frac{-1}{Y_{H,AER}}$							$-f_{P,ZH}$
2	Anoxic growth of heterotrophs on S_{BSC} with N_{H3}	1					$\frac{-1}{Y_{H,ANOX}}$							$-f_{P,ZH}$
3	Aerobic growth of heterotrophs on S_{BSC} with N_{03}	1					$\frac{-1}{Y_{H,AER}}$							$-f_{P,ZH}$
4	Anoxic growth of heterotrophs on S_{BSC} with N_{03}	1					$\frac{-1}{Y_{H,ANOX}}$							$-f_{P,ZH}$
5	Aerobic growth of heterotrophs on S_{BSA} with N_{H3}	1						$\frac{-1}{Y_{H,AER}}$						$-f_{P,ZH}$
6	Anoxic growth of heterotrophs on S_{BSA} with N_{H3}	1						$\frac{-1}{Y_{H,ANOX}}$						$-f_{P,ZH}$
7	Aerobic growth of heterotrophs on S_{BSA} with N_{03}	1						$\frac{-1}{Y_{H,AER}}$						$-f_{P,ZH}$
8	Anoxic growth of heterotrophs on S_{BSA} with N_{03}	1						$\frac{-1}{Y_{H,ANOX}}$						$-f_{P,ZH}$
9	Decay of heterotrophs	-1			$f_{EP,H}$	$1-f_{EP,H}$								$f_{P,ZH} - f_{EP,H} \cdot f_{P,ZEH}$
10	Aerobic hydrolysis of stored/ enmeshed COD					-1	1							
11	Anoxic hydrolysis of stored/ enmeshed COD					-1	E_{ANOX}							
12	Anaerobic hydrolysis of stored/ enmeshed COD					-1	E_{ANA}							
13	Hydrolysis of organic nitrogen													
14	Ammonification													
15	Fermentation of S_{BSC} to S_{BSA}	$Y_{H,ANA}$					-1	$(1-Y_{H,ANA})Y_{AC}$						$-f_{P,ZH} \cdot Y_{H,ANA}$
16	Autotroph growth		1											$-f_{P,ZA}$
17	Autotroph decay		-1		$f_{EP,A}$	$1-f_{EP,A}$								$f_{P,ZA} - f_{EP,A} \cdot f_{P,ZEA}$

Table 6.3: (Continued).

	14	15	16	17	18	19	RATE EQUATION, ρ_i
	N_{BP}	N_{BS}	N_{O3}	N_{H3}	N_{US}	S_O	
1				$-f_{N,ZH}$		$-\frac{(1-Y_{H,AER})}{Y_{H,AER}}$	$\mu_H \cdot \frac{S_{BSC}}{K_{SH}+S_{BSC}} \cdot Z_H \cdot AirYesHet \cdot NH_3Yes \cdot PO_4GroYes$
2			$-\frac{(1-Y_{H,ANOX})}{2.86Y_{H,ANOX}}$	$-f_{N,ZH}$			$\eta_{GRO} \cdot \mu_H \cdot \frac{S_{BSC}}{K_{SH}+S_{BSC}} \cdot Z_H \cdot AirNoHet \cdot NO_3Yes \cdot NH_3Yes \cdot PO_4GroYes$
3			$-f_{N,ZH}$			$-\frac{(1-Y_{H,AER})}{Y_{H,AER}}$	$\mu_H \cdot \frac{S_{BSC}}{K_{SH}+S_{BSC}} \cdot Z_H \cdot AirYesHet \cdot NO_3Yes \cdot NH_3No \cdot PO_4GroYes$
4			$-f_{N,ZH} - \frac{(1-Y_{H,ANOX})}{2.86Y_{H,ANOX}}$				$\eta_{GRO} \cdot \mu_H \cdot \frac{S_{BSC}}{K_{SH}+S_{BSC}} \cdot Z_H \cdot AirNoHet \cdot NO_3Yes \cdot NH_3No \cdot PO_4GroYes$
5				$-f_{N,ZH}$		$-\frac{(1-Y_{H,AER})}{Y_{H,AER}}$	$\mu_H \cdot \frac{S_{BSA}}{K_{SH}+S_{BSA}} \cdot Z_H \cdot AirYesHet \cdot NH_3Yes \cdot PO_4GroYes$
6			$-\frac{(1-Y_{H,ANOX})}{2.86Y_{H,ANOX}}$	$-f_{N,ZH}$			$\eta_{GRO} \cdot \mu_H \cdot \frac{S_{BSA}}{K_{SH}+S_{BSA}} \cdot Z_H \cdot AirNoHet \cdot NO_3Yes \cdot NH_3Yes \cdot PO_4GroYes$
7			$-f_{N,ZH}$			$-\frac{(1-Y_{H,AER})}{Y_{H,AER}}$	$\mu_H \cdot \frac{S_{BSA}}{K_{SH}+S_{BSA}} \cdot Z_H \cdot AirYesHet \cdot NO_3Yes \cdot NH_3No \cdot PO_4GroYes$
8			$-f_{N,ZH} - \frac{(1-Y_{H,ANOX})}{2.86Y_{H,ANOX}}$				$\eta_{GRO} \cdot \mu_H \cdot \frac{S_{BSA}}{K_{SH}+S_{BSA}} \cdot Z_H \cdot AirNoHet \cdot NO_3Yes \cdot NH_3No \cdot PO_4GroYes$
9	$f_{N,ZH} - f_{EP,H} \cdot f_{N,ZEH}$						$b_H \cdot Z_H$
10							$K_H \cdot \frac{S_{ENM}/Z_H}{K_X+S_{ENM}/Z_H} \cdot Z_H \cdot AirYesHet$
11							$\eta_{S,ANOX} \cdot K_H \cdot \frac{S_{ENM}/Z_H}{K_X+S_{ENM}/Z_H} \cdot Z_H \cdot AirNoHet \cdot NO_3Yes$
12							$\eta_{S,ANA} \cdot K_H \cdot \frac{S_{ENM}/Z_H}{K_X+S_{ENM}/Z_H} \cdot Z_H \cdot AirNoHet \cdot NO_3No$
13	-1	1					$\rho_{10} \cdot \frac{N_{BP}}{S_{ENM}}$ or $\rho_{11} \cdot \frac{N_{BP}}{S_{ENM}}$ or $\rho_{12} \cdot \frac{N_{BP}}{S_{ENM}}$
14		-1		1			$K_R \cdot N_{BS} \cdot (Z_H + Z_P)$
15				$-f_{N,ZH} \cdot Y_{H,ANA}$			$K_C \cdot \frac{S_{BSC}}{K_{S,ANA}+S_{BSC}} \cdot Z_H \cdot AirNoHet \cdot NO_3No$
16			$\frac{1}{Y_A}$	$-f_{N,ZA} - \frac{1}{Y_A}$		$-\frac{(4.57-Y_A)}{Y_A}$	$\mu_A \cdot \frac{N_{H3}}{K_{NH}+N_{H3}} \cdot Z_A \cdot AirYesAut$
17	$f_{N,ZA} - f_{EP,A} \cdot f_{N,ZEA}$						$b_A \cdot Z_A$

MODEL COMPONENT FOR POLYP HETEROTROPHS

The general model component proposed for describing the kinetic response of the polyP heterotrophic organism mass is similar to the enhanced culture model of Wentzel *et al.* (1989b), but with a number of modifications described earlier.

The polyP organism component of the general model is presented in matrix format in Table 6.4. Suggested values of the stoichiometric, kinetic, and switching function parameters are listed in Tables 6.5, 6.6 and 6.7.

Space limitations again do not allow for a detailed discussion of this component of the model. The reader is referred to the literature cited above. The following paragraphs briefly summarize this second part of the model.

- *Aerobic growth of polyP heterotrophs on PHB (processes 18 to 21):* There are four different process equations to describe polyP organism growth on stored PHB, depending on whether soluble P is limiting or not, and whether ammonia or nitrate serves as the nitrogen source for cell synthesis. The growth rate, formulated as a Monod expression, is dependent on the amount of stored substrate per unit polyP organism mass. Switching functions enable the model to simulate a change to P limitation or a change in N source. Soluble phosphate uptake and storage as polyP occurs concomitant with growth [$f_{P,UPT1}$ gP (gPHB-COD)$^{-1}$]. Only a fraction (f_{PP}) of the stored phosphate can be released subsequently.

- *Anoxic growth of polyP heterotrophs on PHB (process 22):* The model assumes that a fraction (η_P) of the polyP organisms can use nitrate as an electron acceptor (in the absence of oxygen) for the oxidation of stored PHB and uptake of phosphorus. [Alternately, this factor η_P can be regarded as a reduction in rate of growth and uptake compared to aerobic conditions]. The stoichiometric uptake of phosphate [$f_{P,UPT2}$ gP (gPHB-COD)$^{-1}$] differs from that for aerobic growth.

- *Decay of polyP heterotrophs (processes 23 to 34):* This process is modelled in a slightly different manner to that of the non-polyP heterotrophs to account for the effect of electron acceptor on the polyP organisms, as well as other differences such as

the amount of nitrogen, phosphorus, and stored PHB released due to cell decay. Twelve process rate equations in all are used to simulate aerobic, anoxic, and anaerobic decay of the polyP organisms, and the associated lysis of polyphosphate, PHB, and cellular N and P.

- *Cleavage of polyP for anaerobic maintenance (process 35):* The polyphosphate polymers stored by the polyP organisms are used under anaerobic conditions to supply the maintenance energy requirements. Cleavage of polyphosphate is modelled as a first order process with respect to the polyP organism mass.

- *Sequestration of SCFA by polyP organisms (process 36):* Cleavage of polyphosphate polymers supplies the energy requirements for the storage of the SCFA as PHB by the polyP heterotrophic organisms. The rate of SCFA uptake is assumed to be zero order with respect to the SCFA concentration, and first order with respect to the polyP organism concentration. The stored PHB yield is Y_{PHB} units (as COD) for each unit of SCFA COD taken up. The release of P due to polyphosphate cleavage is assumed to be directly proportional to the uptake of the SCFA. Switching functions allow the process to be switched off if either polyphosphate or SCFA become limiting. [For modelling purposes, the SCFA are assumed to be acetate or similar compounds, and all of the stored organics are assumed to be in the form of PHB].

Table 6.4: Model matrix for the polyP organism component of the general model.

	COMPONENT →	1	2	3	4	5	6	7	8	9	10	11	12	13
	PROCESS ↓	Z_H	Z_A	Z_P	Z_E	S_{ENM}	S_{BSC}	S_{BSA}	S_{PHB}	S_{UP}	S_{US}	$P_{PP\text{-}LO}$	$P_{PP\text{-}HI}$	P_{O4}
18	Aerobic growth of polyP organisms on S_{PHB} with N_{H3}			1					$\frac{-1}{Y_P}$			$f_{PP}\cdot\frac{f_{P,UPT1}}{Y_P}$	$(1-f_{PP})\cdot\frac{f_{P,UPT1}}{Y_P}$	$-f_{P,UPT1}/Y_P$ $-f_{P,ZP}$
19	Aerobic growth of polyP organisms on S_{PHB} with N_{O3}			1					$\frac{-1}{Y_P}$			$f_{PP}\cdot\frac{f_{P,UPT1}}{Y_P}$	$(1-f_{PP})\cdot\frac{f_{P,UPT1}}{Y_P}$	$-f_{P,UPT1}/Y_P$ $-f_{P,ZP}$
20	Process 18 if P_{O4} limited			1					$\frac{-1}{Y_P}$			$-f_{P,ZP}$		
21	Process 19 if P_{O4} limited			1					$\frac{-1}{Y_P}$			$-f_{P,ZP}$		
22	Anoxic growth of polyP organisms on S_{PHB} with N_{H3}			1					$\frac{-1}{Y_P}$			$f_{PP}\cdot\frac{f_{P,UPT2}}{Y_P}$	$(1-f_{PP})\cdot\frac{f_{P,UPT2}}{Y_P}$	$-f_{P,UPT2}/Y_P$ $-f_{P,ZP}$
23	Aerobic decay of polyP organisms			-1	$f_{EP,P}$						$f_{ES,P}$			$f_{P,ZP}$ $-f_{EP,P}\cdot f_{P,ZEP}$
24	$P_{PP\text{-}LO}$ lysis on aerobic decay											-1		1
25	$P_{PP\text{-}HI}$ lysis on aerobic decay												-1	1
26	S_{PHB} lysis on aerobic decay							1	-1					
27	Anoxic decay of polyP organisms			-1	$f_{EP,P}$						$f_{ES,P}$			$f_{P,ZP}$ $-f_{EP,P}\cdot f_{P,ZEP}$
28	$P_{PP\text{-}LO}$ lysis on anoxic decay											-1		1
29	$P_{PP\text{-}HI}$ lysis on anoxic decay												-1	1
30	S_{PHB} lysis on anoxic decay							1	-1					
31	Anaerobic decay of polyP organisms			-1	$f_{EP,P}$						$1-f_{EP,P}$			$f_{P,ZP}$ $-f_{EP,P}\cdot f_{P,ZEP}$
32	$P_{PP\text{-}LO}$ lysis on anaerobic decay											-1		1
33	$P_{PP\text{-}HI}$ lysis on anaerobic decay												-1	1
34	S_{PHB} lysis on anaerobic decay							1	-1					
35	Cleavage of polyP for anaerobic maintenance											-1		1
36	Sequestration of SCFA by polyP organisms							-1	Y_{PHB}			$-f_{P,REL}$		$f_{P,REL}$

Table 6.4: (Continued).

	14	15	16	17	18	19	RATE EQUATION, ρ_i
	N_{BP}	N_{BS}	N_{O3}	N_{HS}	N_{US}	S_O	
18				$-f_{N,ZP}$		$-\frac{(1-Y_P)}{Y_P}$	$\mu_{P1}\cdot\frac{S_{PHB}/Z_P}{K_{SP1}+S_{PHB}/Z_P}\cdot Z_P\cdot AirYesHet\cdot NH_3Yes\cdot PO_4UptYes$
19			$-f_{N,ZP}$			$-\frac{(1-Y_P)}{Y_P}$	$\mu_{P1}\cdot\frac{S_{PHB}/Z_P}{K_{SP1}+S_{PHB}/Z_P}\cdot Z_P\cdot AirYesHet\cdot NO_3Yes\cdot NH_3No\cdot PO_4UptYes$
20				$-f_{N,ZP}$		$-\frac{(1-Y_P)}{Y_P}$	$\mu_{P2}\cdot\frac{S_{PHB}/Z_P}{K_{SP2}+S_{PHB}/Z_P}\cdot Z_P\cdot AirYesHet\cdot NH_3Yes\cdot PO_4UptNo$
21			$-f_{N,ZP}$			$-\frac{(1-Y_P)}{Y_P}$	$\mu_{P2}\cdot\frac{S_{PHB}/Z_P}{K_{SP2}+S_{PHB}/Z_P}\cdot Z_P\cdot AirYesHet\cdot NO_3Yes\cdot NH_3No\cdot PO_4UptNo$
22			$-\frac{(1-Y_P)}{2.86Y_P}$	$-f_{N,ZP}$			$\eta_P\cdot\mu_{P1}\cdot\frac{S_{PHB}/Z_P}{K_{SP1}+S_{PHB}/Z_P}\cdot Z_P\cdot AirNoHet\cdot NO_3Yes\cdot NH_3Yes\cdot PO_4UptYes$
23		$f_{ES,P}\cdot f_{N,SEP}$		$f_{N,ZP}$ $-f_{EP,P}\cdot f_{N,ZEP}$ $-f_{ES,P}\cdot f_{N,SEP}$		$-(1-f_{EP,P}$ $-f_{ES,P})$	$b_P\cdot Z_P\cdot AirYesHet$
24							$\rho_{23}\cdot\frac{P_{PP\text{-}LO}}{Z_P}$
25							$\rho_{23}\cdot\frac{P_{PP\text{-}HI}}{Z_P}$
26							$\rho_{23}\cdot\frac{S_{PHB}}{Z_P}$
27		$f_{ES,P}\cdot f_{N,SEP}$	$-\frac{(1-f_{EP,P}-f_{ES,P})}{2.86}$	$f_{N,ZP}$ $-f_{EP,P}\cdot f_{N,ZEP}$ $-f_{ES,P}\cdot f_{N,SEP}$			$b_P\cdot Z_P\cdot AirNoHet\cdot NO_3Yes$
28							$\rho_{27}\cdot\frac{P_{PP\text{-}LO}}{Z_P}$
29							$\rho_{27}\cdot\frac{P_{PP\text{-}HI}}{Z_P}$
30							$\rho_{27}\cdot\frac{S_{PHB}}{Z_P}$
31		$f_{ES,P}\cdot f_{N,SEP}$		$f_{N,ZP}$ $-f_{EP,P}\cdot f_{N,ZEP}$ $-f_{ES,P}\cdot f_{N,SEP}$			$b_P\cdot Z_P\cdot AirNoHet\cdot NO_3No$
32							$\rho_{31}\cdot\frac{P_{PP\text{-}LO}}{Z_P}$
33							$\rho_{31}\cdot\frac{P_{PP\text{-}HI}}{Z_P}$
34							$\rho_{31}\cdot\frac{S_{PHB}}{Z_P}$
35							$b_{PP}\cdot Z_P\cdot AirNoHet\cdot PolyPYes$
36							$K_P\cdot Z_P\cdot S_{BSA}Yes\cdot PolyPYes$

Table 6.5: Stoichiometric parameters for the general model.

Non-polyP Heterotrophs			
$Y_{H,AER}$	Yield (aerobic)	0.666	g cell COD yield (g COD utilized)$^{-1}$
$Y_{H,ANOX}$	Yield (anoxic)	0.666	g cell COD yield (g COD utilized)$^{-1}$
$Y_{H,ANA}$	Yield (anaerobic)	0.100	g cell COD yield (g COD utilized)$^{-1}$
Y_{AC}	Fermentation S_{BSA} yield	0.50	g S_{BSA} COD (g S_{BSC} COD)$^{-1}$
E_{ANOX}	Hydrolysis efficiency factor (anoxic)	0.90	g S_{BSC} COD (g S_{ENM} COD)$^{-1}$
E_{ANA}	Hydrolysis efficiency factor (anaerobic)	0.60	g S_{BSC} COD (g S_{ENM} COD)$^{-1}$
$f_{N,ZH}$	Nitrogen content of active mass	0.068	g N (g COD active organisms)$^{-1}$
$f_{N,ZEH}$	Nitrogen content of endogenous mass	0.068	g N (g COD endogenous residue)$^{-1}$
$f_{P,ZH}$	Phosphorus content of active mass	0.021	g P (g COD active organisms)$^{-1}$
$f_{P,ZEH}$	Phosphorus content of endogenous mass	0.021	g P (g COD endogenous residue)$^{-1}$
$f_{EP,H}$	Fraction of active mass remaining as endogenous residue	0.08	g COD endog. mass (g COD active mass)$^{-1}$
$f_{CV,H}$	Ratio COD/VSS	1.48	g COD (g VSS)$^{-1}$
PolyP Heterotrophs			
Y_P	Yield	0.639	g cell COD yield (g COD utilized)$^{-1}$
$f_{P,UPT1}$	P uptake/ COD utilized in aerobic growth	0.95	g P (g stored COD)$^{-1}$
$f_{P,UPT2}$	P uptake/ COD utilized in anoxic growth	0.55	g P (g stored COD)$^{-1}$
Y_{PHB}	PHB yield on sequestration of S_{BSA}	0.889	g PHB COD (g S_{BSA} COD)$^{-1}$
$f_{N,ZP}$	Nitrogen content of active mass	0.070	g N (g COD active organisms)$^{-1}$
$f_{N,ZEP}$	Nitrogen content of endogenous mass	0.070	g N (g COD endogenous residue)$^{-1}$
$f_{N,SEP}$	Nitrogen content of soluble unbio. COD	0.070	g N (g COD endogenous residue)$^{-1}$
$f_{P,ZP}$	Phosphorus content of active mass (excluding polyP content)	0.021	g P (g COD active organisms)$^{-1}$
$f_{P,ZEP}$	Phosphorus content of endogenous mass	0.021	g P (g COD endogenous residue)$^{-1}$
$f_{EP,P}$	Fraction of active mass remaining as particulate unbio. endogenous residue	0.25	g COD endog. mass (g COD active mass)$^{-1}$
$f_{ES,P}$	Fraction of active mass remaining as soluble unbio. residue	0.20	g COD (g COD active mass)$^{-1}$
$f_{P,REL}$	P release/SCFA COD uptake for sequestration	0.52	g P (g S_{BSA} COD)$^{-1}$
$f_{CV,P}$	Ratio COD/VSS	1.42	g COD (g VSS)$^{-1}$
f_{PP}	Fraction of taken up P which can be released	0.94	g P (g P)$^{-1}$
Autotrophs			
Y_A	Yield	0.150	g cell COD yield (g N utilized)$^{-1}$
$f_{N,ZA}$	Nitrogen content of active mass	0.068	g N (g COD active organisms)$^{-1}$
$f_{N,ZEA}$	Nitrogen content of endogenous mass	0.068	g N (g COD endogenous residue)$^{-1}$
$f_{P,ZA}$	Phosphorus content of active mass	0.021	g P (g COD active organisms)$^{-1}$
$f_{P,ZEA}$	Phosphorus content of endogenous mass	0.021	g P (g COD endogenous residue)$^{-1}$
$f_{EP,A}$	Fraction of active mass remaining as endogenous residue	0.08	g COD endog. mass (g COD active mass)$^{-1}$
$f_{CV,A}$	Ratio COD/VSS	1.42	g COD (g VSS)$^{-1}$

Table 6.6: Kinetic parameters for the general model.

Non-polyP Heterotrophs				θ
μ_H	Maximum specific growth rate	3.2	d^{-1}	1.029
$K_{S,H}$	Half saturation coefficient for growth	5.0	g COD m^{-3}	1.000
b_H	Organism decay rate	0.62	d^{-1}	1.029
$\eta_{S,ANOX}$	Anoxic solubilization factor	1.00	-	-
$\eta_{S,ANA}$	Anaerobic solubilization factor	0.50	-	-
η_{GRO}	Anoxic growth factor	0.37	-	-
K_H	Maximum specific hydrolysis rate	2.81	d^{-1}	1.050
K_X	Half saturation coefficient for hydrolysis	0.15	g COD (g COD)$^{-1}$	1.000
K_C	Maximum specific fermentation growth rate	4.0	d^{-1}	1.029
$K_{S,ANA}$	Fermentation half saturation coefficient	2.0	g COD m^{-3}	1.000
K_R	Ammonification rate	0.08	m^3 (g COD . d)$^{-1}$	1.029
PolyP Heterotrophs				
μ_{P1}	Maximum specific growth rate (no P limit)	0.95	d^{-1}	1.000
μ_{P2}	Maximum specific growth rate (P limit)	0.42	d^{-1}	1.000
K_{SP1}	Half saturation coefficient (no P limit)	0.10	g COD (g COD . d)$^{-1}$	1.000
K_{SP2}	Half saturation coefficient (P limit)	0.05	g COD (g COD . d)$^{-1}$	1.000
η_P	Anoxic growth factor	0.40	-	-
b_P	Organism endogenous mass loss rate	0.04	d^{-1}	1.000
b_{PP}	PolyP cleavage rate for anaerobic "maintenance" energy generation	0.03	d^{-1}	1.000
K_P	Specific rate of SCFA sequestration	2.00	g COD (g COD . d)$^{-1}$	1.000
Autotrophs				
μ_A	Maximum specific growth rate	0.2-1.0	d^{-1}	1.123
K_{NH}	Half saturation coefficient for growth	1.0	g N m^{-3}	1.123
b_A	Organism decay rate	0.04	d^{-1}	1.029

TEMPERATURE ADJUSTMENT OF KINETIC PARAMETERS:

$$K_T = K_{20} \cdot \theta^{(T-20)}$$

where K_T = parameter value at T°C

K_{20} = parameter value at 20°C

θ = temperature adjustment coefficient

Table 6.7: Switching function parameters for the general model.

$K_{O,HET}$	Aerobic/anoxic growth of heterotrophs	0.002	g O_2 m^{-3}
$K_{O,AUT}$	Aerobic growth of autotrophs	0.50	g O_2 m^{-3}
K_{NA}	Ammonia limit	0.005	g N m^{-3}
K_{NO}	Nitrate limit	0.10	g N m^{-3}
$K_{LP,UPT}$	Phosphate limit	0.25	g P m^{-3}
$K_{LP,GRO}$	Phosphate limit	0.005	g P m^{-3}
K_{XP}	PolyP limit	0.01	g P (g COD)$^{-1}$
K_{SSEQ}	SCFA limit	2.50	g COD m^{-3}

CALIBRATION AND EVALUATION OF THE GENERAL MODEL

The general model incorporates a large number of stoichiometric and kinetic parameters relating to the three organism masses. The suggested parameter values reported in this paper were derived from an extensive calibration exercise involving three parts:

- The model evolved from a number of earlier models, as discussed. In many instances parameter values taken from these models were found satisfactory (or with minor adjustment).

- A number of "new" parameters were based on experimental data presented in the literature; for example, the anoxic P uptake ratio ($f_{P,UPT2}$).

- Other "new" parameters were established through application of the model to a number of experimental systems, adjusting parameter values to give the best fit.

The general model has been applied to a wide range of systems operated over a range of conditions (sludge age, recycle rates, etc.); for example, aerobic systems (with and without nitrification), ND systems, BEPR systems, NDBEPR systems (under steady state and dynamic conditions). The model simulates the organism mass distribution and satisfactorily tracks the changes in a range of key parameters such as soluble phosphorus and nitrate concentrations. What is most important is that the volatile suspended solids concentration and the oxygen utilization rates in the aerated reactors also are predicted

reasonably. This is of particular significance given the model assumptions on COD loss. Results from simulations of a number of systems are presented in a Part II paper.

An important feature of the model calibration exercise is that a single set of kinetic and stoichiometric model parameters produced quite accurate predictions for all systems. [One exception is the maximum specific growth rate of the nitrifiers, μ_A - see comments later]. This provides a degree of support for the model structure and integrity.

CLOSURE

This paper has outlined a general activated sludge dynamic model with the capacity for modelling the biological processes of carbonaceous energy removal, nitrification, denitrification and biological excess phosphorus removal. The satisfactory results from use of the model provide a basis for further model evaluation and refinement. Improvements to the model no doubt will come about as the understanding of the complex interactions occurring within biological nutrient removal systems is expanded. Many aspects require further investigation; for example:

- The mechanisms, kinetics and temperature dependency of enzymatic hydrolysis of slowly biodegradable colloidal and particulate organic substrate. Current understanding of this behaviour is limited, particularly for anoxic and anaerobic conditions important to nutrient removal systems.

- Fermentation behaviour under anaerobic (and possibly anoxic) conditions.

- How the above two aspects impact denitrification behaviour, and the competition between polyP and non-polyP denitrifiers.

- The temperature dependency of the polyP organism kinetic behaviour.

- The fate of "unbiodegradable" COD generated by the endogenous processes of polyP organisms.

The most important unresolved aspect of NDBEPR modelling is the COD loss phenomenon. In the model COD loss is assumed to occur through three different biological processes: fermentation, sequestration, and hydrolysis under anoxic/anaerobic conditions. Empirical parameters have been incorporated which allow the model to predict the COD loss observed in a range of systems. While these empirical relationships appear to give reasonable results, an understanding of the underlying mechanisms is required in order to optimize system performance.

There is no doubt that modelling and simulation are assuming a prominent role in nutrient removal system design, operation and control. It should be recognized that the model described here considers only the activated sludge system. This is only one part of the wastewater treatment cycle. Other unit operations within the treatment plant (and operating procedures) are very important to overall system performance. A comprehensive treatment plant simulator should incorporate all of these aspects; for example, settling tanks, sludge fermenters, digesters, handling of supernatant streams, and so on.

A final comment is worth making regarding the importance of a key aspect which is perhaps not emphasized explicitly in this paper; namely selection of modelling parameters. In applying the model to predict system behaviour, the model requires values for *stoichiometric and kinetic parameters*; for example, yields and growth rates. In addition, a number of parameters which define the *characteristics of the influent wastewater* must be specified; for example, the readily biodegradable COD content, the fraction of unbiodegradable COD which is soluble and particulate, and so on.

References are available which discuss measurement techniques for the stoichiometric and kinetic parameters and influent wastewater characteristics [WRC (1984); Ekama *et al.*(1986); Henze *et al.* (1986, 1987, 1994c); Lesouef *et al.*(1992); Kappeler and Gujer (1992); Gibson (1991); Mamais *et al.*(1993)]. However, several studies have shown that the stoichiometric and kinetic parameters (with one notable exception discussed below) do not change appreciably for different systems *treating municipal wastewaters* [Dold and Marais (1986); Gibson (1991)]. For example, the decay rate estimated from the decline in oxygen utilization rate in a batch aerobic sludge digestion test is the same for sludge drawn from aerobic systems in Canada or South Africa (at least at 20°C). Therefore, it is

proposed that the values for the stoichiometric and kinetic model parameters tabulated in this paper (largely derived from previous studies on a range of treatment systems) should be acceptable initial estimates, and should not require substantial adjustment in model calibration exercises.

The exception referred to above is the maximum specific growth rate of the nitrifiers, μ_A. This parameter shows marked variations between systems treating different wastewaters. The oxidation of saline ammonia first to nitrite ions and then to nitrate is due to two specific genera of autotrophic bacteria, the *Nitrosomonas* and the *Nitrobacter*. The *Nitrosomonas* oxidize free and saline ammonia to nitrite and the *Nitrobacter* oxidize nitrite to nitrate. The first step (i.e. conversion of ammonia to nitrite) usually is the rate limiting one in the two-step nitrification process. As a result, nitrification usually is considered as a single step process mediated by one group of nitrifying autotrophic bacteria. The growth rate parameter for the nitrifiers (μ_A) defines the maximum specific growth rate of this surrogate organism mass. Values for μ_A (at 20°C) ranging from 0.2 to 1.0 d^{-1} have been observed in activated sludge systems treating a number of different wastewaters (WRC, 1984). The variation appears to correlate with the extent of the industrial component in the wastewater; it has been suggested that with increased industrial input there is an increased possibility of inhibition of nitrifying organisms. Another factor influencing the rate between wastewaters may be differences in pH. This parameter has a major impact on nutrient removal system design and performance, and obviously on model predictions as well. Therefore, special attention should be paid to measurement or estimation of μ_A. In a sense, μ_A can be regarded as a wastewater characteristic.

Regarding the *influent wastewater characteristics* (see Appendix), studies have demonstrated that these do change, often appreciably, from one municipal waste to another. Wastewater characteristics have a very significant impact on system performance, particularly for nutrient removal systems. A single characteristic such as the readily biodegradable COD fraction can determine whether or not a system designed for excess P removal will in fact remove phosphorus. Therefore, if the model is to provide reasonable predictions of system behaviour, adequate knowledge of wastewater characteristics is extremely important. It is likely that the importance of the measurement (or appropriate estimation) of wastewater characteristics will receive increasing attention through wider application of models such as the one presented here.

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APPENDIX TO CHAPTER SIX:

INFLUENT WASTEWATER CHARACTERIZATION

Studies have demonstrated that the influent wastewater characteristics change, often appreciably, from one municipal wastewater to another. Differences in characteristics usually are a function of a combination of the following factors: (1) socio-economic factors; (2) water usage; (3) degree of inflow and infiltration; (4) use of garbage grinders; (5) presence, magnitude and nature of any industrial content; (6) size, retention time and storage capacity within the sewage collection system; and (7) presence of a phosphate detergent ban.

Organic Material

Characterization of the carbonaceous material in municipal wastewater is in terms of the chemical oxygen demand (COD). The advantage of selecting COD as the parameter for quantifying the "strength" of organic material in the influent, as opposed to BOD or TOC, is that it provides a consistent basis for description of the activated sludge process. The division of the total influent COD (S_{Ti}) into the various fractions used in nutrient removal system design and modelling is shown diagrammatically in Fig. 6.2.

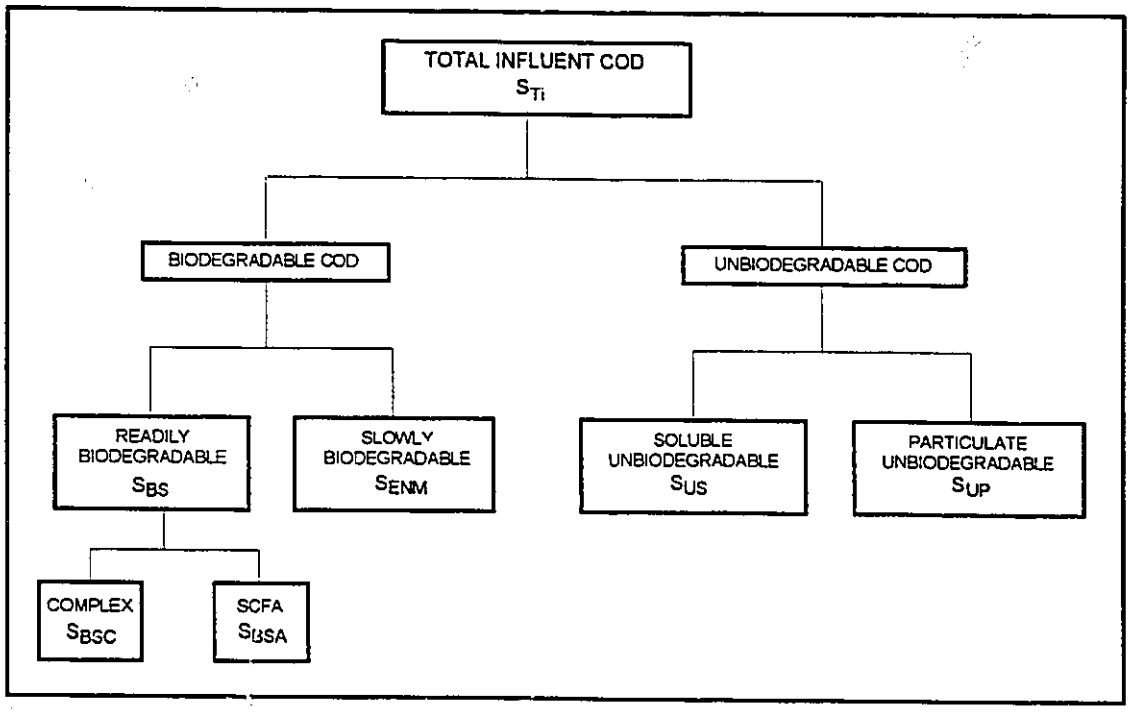

Figure 6.2 Division of municipal wastewater COD into constituent fractions.

Biodegradable and unbiodegradable fractions: The first division of the influent COD is into biodegradable COD and unbiodegradable COD. Each of these fractions is divided further into two sub-fractions.

Biodegradable sub-fractions: The biodegradable material is divided into a readily biodegradable fraction (S_{BS}) and a slowly biodegradable fraction (S_{ENM}). The readily biodegradable fraction is hypothesized to consist of material that can be absorbed readily by the organism and metabolized for energy and synthesis. The slowly biodegradable fraction is assumed to be made up of particulate/colloidal material and complex organic molecules that require extracellular enzymatic breakdown prior to absorption and utilization. The apportionment between readily and slowly biodegradable COD has a major influence on process dynamic behaviour (for example, oxygen demand) and is of crucial importance in the design of biological nitrogen and phosphorus removal systems. For purposes of modelling biological excess phosphorus removal systems it is necessary to

distinguish a further division of the readily biodegradable material (S_{BS}). The readily biodegradable fraction is hypothesized to consist of complex readily biodegradable COD (S_{BSC}) and readily biodegradable COD in the form of short chain volatile fatty acids (S_{BSA}).

Unbiodegradable sub-fractions: The unbiodegradable material is divided into an unbiodegradable soluble fraction (S_{US}) and an unbiodegradable particulate fraction (S_{UP}). Both components are hypothesized to be unaffected by biological action in the system. In an activated sludge system the S_{US} leaves via the secondary clarifier overflow at a concentration equal to that in the influent. The S_{UP} is enmeshed in the sludge mass and accumulates in the system. At steady state the mass of S_{UP} entering the system in the influent will be balanced by the mass leaving via the sludge wastage stream. From a mass balance standpoint, the mass of S_{UP} in the system will equal the influent mass per day multiplied by the system sludge age. In systems operated at a long sludge age the S_{UP} can constitute a significant fraction of the mixed liquor settleable solids concentration.

Quantifying the division: From certain practical considerations the division of the influent wastewater COD into fractions usually is defined by fractional parameters: f_{US}, f_{UP} and f_{BS}.

f_{US} = fraction of the total influent COD which is unbiodegradable soluble;

f_{UP} = fraction of the total influent COD which is unbiodegradable particulate;

f_{BS} = fraction of the total influent COD which is readily biodegradable.

Using these fractions the division of the total influent COD (S_{Ti}) into the various sub-fractions may be expressed as follows:

$$S_{USi} = f_{US}\ S_{Ti} \qquad (A.1)$$

$$S_{UPi} = f_{UP}\ S_{Ti} \qquad (A.2)$$

$$S_{BSi} = f_{BS}\ S_{Ti} \qquad (A.3)$$

$$S_{ENMi} = (1 - f_{BS} - f_{US} - f_{UP})\ S_{Ti} \qquad (A.4)$$

The division of influent organic material as outlined here does not incorporate heterotrophic biomass as a component of influent wastewater. Studies in Europe (e.g. Kappeler & Gujer, 1992) indicate that this component may be significant.

Nitrogenous Material

Characterization of the nitrogenous material in the influent (N_{Ti}) is in terms of the total Kjeldahl nitrogen (TKN). [In a limited number of cases, mainly in Europe, appreciable influent concentrations of nitrate/nitrite have been encountered in municipal wastewaters. This has a significant impact on nutrient removal system design and performance. For these cases the influent nitrate/nitrite concentration must be included as an additional wastewater characteristic, separate from the TKN]. For design and modelling purposes it is necessary to specify the magnitudes of the various fractions of the influent TKN according to the division shown diagrammatically in Fig. 6.3.

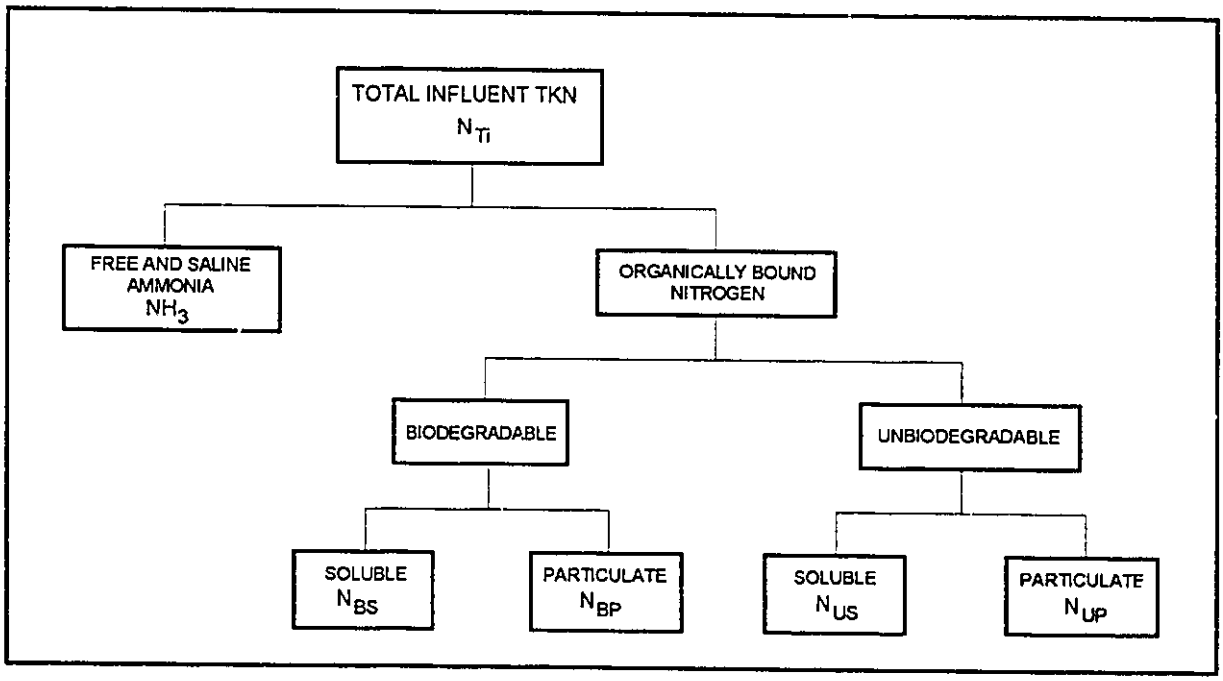

Figure 6.3 Division of municipal wastewater TKN into constituent fractions.

Free and saline ammonia and organically bound fractions: The first division of the influent TKN is into free and saline ammonia (N_{H3}) and organically bound TKN. The organically bound TKN is divided further into two fractions (biodegradable and unbiodegradable) each with soluble and particulate portions.

Biodegradable organically bound TKN: The biodegradable organic nitrogen is divided into a soluble fraction (N_{BS}) and a particulate fraction (N_{BP}).

Unbiodegradable organically bound TKN: This component of the organic nitrogen is divided into an unbiodegradable soluble fraction (N_{US}) and an unbiodegradable particulate fraction (N_{UP}). The unbiodegradable fractions are hypothesized to be unaffected by biological action in the system. In an activated sludge system the soluble unbiodegradable material leaves via the secondary clarifier overflow at a concentration equal to that in the influent. The particulate unbiodegradable fraction is material associated with the unbiodegradable particulate COD in the influent and leaves the system via the sludge wastage stream.

Quantifying the division: Again, from practical considerations the nitrogen fractions of the influent wastewater TKN are defined by fractional constants: f_{NA}, f_{NUS} , f_{NUP} and f_{NOP}:

f_{NA} = fraction of the total influent TKN which is free and saline ammonia;

f_{NUS} = fraction of the total influent TKN which is unbiodegradable soluble;

f_{NUP} = fraction of the total influent TKN which is unbiodegradable particulate;

f_{NOP} = fraction of the biodegradable organic TKN which is particulate.

The division of the influent TKN (N_{Ti}) into the various sub-fractions may be expressed as follows:

$$N_{USi} = f_{NUS}\ N_{Ti} \quad (A.6)$$

$$N_{UPi} = f_{NUP}\ N_{Ti} \quad (A.7)$$

The biodegradable organic nitrogen (N_{OBi}) is given by the total influent TKN less the sum of N_{H3}, N_{US} and N_{UP}.

$$N_{OBi} = (1 - f_{NA} - f_{NUS} - f_{NUP})\ N_{Ti} \quad (A.8)$$

The soluble (N_{BS}) and particulate (N_{BP}) influent biodegradable organic nitrogen concentrations are respectively:

$$N_{BSi} = (1 - f_{NOP})\ N_{OBi} \quad (A.9)$$

$$N_{BPi} = f_{NOP}\ N_{OBi} \quad (A.10)$$

Phosphorus Content

Characterization of the phosphorus content of the influent (P_{Ti}) is in terms of the total phosphorus concentration (TP). In the context of nutrient removal, division of the TP into subfractions has not received as much attention as the COD and TKN. The approach in modelling and design has been to assume that a portion of the influent TP is associated with the unbiodegradable influent COD (approximately 10 to 15 percent of TP), and that the remainder can be considered as orthophosphate. Limited data on influent soluble reactive phosphorus (SRP - generally considered to be orthophosphate) would indicate this approach to be reasonable. That is, measurements of influent SRP are similar to TP less P associated with the unbiodegradable influent COD (assuming a P content of approximately 0.02 mg P per mg unbiodegradable particulate COD).

Several factors support the need for a more rigorous accounting of phosphorus fractions, considering the increasing emphasis on low effluent phosphorus concentrations (< 0.3 mgP/L). For example, up to 90 per cent of the total soluble phosphorus (TSP) in aquatic systems can be comprised of soluble unreactive phosphorus (SUP) (Minear, 1972). If SUP is an appreciable fraction of the influent TP this likely would impact the attainable minimum effluent P concentration for biological nutrient removal systems. A suitable

methodology of accounting for the various influent phosphorus fractions would be analogous to the division of influent TKN, and is shown in Fig. 6.4.

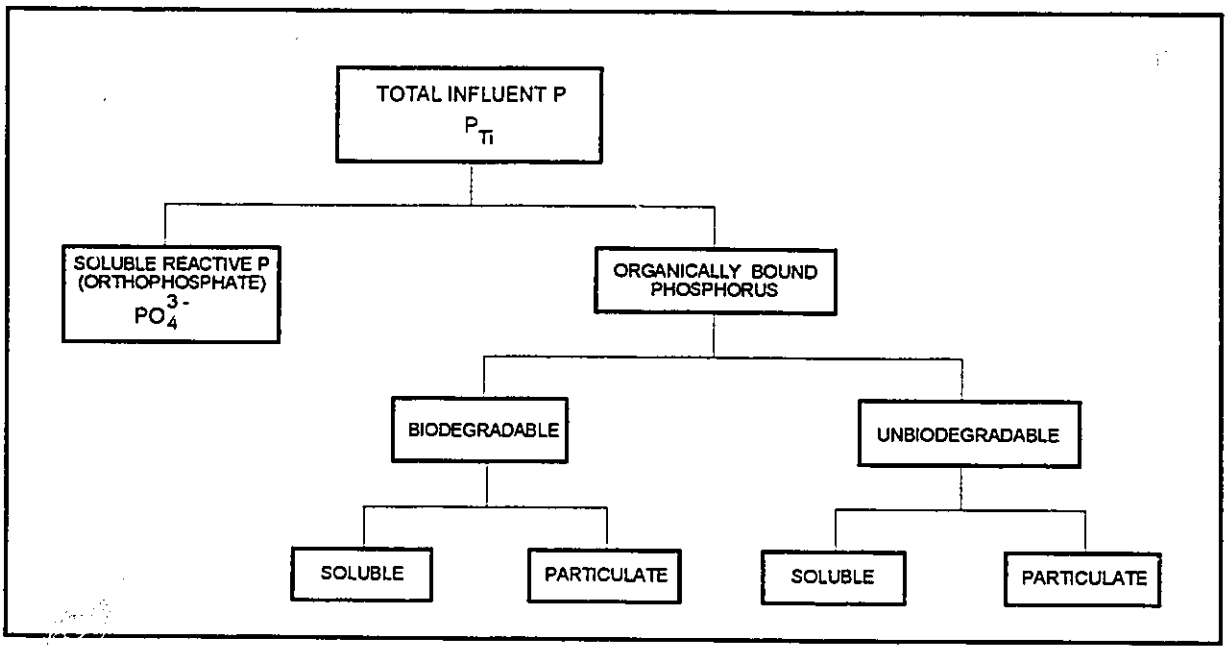

Figure 6.4 Division of municipal wastewater phosphorus into constituent fractions.

CHAPTER SEVEN

GENERAL MODEL FOR BIOLOGICAL NUTRIENT REMOVAL ACTIVATED SLUDGE SYSTEMS

PART II: MODEL APPLICATION

P. S. Barker and P. L. Dold

GENERAL MODEL FOR BIOLOGICAL NUTRIENT REMOVAL ACTIVATED SLUDGE SYSTEMS

PART II: MODEL APPLICATION

P. S. Barker and P. L. Dold

Abstract

The application of a general model for nitrification denitrification biological excess phosphorus removal (NDBEPR) activated sludge systems is demonstrated. Results of simulations show the model is capable of predicting sludge production and oxygen utilization for a range of system types and configurations, as well as tracking changes in a number of parameters including soluble phosphorus and nitrate concentrations. Application of the model is demonstrated for aerobic and anoxic-aerobic systems, as well as a number of nutrient removal systems for both steady state and dynamic conditions.

Key words: Activated sludge, biological excess phosphorus removal, biological nutrient removal, modeliing, nitrogen, phosphorus.

INTRODUCTION

A general model for activated sludge systems incorporating carbonaceous energy removal, nitrification and denitrification, as well as biological excess phosphorus removal, was presented in the Part I paper (Barker and Dold, 1995c). The model is termed general in that it can be applied to simulation of systems with or without nitrification and/or biological excess phosphorus removal.

This paper presents the results of model simulations for a large number of systems operated over a range of conditions (sludge age, recycle rates, etc.). These include aerobic systems (with and without nitrification), nitrification-denitrification (ND) systems, biological excess phosphorus removal (BEPR) systems, and NDBEPR systems (under steady state and dynamic conditions). Configurations of the various system types are shown in Fig. 7.1. It should be noted that each zone (aerobic, anoxic, anaerobic) shown in Fig. 7.1 possibly consisted of a number of compartments in series; the reader is referred to the individual references for specific details of system configuration, reactor volumes, recycle rates, and so on.

An important feature of the model application is that a single set of kinetic and stoichiometric model parameters has been applied for all systems. [One exception is the maximum specific growth rate of the nitrifiers, μ_A - see comments in Part I]. The sensitivity of model predictions to a number of parameters is discussed and demonstrated.

DATABASE FOR SIMULATIONS

For purposes of evaluating the general model it is necessary to consider application to a range of system types. An important requirement within this context is the capacity to predict the appropriate active heterotrophic organism mass structure in a system with respect to the polyP and non-polyP organisms. Typically three "normal" situations are possible:

- In completely aerobic systems the active organism mass should consist only of non-polyP organisms, and should not exhibit excess phosphorus removal. The general model predictions in this case should reduce to those of the modified ASM1 model.

- In BEPR systems incorporating unaerated zones and with *only SCFA as substrate* the active heterotrophic organism mass should consist almost entirely of polyP organisms, and should exhibit excess phosphorus removal. This would correspond to the enhanced culture systems of Wentzel *et al.* (1988, 1989a).

The general model predictions in this case should reduce to those of the enhanced culture polyP model.

- In BEPR systems with municipal wastewater as influent, and which exhibit phosphorus removal, the active organism mass should reflect the co-existence of both polyP and non-polyP organisms.

Data from six sources for three different types of activated sludge system were used for model simulation purposes:

- Aerobic systems - Schroeter *et al.* (1982), Arkley and Marais (1982);
- Anoxic-aerobic systems - Power *et al.* (1992);
- Anaerobic-anoxic-aerobic systems - Wentzel *et al.* (1989a, 1990), Malmo (1992).

The data sets include influent and effluent concentrations of COD, TKN, nitrate, and phosphorus (P), oxygen utilization rates (OUR), and volatile suspended solids (VSS) concentrations, as well as information on operating parameters (flows, recycle rates, sludge wastage, etc.) and system configuration. Certain of the data sets also include influent readily biodegradable COD concentrations and reactor concentrations of nitrate and soluble P. [It should be noted that the reported nitrate concentrations also include a small amount of nitrite.] For modelling purposes, for systems operated at steady state conditions, all parameters were averaged over an extended period (approximately 3-4 sludge ages, where possible). For the dynamic system, the influent COD, TKN, and P, as well as the anaerobic, anoxic, and effluent nitrate and PO_4-P concentrations, were reported at hourly intervals. [VSS was reported for average steady state conditions only; OUR data were not available for Malmo (1992) data on a dynamic basis.] Mass balances for nitrogen were used as a check for data reliablity, resulting in the exclusion of a number of systems from the data set of Wentzel *et al.* (1990) [see Barker and Dold, 1995a].

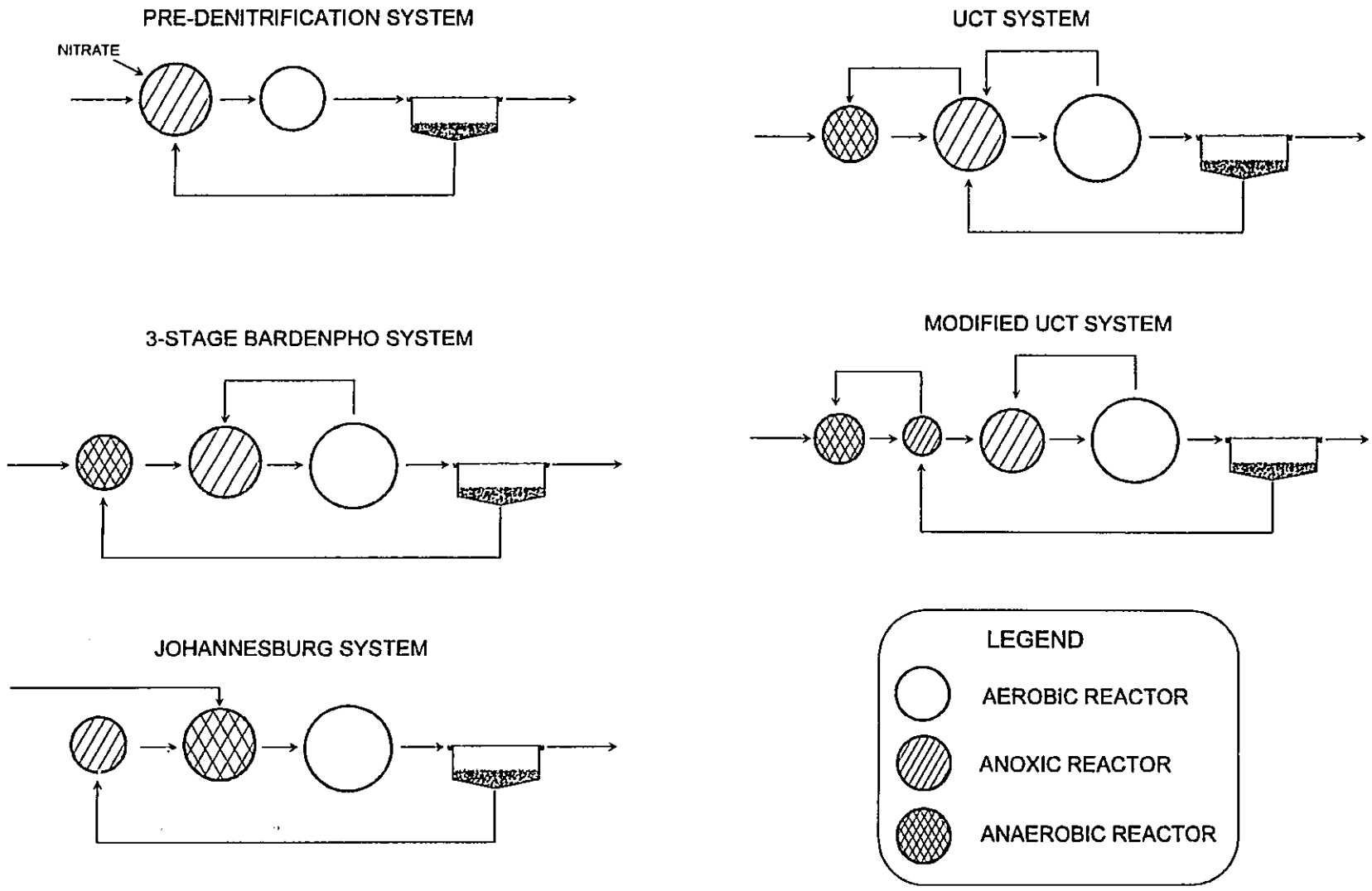

Figure 7.1 **Activated sludge system configurations utilized in the model application.**

AEROBIC SYSTEMS

Schroeter *et al.* (1982) operated three pairs of aerobic laboratory scale systems at temperatures of 12 and 20°C. The systems were operated at sludge ages of 3, 8, and 20 days. The influent consisted of domestic wastewater, diluted with tap water to a concentration of 500 mgCOD/L. All systems were single reactor systems with return activated sludge (RAS) recycle. Arkley and Marais (1981) also operated laboratory scale aerobic systems. These systems were operated at a 20 day sludge age with municipal wastewater as influent. System 1 was a single reactor system; systems 2, 3 and 4 were two-in-series reactor configurations.

Results of model simulations for the aerobic systems of Schroeter *et al.* (1982) and Arkley and Marais (1981) are shown in Tables 7.1 & 7.2 and Fig. 7.2. The model correctly predicts that the active mass in these systems is comprised entirely of non-polyP organisms (and a small nitrifier mass). The model provides quite accurate predictions for effluent nitrate and soluble TKN for most systems (with the exception of the 3 day system at 12°C where nitrification was borderline). Oxygen utilization (mass/day) and VSS predictions are also reasonable. The dotted lines in Fig. 7.2 show where the predicted and observed values are equal. Predicted and observed OUR's are shown in Tables 1 & 2. Phosphorus data were not reported.

ANOXIC-AEROBIC SYSTEMS

Power *et al.* (1992) operated a two reactor anoxic-aerobic system with a 70% unaerated mass fraction receiving municipal wastewater (operating temperature 20°C). In this system nitrate was added to the large pre-denitrification reactor to ensure that the reactor remained anoxic (system configuration shown in Fig. 7.1). The objective of nitrate addition was to prevent biological excess phosphorus removal. The system was operated at a 20 day sludge age for a total of 305 days. During this time influent and effluent concentrations of COD, TKN, P, and nitrate were measured, as well as reactor VSS concentrations and oxygen utilization rates. From this extensive data set, Power *et al.* (1992) identified a number of "steady state" operating periods. Averaged concentrations from these periods have been used for modelling purposes.

Table 7.1: Model predictions for aerobic systems of Schroeter *et al.* (1982).

System	3 day (20°C)		8 day (20°C)		20 day (20°C)		3 day (12°C)		8 day (12°C)		20 day (12°C)	
	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.
Influent:												
COD (gCOD m^{-3})	515	-	516	-	503	-	504	-	503	-	504	-
TKN (gN m^{-3})	47.4	-	47.1	-	46.2	-	45.5	-	46.1	-	46.2	-
Reactor:												
VSS (gVSS m^{-3})	1400	1568	1266	1427	1763	1896	1085	1326	1773	1821	2857	2878
OUR (gO m^{-3} h^{-1})	41.9	42.6	29.2	28.9	24.2	24.2	-	26.4	25.5	25.6	22.1	22.7
Effluent:												
TKN (gN m^{-3})	11.0	10.4	6.1	6.0	6.2	5.9	32.6	29.0	4.4	4.3	3.3	3.2
NO3 (gN m^{-3})	20.4	20.3	28.8	28.7	32.7	31.0	1.0	0.0	27.4	27.4	31.0	31.6

Table 7.2: Model predictions for aerobic systems of Arkley and Marais (1981).

System	1		2		3		4	
	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.
Influent								
COD (gCOD m^{-3})	507	-	495	-	497	-	495	-
TKN (gN m^{-3})	50.1	-	50.6	-	50.6	-	50.6	-
Reactor								
VSS (gVSS m^{-3})	2001	2009	1876	1886	1600	1754	1770	1788
OUR (s)	19.2	20.8	29.7	31.9	25.4	26.4	22.2	23.0
(gO m^{-3} h^{-1})			12.2	13.0	13.1	13.5	14.8	14.6
Effluent								
TKN (gN m^{-3})	0.2	0.9	2.7	2.6	2.6	2.7	2.5	2.3
NO3 (gN m^{-3})	39.4	39.2	39.7	38.5	40.2	39.1	40.3	39.3

*All Systems operated at a 20 day sludge age (operating temperature 20°C).

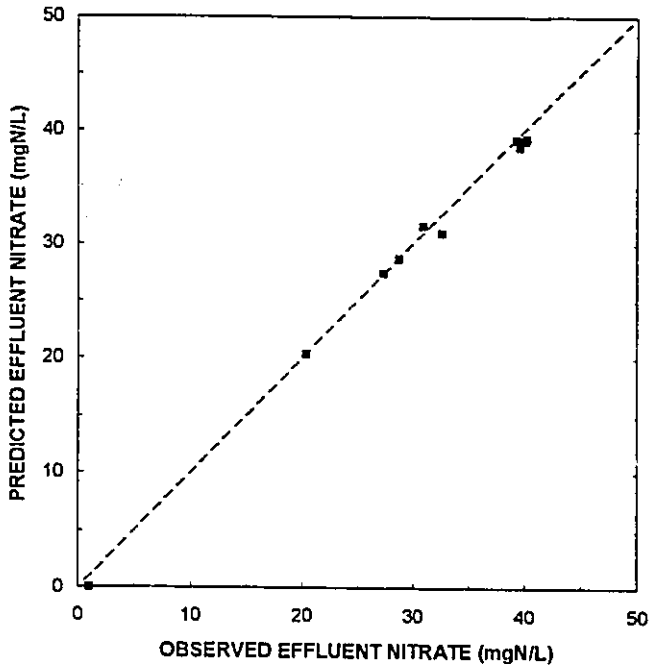

Figure 7.2a Model predictions of effluent nitrate concentration for aerobic systems of Arkley and Marais (1981) and Schroeter *et al.* (1982).

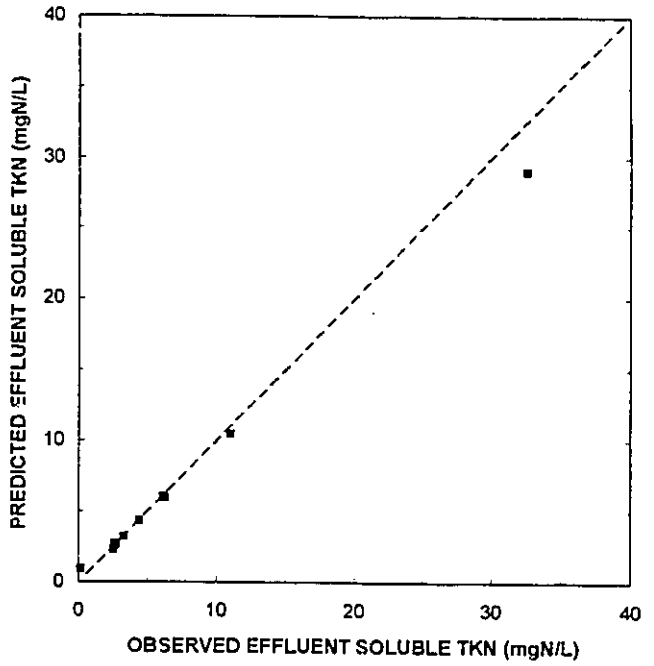

Figure 7.2b Model predictions of effluent soluble TKN concentration for aerobic systems of Arkley and Marais (1981) and Schroeter *et al.* (1982).

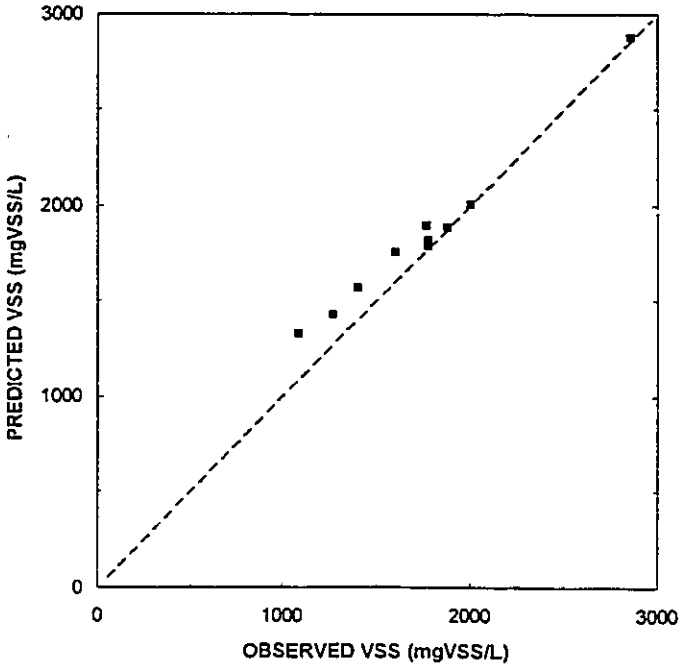

Figure 7.2c Model predictions of volatile solids concentration for aerobic systems of Arkley and Marais (1981) and Schroeter *et al.* (1982).

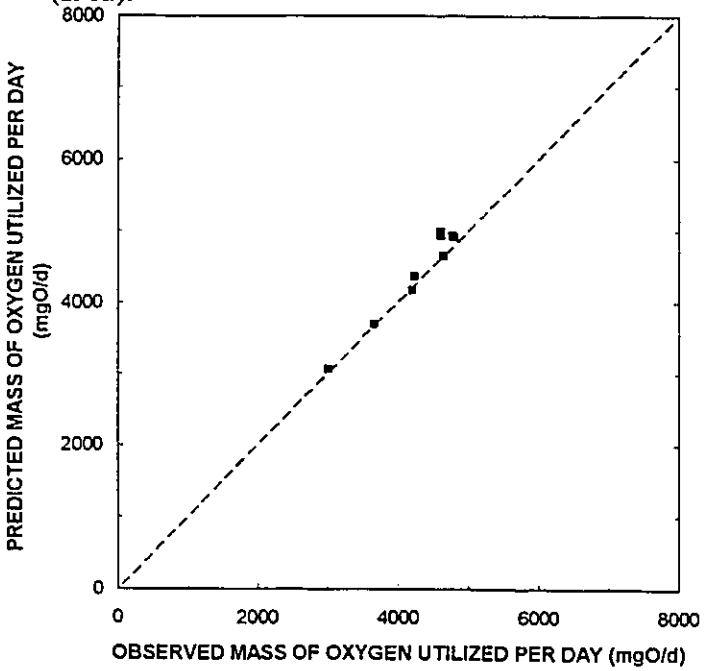

Figure 7.2d Model predictions of mass oxygen consumed per day for aerobic systems of Arkley and Marais (1981) and Schroeter *et al.* (1982).

Results of model simulations for the pre-denitrification systems of Power *et al.* (1992) are shown in Fig. 7.3. While predictions of effluent P are reasonable, effluent nitrate concentrations are under-predicted for all periods modelled. This may be due to differences in denitrification kinetics in this system, resulting in less denitrification occurring than is assumed by the model. This aspect is discussed later in the section on model sensitivity. Predictions of oxygen utilization and VSS concentrations are reasonable for all periods.

BIOLOGICAL EXCESS PHOSPHORUS REMOVAL SYSTEMS (STEADY STATE)

Systems Receiving Domestic Wastewater

Wentzel *et al.* (1990) provided comprehensive data for 30 laboratory scale nutrient removal systems treating municipal wastewater. These systems varied in configuration, reactor sizes, recycle ratios, influent flowrates, and were operated over a range of sludge ages from 3 to 21 days (all at 20°C). There were four basic configurations as shown in Fig. 7.1: 3-stage Bardenpho, Johannesburg, University of Cape Town (UCT), and the modified UCT (MUCT) configuration. The influent to these systems was supplemented with KH_2PO_4 to ensure that soluble P remained in the effluent, and the BEPR processes did not become P limited. Data were reported for each system for a number of different batches of influent wastewater (denoted by a letter appended to the system number). Only systems with reasonable nitrogen balances (between 90 and 110%) were used for modelling purposes [see Barker and Dold (1995a)].

Figure 7.4 shows results of model simulations [for reactor and effluent concentrations of a number of parameters] for the mixed culture BEPR systems of Wentzel *et al.* (1990). Reasonable predictions were obtained for effluent concentrations of soluble P and nitrate, as well as for oxygen utilization and VSS concentrations. It is also instructive to consider predictions of the concentrations of various key components from reactor to reactor in individual systems. Soluble P and nitrate profiles for a 5 reactor UCT system are shown in Fig. 7.5.

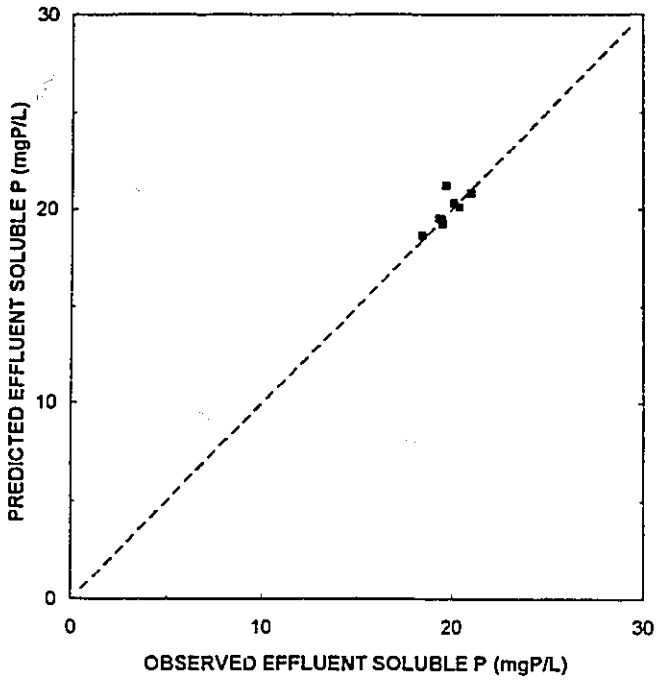

Figure 7.3a Model predictions of effluent soluble phosphorus concentration for anoxic-aerobic system of Power *et al.* (1992).

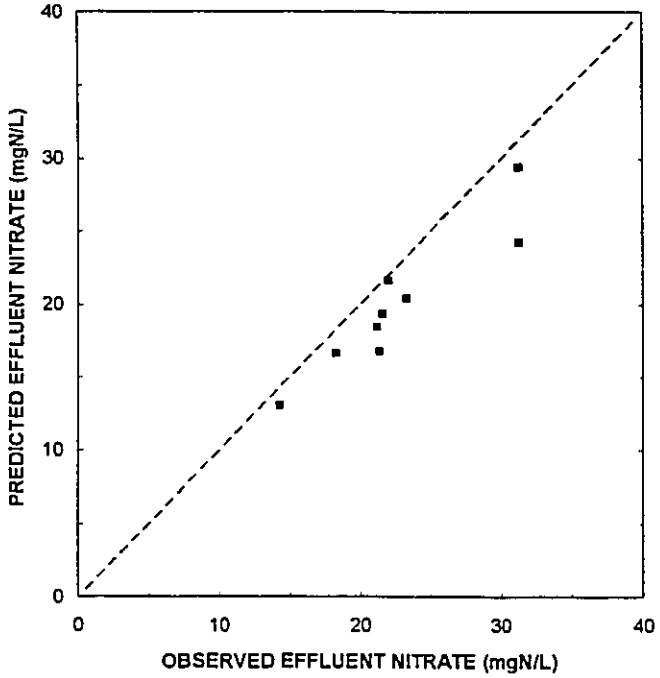

Figure 7.3b Model predictions of effluent nitrate concentration for anoxic-aerobic system of Power *et al.* (1992).

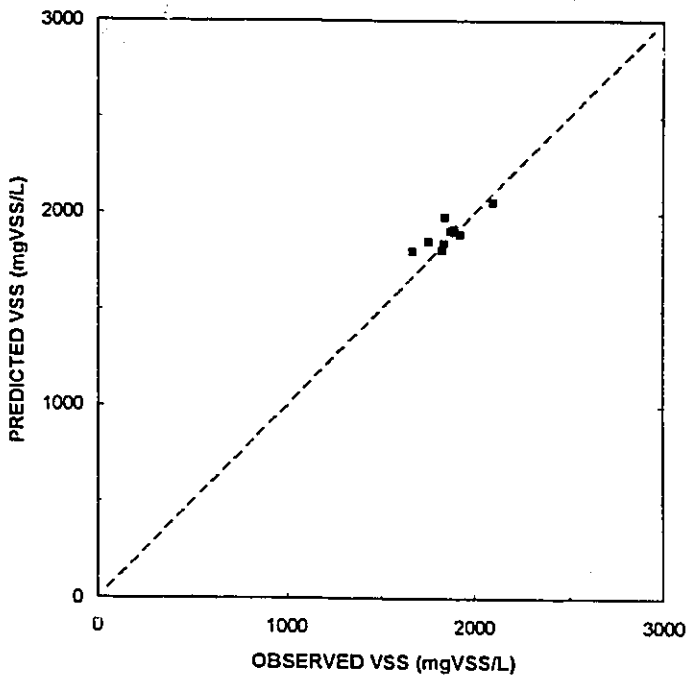

Figure 7.3c Model predictions of volatile solids concentration for anoxic-aerobic system of Power *et al.* (1992).

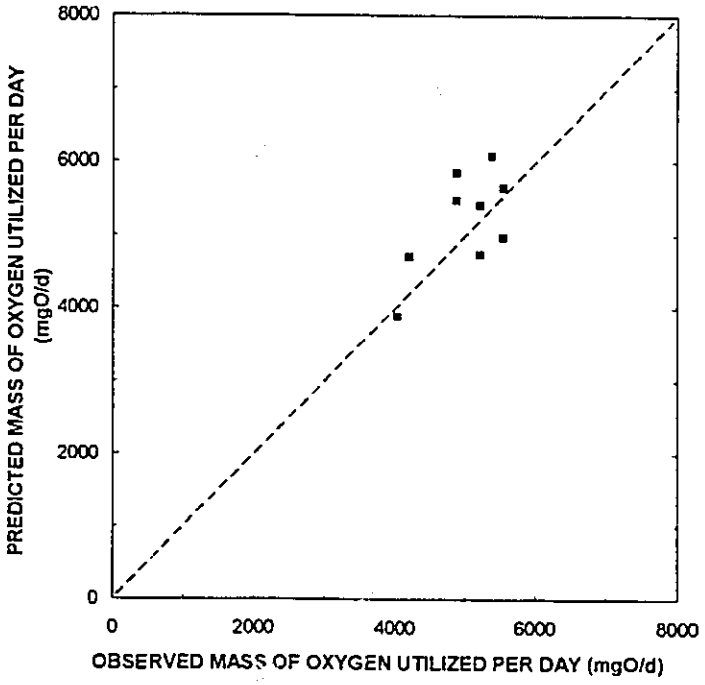

Figure 7.3d Model predictions of mass oxygen consumed per day for anoxic-aerobic system of Power *et al.* (1992).

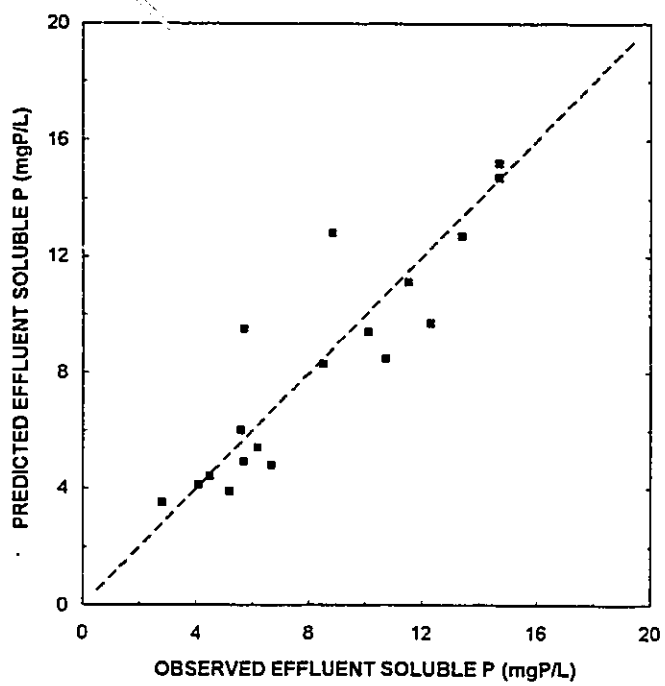

Figure 7.4a Model predictions of effluent soluble phosphorus concentration for anaerobic-anoxic-aerobic (NDBEPR) systems of Wentzel *et al.* (1990).

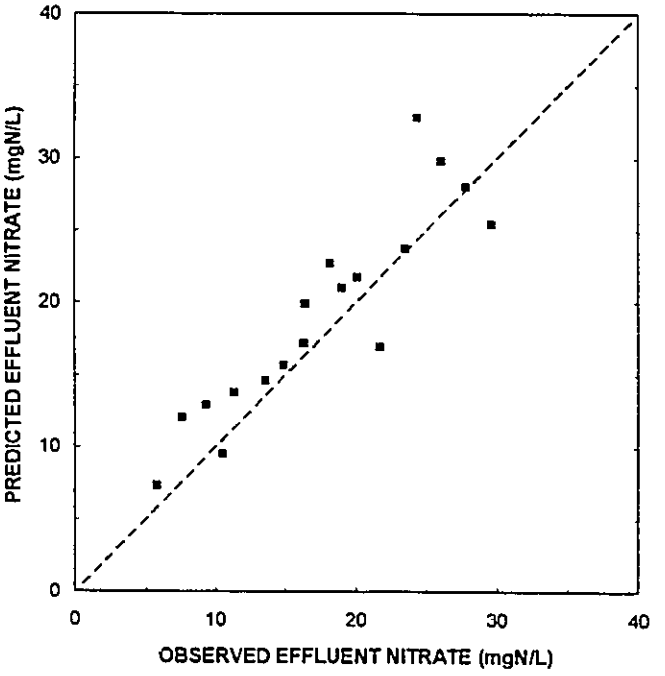

Figure 7.4b Model predictions of effluent nitrate concentration for anaerobic-anoxic-aerobic (NDBEPR) systems of Wentzel *et al.* (1990).

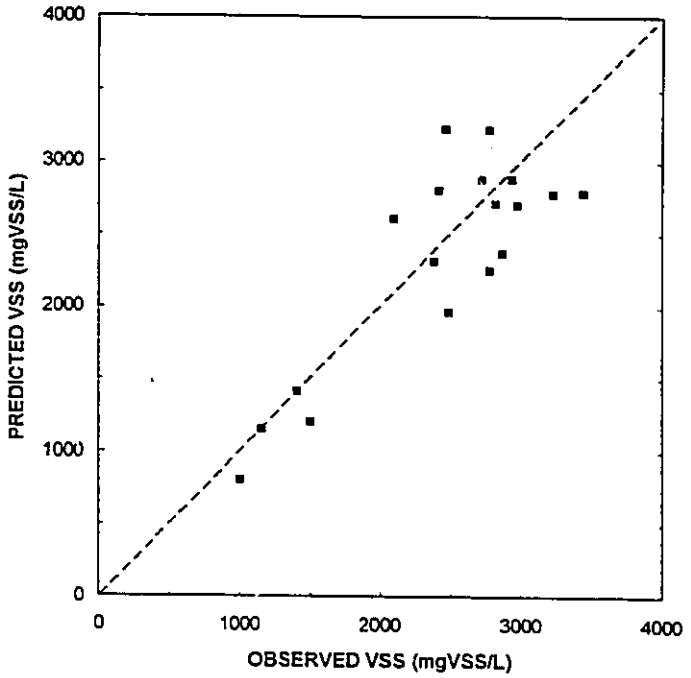

Figure 7.4c Model predictions of volatile solids concentration for anaerobic-anoxic-aerobic (NDBEPR) systems of Wentzel *et al.* (1990).

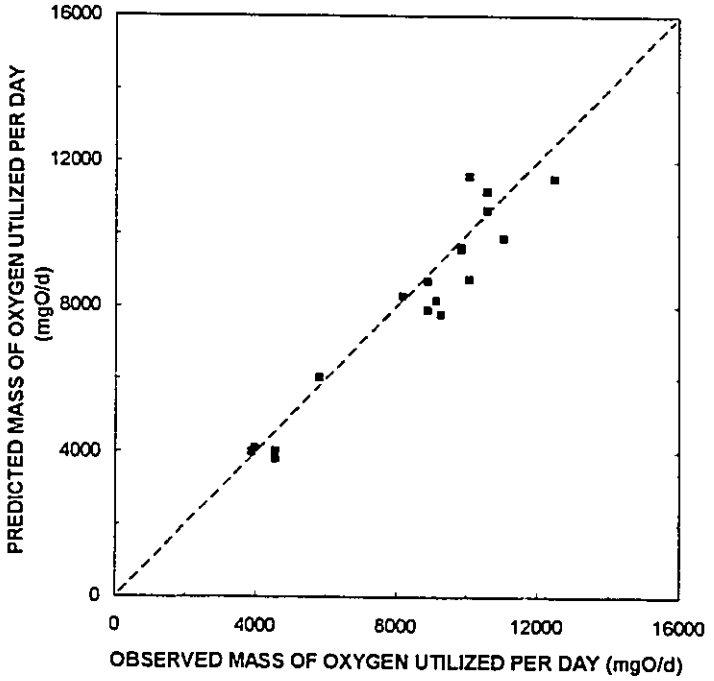

Figure 7.4d Model predictions of mass oxygen consumed per day for anaerobic-anoxic-aerobic (NDBEPR) systems of Wentzel *et al.* (1990).

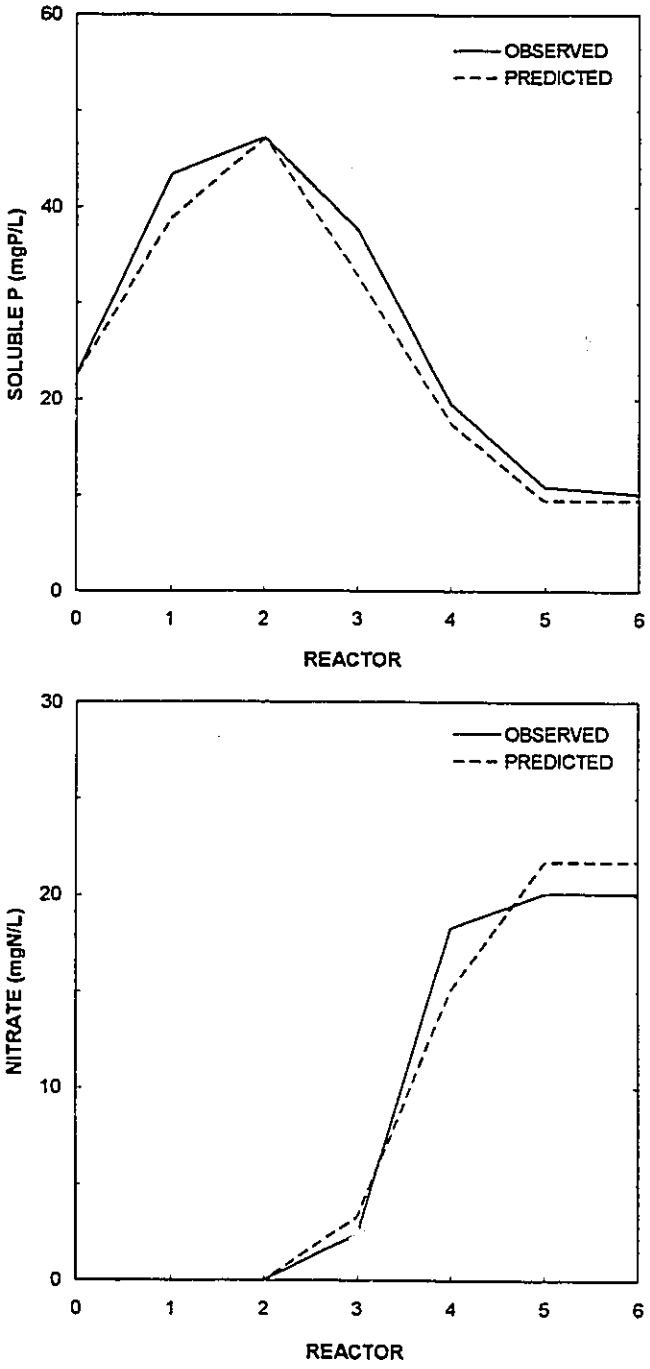

Figure 7.5 Model predictions for anaerobic-anoxic-aerobic (NDBEPR) UCT system 11a of Wentzel *et al.* (1990): (a) observed and predicted soluble phosphorus profiles; (b) observed and predicted nitrate profiles ['0' indicates influent concentration; '1' and '2' represent anaerobic reactor concentrations; '3' indicates anoxic concentration; '4' and '5' represent aerobic concentrations; '6' indicates effluent concentration].

Systems Receiving SCFA Only

Wentzel *et al.* (1989a) reported data for four different laboratory scale enhanced culture BEPR systems with acetate as influent. These "enhanced" cultures (greater than 90% polyP organisms) were developed using modified Bardenpho and UCT systems operated at sludge ages of 7.5, 10 and 20 days (all at 20°C).

Results of model simulations for the enhanced culture BEPR systems of Wentzel *et al.* (1989a) are shown in Table 7.3 and Fig. 7.6. For these systems the model correctly predicts that the organism mass will be mainly polyP organisms (plus a small mass of nitrifiers), with the non-polyP heterotrophic mass comprising less than 10% of the total mass of active organisms. Reasonable predictions were obtained for effluent concentrations of soluble P, nitrate and TKN, as well as for OUR's (shown in Table 7.3). Excellent predictions were obtained for oxygen utilization (mass/day) and VSS concentrations (Fig. 7.6). Predictions of aerobic zone P/VSS ratios also were reasonable.

Reactor concentration profiles for nitrate and soluble P are shown in Fig. 7.7 for the 10 day UCT system receiving acetate only.

BIOLOGICAL EXCESS PHOSPHORUS REMOVAL SYSTEMS (DYNAMIC)

Observations from a pilot plant in Malmo, Sweden, were used to test the predictive capabilities of the NDBEPR model under dynamic conditions. The UCT system was comprised of 7 equal volume 5 m^3 reactors: one anaerobic, three anoxic, and three aerobic. The system received municipal wastewater of varying concentration at a constant rate of 43.2 $m^3\ d^{-1}$, and the sludge age was maintained at 23 days. Over one 24 hour period, the influent COD, TKN, and soluble P were measured at hourly intervals, as well as the soluble P and nitrate in the anaerobic reactor, anoxic reactors and in the effluent (VSS and OUR's were not reported on a dynamic basis).

Results of model simulations for the Malmo dynamic system are shown in Fig. 7.8. The anaerobic P release appears somewhat under-predicted for this system; also the observed values show considerably more variaton than the predicted values. As this was the only system for which sufficient dynamic data was available for modelling, it is unknown

whether this is indicative of the model performance under dynamic conditions, or a characteristic of this system in particular. Reasonable predictions were obtained for effluent concentration of soluble P and nitrate, as well as for reactor concentrations of nitrate. The observed VSS concentration in the aerobic zone was reportedly approximately 2450 gm^{-3}, which is very close to the average predicted value of 2400 gm^{-3}. [The accuracy of this prediction is difficult to check since the OUR is unknown.]

Table 7.3: Model predictions for enhanced culture systems of Wentzel *et al.* (1989a).

	System 1 (20d)		System 2 (10d)		System 3 (10d)		System 4 (7.5d)	
	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.	Obs.	Pred.
Influent								
COD ($gCOD\ m^{-3}$)	544	-	543	-	417	-	410	-
TKN ($gN\ m^{-3}$)	35.2	-	36.0	-	26.9	-	26.3	-
P ($gP\ m^{-3}$)	53.6	-	63.7	-	43.8	-	46.0	-
Reactor								
VSS ($gVSS\ m^{-3}$)	2998	3194	2397	2443	1167	1305	1036	1018
P/VSS ($gP\ gVSS^{-1}$)	0.38	0.35	0.38	0.38	0.34	0.31	0.32	0.32
OUR (s) ($gO\ m^{-3}\ h^{-1}$):								
Aerobic Reactor #1	38.5	41.0	39.5	41.5	23.0	22.9	20.4	20.2
#2	17.8	17.5	17.5	19.6	8.9	9.0	7.6	9.9
#3	9.5	8.2	9.0	9.1				
Underflow Reactor	14.0	13.9						
Effluent								
P (gPm^{-3})	3.9	5.1	2.9	3.0	5.2	5.7	3.4	5.1
NO3 (gNm^{-3})	11.5	6.3	7.0	6.1	3.7	2.9	3.3	3.1
TKN (gNm^{-3})	2.7	2.7	2.7	2.7	2.5	2.1	2.5	2.3

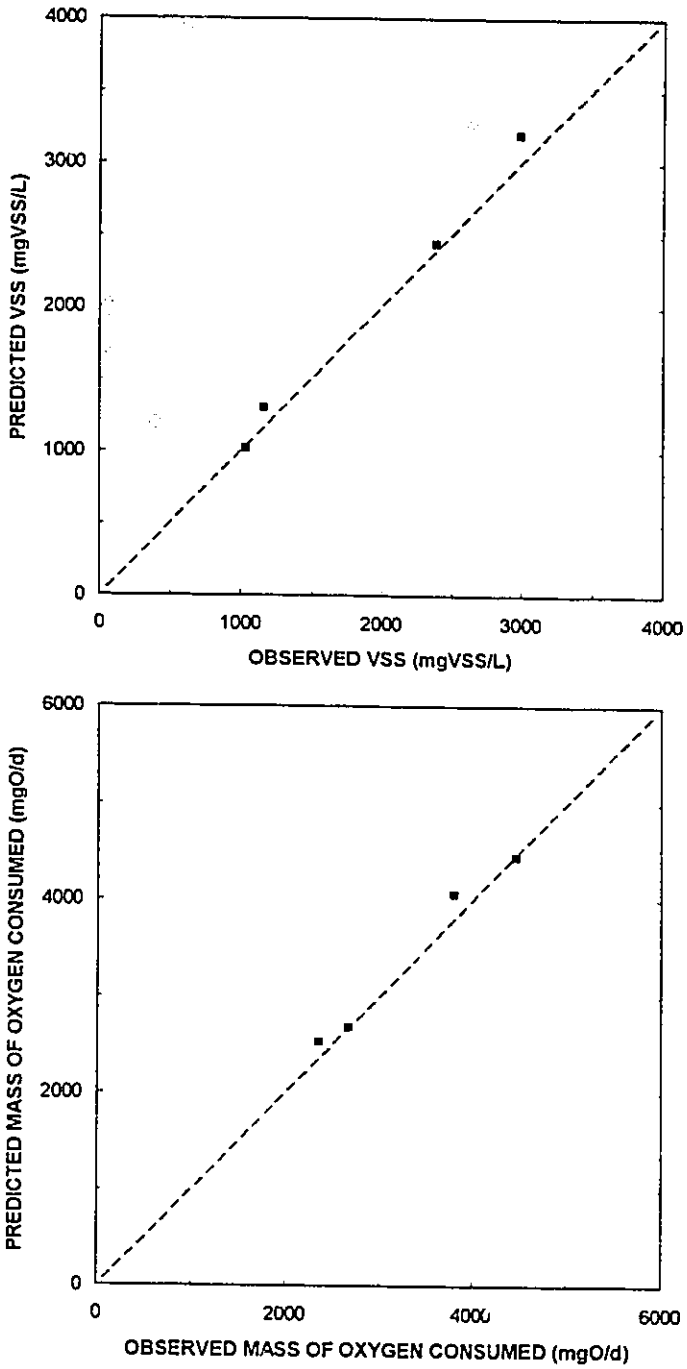

Figure 7.6 Model predictions for enhanced culture BEPR systems of Wentzel *et al.* (1989a): (a) volatile solids concentration; (b) mass oxygen consumed per day.

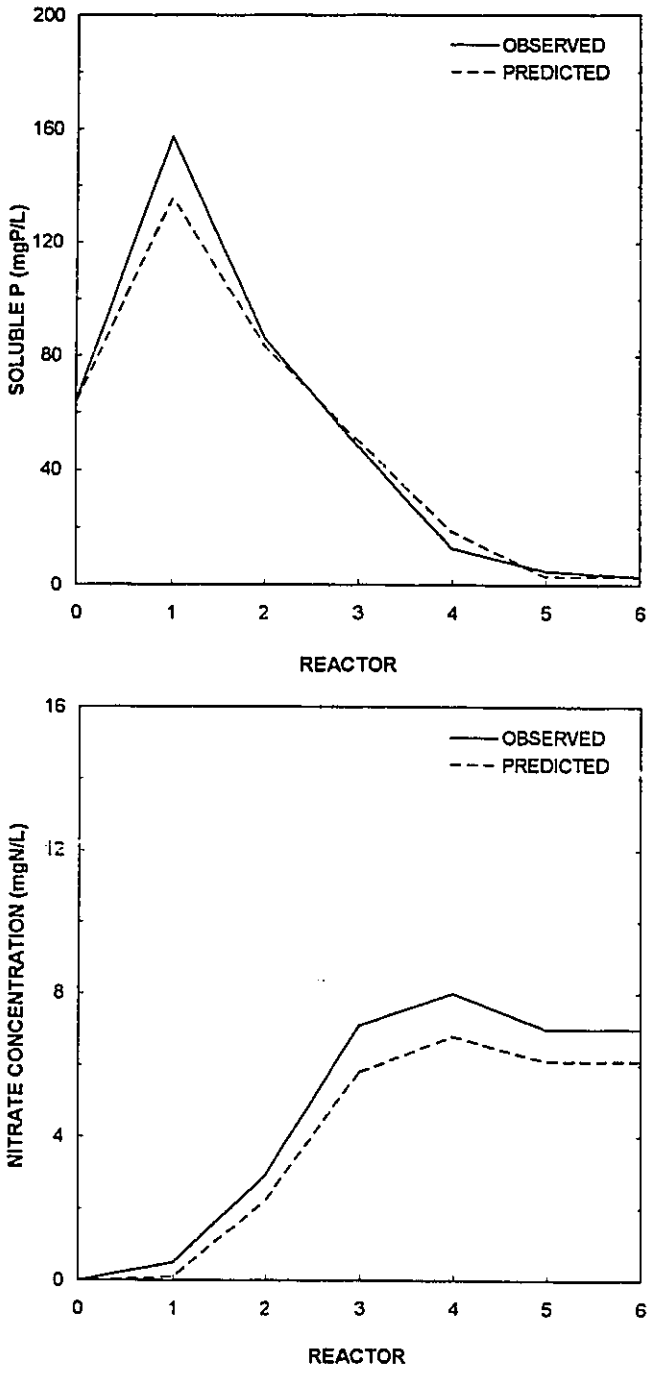

Figure 7.7 Model predictions for Wentzel *et al.* (1989a) enhanced culture BEPR UCT system 2: (a) observed and predicted soluble phosphorus profiles; (b) observed and predicted nitrate profiles ['0' indicates influent concentration; '1' represents anaerobic reactor concentration; '2' indicates anoxic concentration; '3','4' and '5' represent aerobic concentrations; '6' indicates effluent concentration].

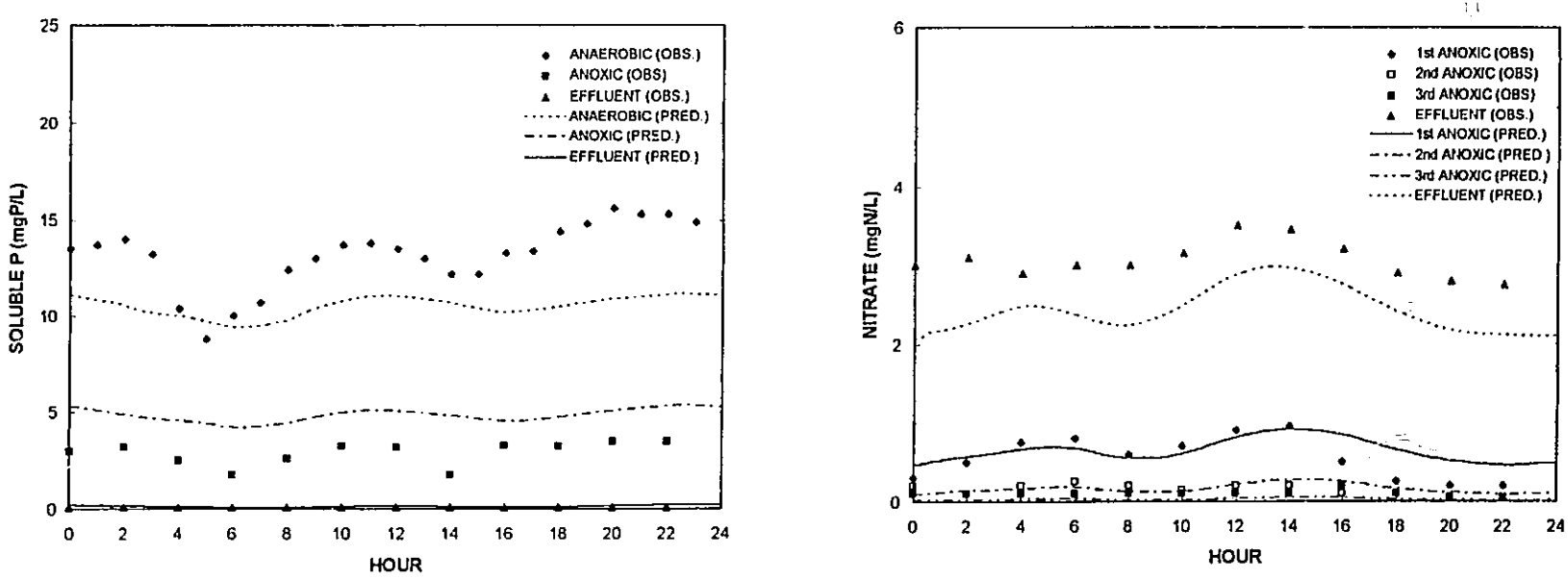

Figure 7.8 **Model predictions for dynamic anaerobic-anoxic-aerobic (NDBEPR) system: (a) soluble phosphorus (note: the P concentration did not change appreciably from one anoxic zone to another, therefore only the first anoxic zone P concentration is shown); (b) nitrate concentration.**

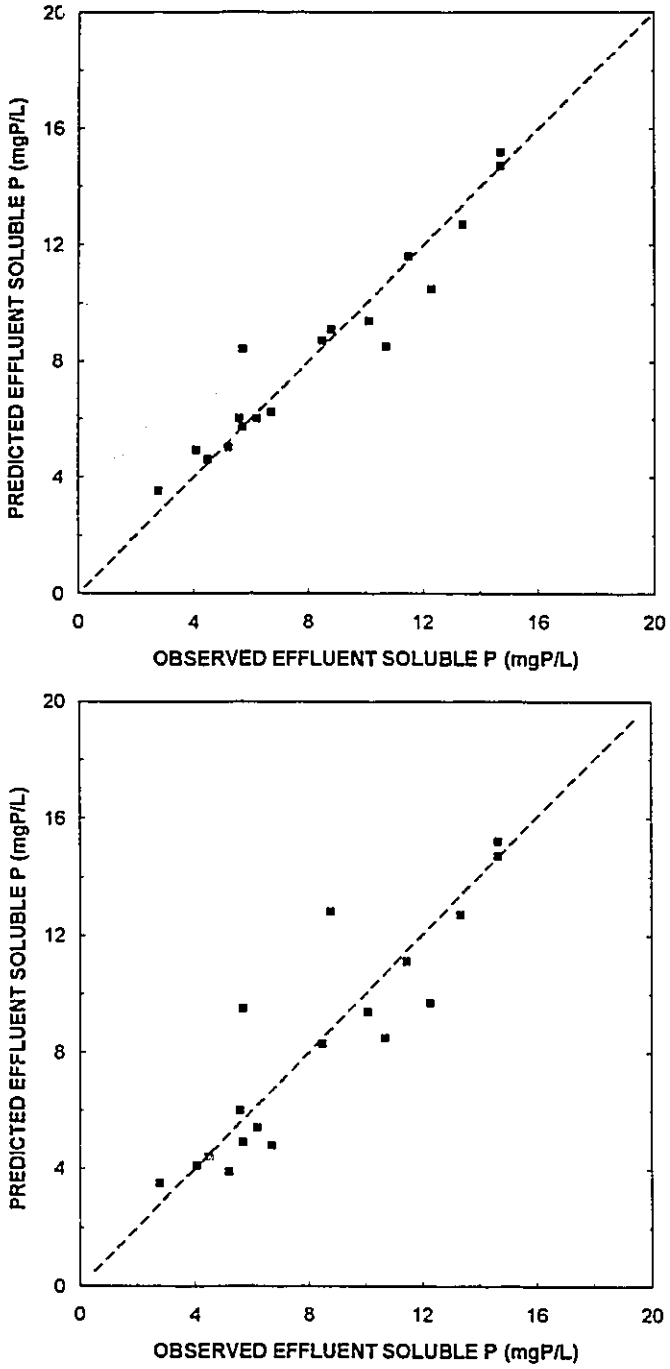

Figure 7.9 Effluent soluble phosphorus predictions for anaerobic-anoxic-aerobic (NDBEPR) systems of Wentzel *et al.* (1990): (a) adjusting the denitrifying fraction of the polyP organism mass for each system (in the range 20 to 70%); (b) assuming 40% of the polyP organism mass can denitrify (as in Fig. 7.4).

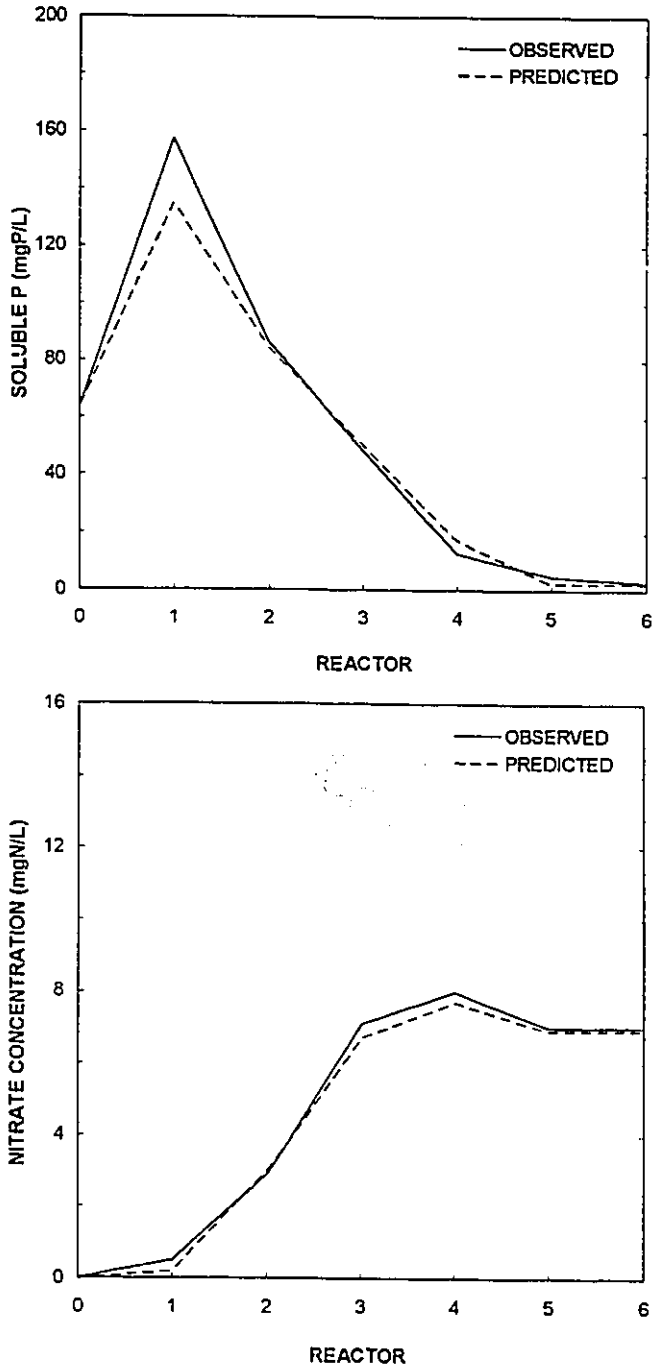

Figure 7.10 Model predictions (assuming only 20% of the polyP organism mass can denitrify) for Wentzel *et al.* (1989a) enhanced culture BEPR UCT system 2: (a) observed and predicted soluble phosphorus profiles; (b) observed and predicted nitrate profiles.

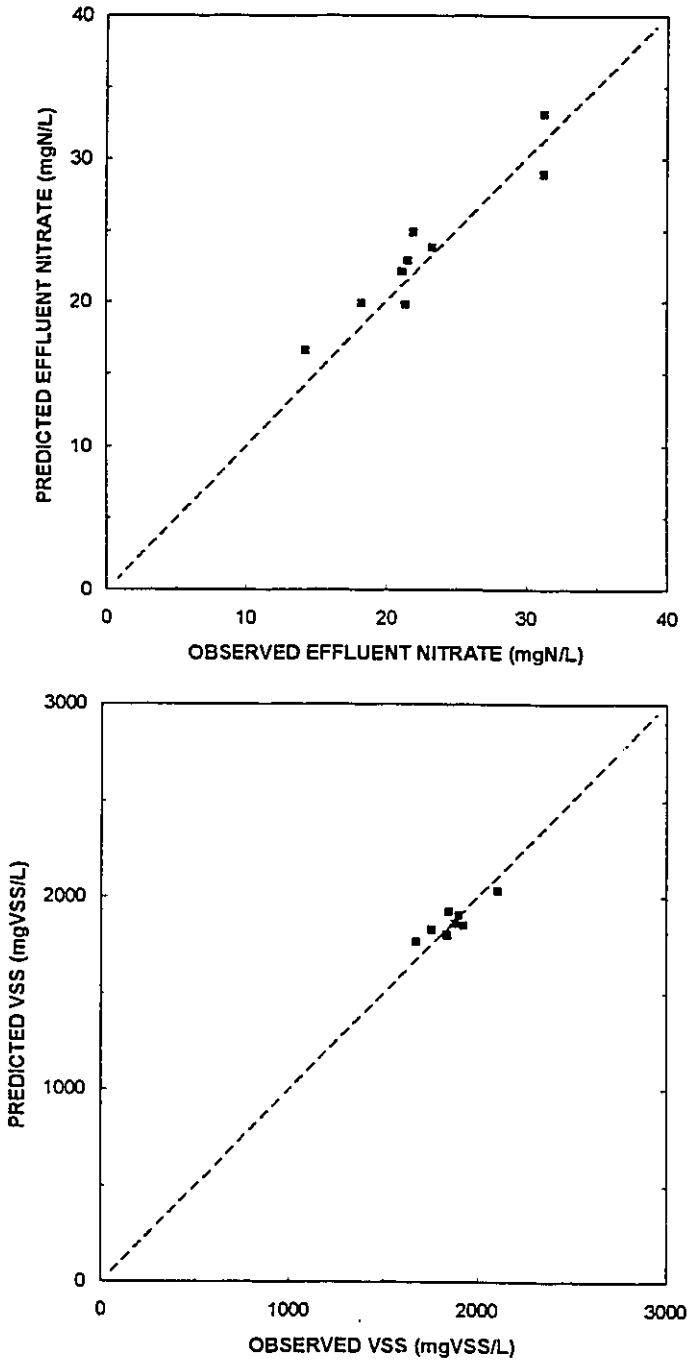

Figure 7.11 Model predictions for anoxic-aerobic system of Power *et al.* (1992) (after increasing the denitrification switching function parameter to 0.50 mgN/L from 0.10 mgN/L): (a) effluent nitrate concentration; (b) volatile solids concentration.

MODEL SENSITIVITY

The objective of this study has been to test the predictive capabilities of the model using a single set of kinetic and stoichiometric parameters (with the exception of the nitrifier growth rate). The model parameters (listed in Part I) were derived from a detailed calibration exercise discussed in Part I (Barker and Dold, 1995c). This included calibrating model parameters to give the best overall predictions for an extensive range of systems to which the model was applied. However, this does not necessarily lead to the selection of parameters which give the best results for a particular system. In fact, the predictions for any system could be improved by adjusting model parameters to "force" a fit to observed data. The following section demonstrates how changes to two model parameters lead to improved model predictions for two of the systems considered earlier.

Fraction of PolyP Denitrifiers

The fraction of the polyP organisms which can denitrify (η_P) is assumed to be 40% in the model predictions shown above. For certain systems this value may be significantly lower or higher. If the fraction of denitrifiers is allowed to vary in the range of 20 to 70%, the results of model predictions for effluent soluble P (shown in Fig. 7.9) can be improved for the individual mixed culture BEPR systems of Wentzel *et al.* (1990). [Note that since it is assumed that more stored PHB is consumed/mole P taken up when nitrate is the electron acceptor in place of oxygen, the effect of reducing the number of denitrifying polyP organisms in a system where P uptake is limited by the amount of stored PHB available is to decrease the effluent (aerobic) P, without significantly affecting the concentration of soluble P in anaerobic and anoxic zones]. Predictions of other parameters such as oxygen utilization, VSS and nitrate concentrations were relatively unaffected by adjusting this fraction for mixed culture systems.

As expected, predictions for enhanced culture systems (comprised mainly of polyP organisms) show a greater sensitivity to η_P than those for mixed culture systems. Wentzel *et al.* (1989a,b) noted that minimal denitrification occurred in the enhanced culture systems, contrary to the polyP organism behaviour which has been observed in other studies (see Barker and Dold, 1995b). Assuming that only 20% of the polyP organisms in these systems could denitrify leads to the soluble P and nitrate concentration predictions shown in Fig. 7.10. A comparison of these plots with those shown in Fig. 7.7 suggests

that a value of 20% may be more appropriate for this system than the value of 40% used earlier for all systems. However, the effect on model predictions of soluble P and nitrate is minimal, and there is no significant effect on predictions of other parameters.

Switching Function Values

The selection of the most appropriate values for the switching function parameters also appears to be somewhat system dependent. For example, the threshold value for denitrification of 0.10 gNO_3-N m^{-3} leads to reasonable nitrate predictions for most of the systems studied. However, for the anoxic-aerobic systems of Power *et al.* (1992), a value of 0.50 gNO_3-N m^{-3} gives improved predictions overall for both effluent nitrate and aerobic VSS concentration [comparing Fig. 7.11 with Fig. 7.3]. Oxygen utilization and effluent P predictions were not affected significantly. It has been suggested that ND systems may exhibit lower rates of denitrification compared to NDBEPR systems (Clayton *et al.*, 1991; Wentzel *et al.*, 1992). This could lead to under-predictions of the effluent nitrate concentrations in ND systems modelled here as a single set of kinetic parameters are assumed for all system types.

CLOSURE

This paper has demonstrated application of the general activated sludge model presented in Part I (Barker and Dold, 1995c). The systems considered range in complexity from single aerobic reactors to multi-reactor nutrient removal configurations. The latter involve extensive interactions between different organism masses in different environmental regimes. Model predictions are very reasonable, even for these systems. Nevertheless, it is stressed that these are predictions, and that the model incorporates a number of empirical assumptions to account for a lack of complete knowledge concerning the processes being modelled.

The fact that model predictions using a single set of model parameters are not perfect for all systems may point to deficiencies in the model (and/or inaccuracies in experimental data, or physical characteristics such as mixing conditions). This begs the question: if the model predictions are not perfect, are there certain model parameters which must be adjusted each time the model is applied? From extensive application of the model, perhaps

the aspect where there is the most uncertainty is denitrification. However, it is very difficult to identify a specific model process or kinetic/stoichiometric parameter which must be "calibrated" for each system to obtain accurate denitrification predictions. This is because of the interactive nature of many of the model processes. In this regard it should be noted that quite significant changes to the parameters considered in the previous section do not have a major impact on model predictions. This is not the case for all parameters. For example, significantly changing a heterotrophic yield coefficient would impact sludge production, oxygen demand, nitrate utilization, hydrolysis rates, and a range of other factors. The point to note is that models are only tools, and should be used judiciously.

ACKNOWLEDGEMENTS

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CHAPTER EIGHT

SLUDGE PRODUCTION AND OXYGEN DEMAND IN NUTRIENT REMOVAL ACTIVATED SLUDGE SYSTEMS

P. S. Barker and P. L. Dold

This chapter contains the complete text of a paper submitted to the IAWQ Conference, Singapore, July, 1996 (submitted June, 1995).

SLUDGE PRODUCTION AND OXYGEN DEMAND IN NUTRIENT REMOVAL ACTIVATED SLUDGE SYSTEMS

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Abstract

Results of model simulations indicate that without the assumption of COD loss, predictions of oxygen consumption and volatile suspended solids production are significantly over-estimated for biological excess phosphorus removal (BEPR) activated sludge systems (and to a lesser extent anoxic-aerobic systems). These systems apparently consume less oxygen and produce less volatile solids than aerobic systems for the same amount of COD removal. A general model for biological nutrient removal systems has been presented (Barker and Dold, 1995b,c). Three mechanisms for COD loss are suggested, based on results of COD balances for different types of activated sludge system. Model simulation results with and without the assumption of COD loss are discussed, as well as the influence of influent COD composition on predictions of volatile suspended solids concentration/production and oxygen consumption.

Key words: Activated sludge, biological excess phosphorus removal (BEPR), COD, oxygen utilization, volatile solids production.

INTRODUCTION

Typically sludge disposal and aeration requirements represent the greatest proportion of operating costs for activated sludge treatment of domestic wastewater. Also, for system design (e.g. reactor and final settler sizing, aeration system design) the predicted sludge production and oxygen requirements are important factors. A number of factors influence the quantity of sludge produced and oxygen demand in an activated sludge system, including operational parameters (e.g. sludge age, loading patterns), wastewater characteristics (e.g. wastewater strength, unbiodegradable particulate fraction), system configuration, chemical addition, and effluent quality.

In the development of a model for nitrification, denitrification, biological excess phosphorus removal (NDBEPR) systems, the over-prediction of oxygen utilization and volatile suspended solids production in systems with anaerobic zones lead to the analysis of COD and nitrogen (N) data from different types of laboratory-scale system. COD and N mass balances were performed on aerobic, anoxic, anoxic-aerobic, and anaerobic-anoxic-aerobic activated sludge systems, with a range of influent wastewater characteristics and operating parameters (Barker and Dold, 1995a). The results show that while good COD balances are to be expected in aerobic systems, systems incorporating anaerobic zones (i.e. BEPR systems) tend to exhibit low COD balances (less than 80%); that is, there is a significant amount of COD entering the system which cannot be accounted for in the effluent stream, wastage stream, or is the mass of COD oxidized (under either aerobic or anoxic conditions). This "loss" of COD translates into a reduction in sludge production and oxygen demand in BEPR systems compared to non-BEPR systems for the same organics load. Anoxic-only systems also appear to exhibit a loss of COD, but to a lesser extent. Further analysis of anoxic-aerobic systems (Barker and Dold, 1995b) suggests that these systems also may exhibit COD loss. The phenomenon of reduced solids production and oxygen consumption has been noted elsewhere (Ip *et al.*, 1987; McClintock *et al.*, 1988).

A general mechanistic model has been developed which is capable of predicting sludge production and oxygen utilization for a range of system types and configurations, as well as tracking changes in soluble phosphorus (P), nitrate, and TKN (Barker and Dold, 1995b). The model is based on the IAWPRC (now IAWQ) model for carbonaceous

energy removal, nitrification, and denitrification (Henze *et al.*, 1987a,b), and the Wentzel *et al.* (1989a,b) model for biological phosphorus removal, with a number of modifications.

Among the modifications made to the combined models are the assumptions regarding COD loss. From the analysis of COD mass balance results, empirical factors were developed which allow the model to mimic the COD balances observed in the laboratory scale anoxic-aerobic, and anaerobic-anoxic-aerobic systems. The model has been tested extensively on aerobic, anoxic-aerobic, and anaerobic-anoxic-aerobic (NDBEPR) systems (Barker and Dold, 1995c). In the model COD loss is assumed to occur through three different biological processes depicted in Fig. 8.1: fermentation of readily biodegradable COD to short-chain fatty acids (SCFA), sequestration of SCFA by polyP organisms, and hydrolysis of enmeshed slowly biodegradable COD under anaerobic/anoxic conditions. These processes are outlined in the subsequent section, following which application of the model (with and without the COD loss assumptions) is demonstrated for a number of ND and NDBEPR systems.

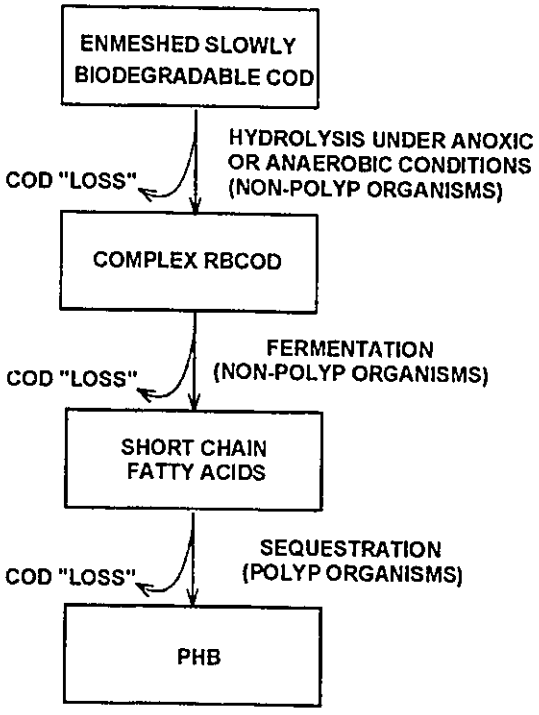

Figure 8.1 **Three stages of COD loss incorporated in the model.**

MODELLING COD LOSS

Conversion of Soluble Readily Biodegradable COD to SCFA

The principal linkage between the polyP and non-polyP heterotrophic organism masses in BEPR systems treating municipal wastewater is the conversion, by non-polyP organisms, of "complex" readily biodegradable soluble COD to SCFA. This process is the source of SCFA (S_{BSA}) to sustain polyP organism growth in the mixed culture system as the influent SCFA content usually is minimal. Wentzel *et al.* (1985) established the kinetics of this phenomenon and incorporated the process in the enhanced culture model for completeness even though all of the influent COD to the enhanced cultures was in the form of SCFA (acetate). The process was modelled as being first order with respect to the concentrations of "complex" readily biodegradable soluble COD (S_{BSC}) and non-polyP heterotrophs. In terms of stoichiometry the process was assumed to yield one unit of S_{BSA} for each unit of S_{BSC} converted.

Barker and Dold (1995b) adopted the following approach for modelling of the readily biodegradable COD conversion process, including an empirical factor for modelling loss of COD due to fermentation:

- The process is assumed to be a fermentation; that is, a growth process under anaerobic conditions. This is modelled using a Monod growth expression, with a yield of non-polyP heterotrophic organisms ($Y_{H,ANA}$); correspondingly, the yield of fermentation products is ($1 - Y_{H,ANA}$).

- Further, it is assumed that only a portion (Y_{AC}) of the fermentation products is S_{BSA}. The remainder is assumed to be COD lost from the system. Whether this COD loss is a direct result of fermentation (e.g. through the generation of gas which evolves during the fermentation process), or an indirect result (e.g. through the production of volatile compounds which are released from the system under aerated conditions), remains to be determined.

Sequestration of SCFA by PolyP Organisms

In the anaerobic sequestration of SCFA by polyP organisms (for PHB storage, with associated P release), it is assumed that the yield of PHB is Y_{PHB} units of PHB (as COD) per unit SCFA COD taken up. A value of 0.89 gCOD.(gCOD)$^{-1}$ is suggested for Y_{PHB} based on the assumption that for an initial amount of 2.25 moles acetate, 2 moles enter the PHB formation pathway directly and 0.25 moles are directed to the TCA cycle [see biochemical model of Wentzel *et al.* (1986)]. That is, the model also incorporates COD loss in the sequestration reaction. This provides a second mechanism for "losing" COD, and allows the general model to mimic the COD balances (approximately 90%) observed in the Wentzel enhanced culture BEPR systems receiving acetate as influent. It should be noted, however, that this COD loss is not suggested in the biochemical model because it is assumed that the available electrons from the 0.25 moles acetate are returned to the PHB formation pathway from the TCA cycle.

Hydrolysis/Solubilization of Slowly Biodegradable COD

In the IAWPRC model (ASM1) the biodegradable material is divided into a readily biodegradable fraction (S_{BS}) and a slowly biodegradable fraction (S_{ENM}). The readily biodegradable fraction is hypothesized to consist of material that can be absorbed readily by the organism and metabolized for energy and synthesis, whereas the slowly biodegradable fraction is assumed to be made up of particulate/colloidal material and complex organic molecules that require extracellular enzymatic breakdown prior to absorption and utilization. In the ASM1 model the rate of solubilization under *anoxic* conditions is assumed to be reduced by a factor η_{SOL} compared to the rate under aerobic conditions. Under anaerobic conditions the rate is assumed zero. Recent research on enzymatic hydrolysis (Dold et al., 1991, San Pedro et al., 1994) indicates that hydrolysis does in fact occur under anaerobic conditions, and under anoxic conditions the rate of hydrolysis appears similar to that under aerobic conditions. This behaviour requires further research. To provide flexibility in the model two η_{SOL} factors are incorporated: $\eta_{S,ANOX}$ and $\eta_{S,ANA}$.

Initially it was surmised by Barker and Dold (1995a) that COD loss was induced by the inclusion of an anaerobic zone, and that all COD loss was related to the fermentation

process in the anaerobic zone. However, analysis of data from a number of anoxic-only and anoxic-aerobic systems indicates that COD loss also occurs under anoxic conditions. For example, Power *et al.* (1992) observed COD balances in the range 70-85% in a two reactor anoxic-aerobic system (see below). In order to model COD loss under anoxic conditions, it is assumed that the loss occurs during the breakdown of the enmeshed slowly biodegradable material to readily biodegradable ("soluble") material. Two 'hydrolysis efficiency factors' E_{ANOX} and E_{ANA} have been included in the model to allow for the possibility of COD loss occurring during hydrolysis. That is, in the hydrolysis of one COD unit of slowly biodegradable substrate there is a production of E units of S_{BSC} and a "loss" of (1-E) units of COD. This third mechanism for COD loss allows the model to simulate the COD loss observed in anoxic-aerobic and anoxic-only systems.

DATA BASE FOR MODEL SIMULATION

Anoxic-aerobic Systems: Power *et al.* (1992) operated a non-BEPR two reactor pre-denitrification system with a 70% unaerated mass fraction receiving municipal wastewater. In this system nitrate was added to the large anoxic zone to ensure that the reactor did not become anaerobic. The system was operated at a 20 day sludge age for a total of 305 days. Influent and effluent concentrations of COD, TKN, phosphorus (P), and nitrate were measured, as well as VSS concentrations and oxygen utilization rates. From this extensive data set, Power *et al.* (1992) identified a number of "steady state" periods. Averaged concentrations from the nine periods have been used for modelling purposes (all periods showed N balances between 95 and 100%).

Anaerobic-anoxic-aerobic Systems: Wentzel *et al.* (1990) provided comprehensive data for 30 laboratory scale NDBEPR systems treating municipal wastewater. These systems varied in configuration, reactor sizes, recycle ratios, influent flowrates, and were operated over a range of sludge ages from 3 to 21 days. There were five basic configurations: Phoredox, 3-stage Bardenpho, Johannesburg, University of Cape Town (UCT), and the modified UCT (MUCT) configuration. The influent to these systems was supplemented with KH_2PO_4 to ensure that soluble P remained in the effluent, and the BEPR processes did not become P limited. Data were reported for each system for a number of different batches of influent wastewater (denoted by a letter appended to the system number). Only

systems with reasonable nitrogen balances (between 90 and 110%) were used for modelling purposes (see Barker and Dold, 1995a). In addition, Wentzel *et al.* (1989a) reported data for four different laboratory scale enhanced culture BEPR systems with acetate as influent. The enhanced cultures (greater than 90% polyP organisms) were developed using modified Bardenpho and UCT systems operated at sludge ages of 7.5, 10 and 20 days.

ANOXIC-AEROBIC SYSTEMS

Results of model simulations for the pre-denitrification systems of Power *et al.* (1992) are shown in Fig. 2 for oxygen consumption and VSS production. The results are presented in terms of the masses of oxygen consumed and VSS produced per day. Accurate predictions for observed values would yield data points lying on the diagonal. Simulations were performed assuming both COD loss from the system, and assuming no COD loss. The "no COD loss" results shown in Fig. 2 (open squares) were obtained by assuming a value of 1 for: the portion of the fermentation products which is S_{RSA} (Y_{AC}), the yield of PHB per unit SCFA COD taken up in COD units (Y_{PHB}), and the hydrolysis efficiency factors, E_{ANOX} and E_{ANA}.

In order to simulate an activated sludge system, it is necessary to estimate values for the fraction of unbiodegradable soluble (f_{US}) and unbiodegradable particulate (f_{UP}) organic material in the influent to the system [for a brief outline of wastewater characterization refer to Barker and Dold (1995b)]. These fractions can be estimated if the observed effluent soluble COD and VSS concentrations, and oxygen utilization rates are known. The predictions shown in Fig. 8.2 were obtained by using the f_{US} and f_{UP} values estimated using the model incorporating COD loss. Fig. 8.3 shows predictions made after reducing the f_{UP} value (to zero) for the no COD loss case in order to improve VSS predictions. Clearly any improvement in VSS predictions has been at the expense of oxygen consumption predictions, and has not significantly improved the overall results.

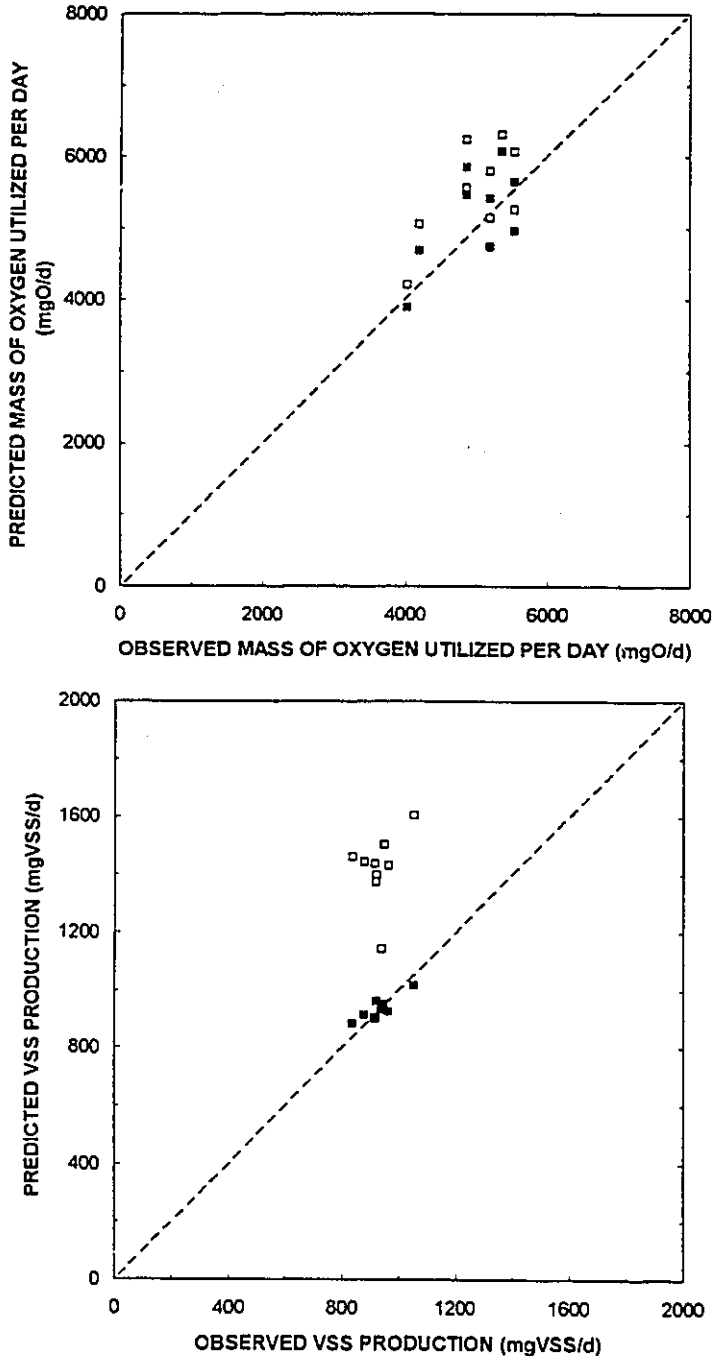

Figure 8.2 Predicted *versus* observed values for oxygen consumption and VSS production for anoxic-aerobic systems of Power *et al.* (1992). [■ assuming COD loss, □ assuming no COD loss].

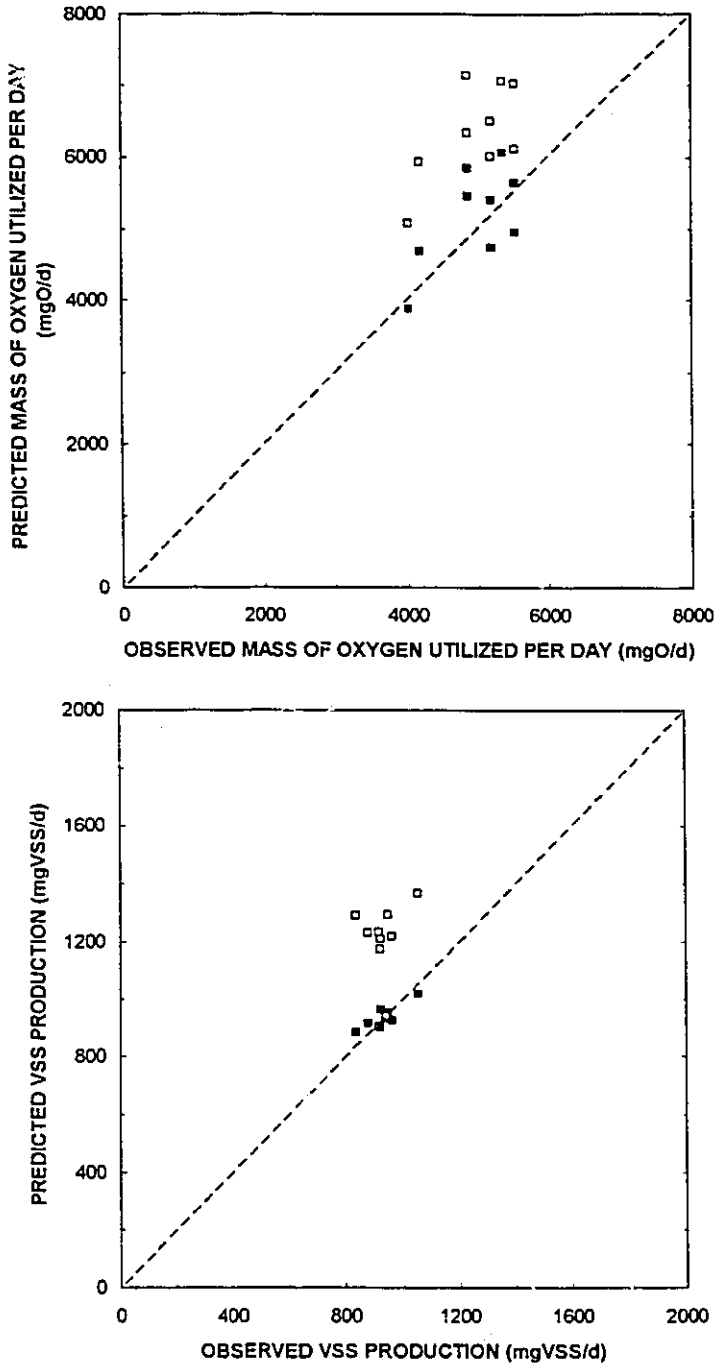

Figure 8.3 Predicted *versus* observed values for oxygen consumption and VSS production for anoxic-aerobic systems of Power *et al.* (1992) with f_{UP} reduced for the no loss case. [■ assuming COD loss, □ assuming no COD loss].

Figure 8.4 presents predicted and observed results for one "steady state" period (the third). Model predictions of oxygen utilization rates and VSS concentrations with and without assuming COD loss are shown. These predictions were obtained using the f_{US} and f_{UP} values estimated for the model incorporating COD loss.

After eliminating COD loss from the model it was necessary to adjust a number of model parameters to obtain reasonable predictions for soluble P and nitrate concentrations. [This involved reducing the maximum hydrolysis rate, reducing the anoxic and anaerobic hydrolysis rate factors, $\eta_{S,ANOX}$ and $\eta_{S,ANA}$, decreasing the rate of fermentation, and increasing the P uptake switching function constant]. Predicted oxygen utilization rates and VSS concentrations after re-calibration are shown in Fig. 8.5. Although re-calibration of the model results in an improved prediction of the VSS concentration in this system, clearly the oxygen utilization prediction is much worse. Another attempt to improve model predictions for OUR and VSS concentration while assuming no COD loss was through reducing the influent unbiodegradable particulate fraction. The results are shown in Fig. 8.6. Again, the VSS prediction is improved slightiy, but at the expense of the OUR prediction.

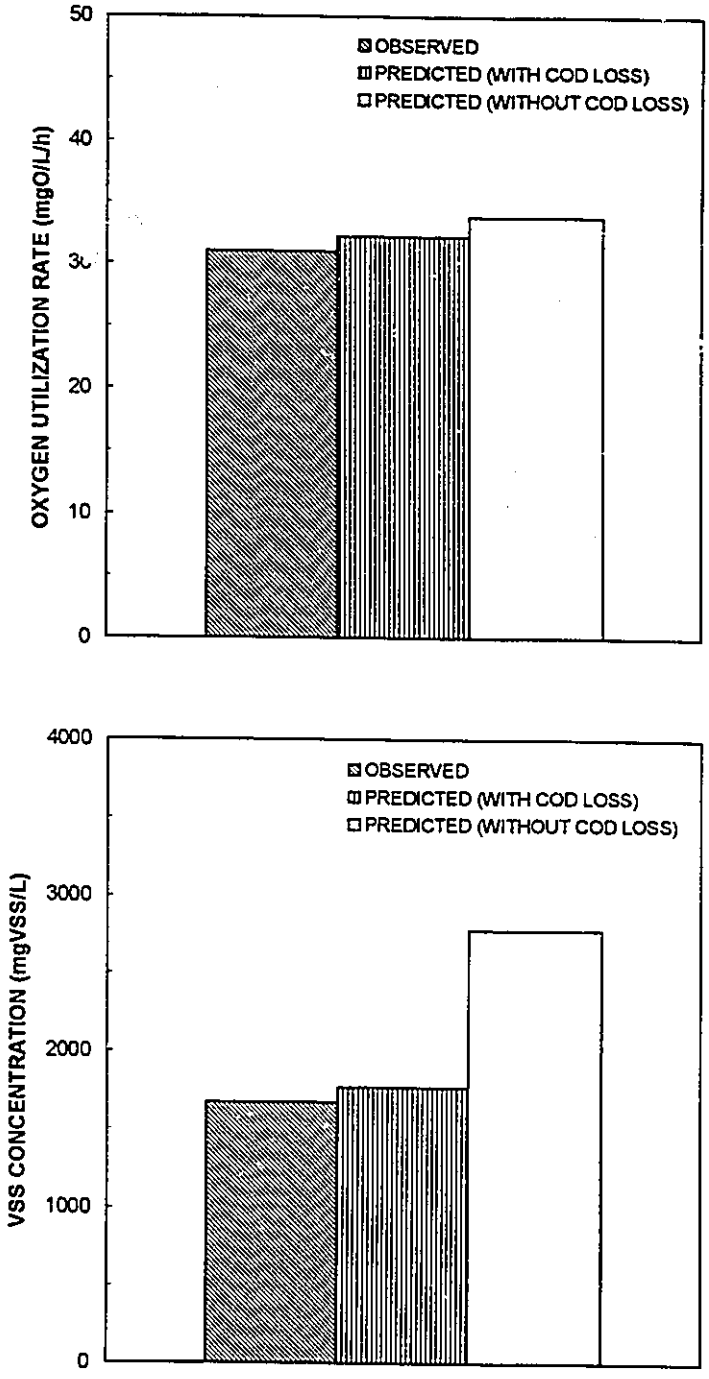

Figure 8.4 Predicted *versus* observed values for oxygen utilization rates and VSS concentration for the anoxic-aerobic system of Power *et al.* (1992) with and without assuming COD loss.

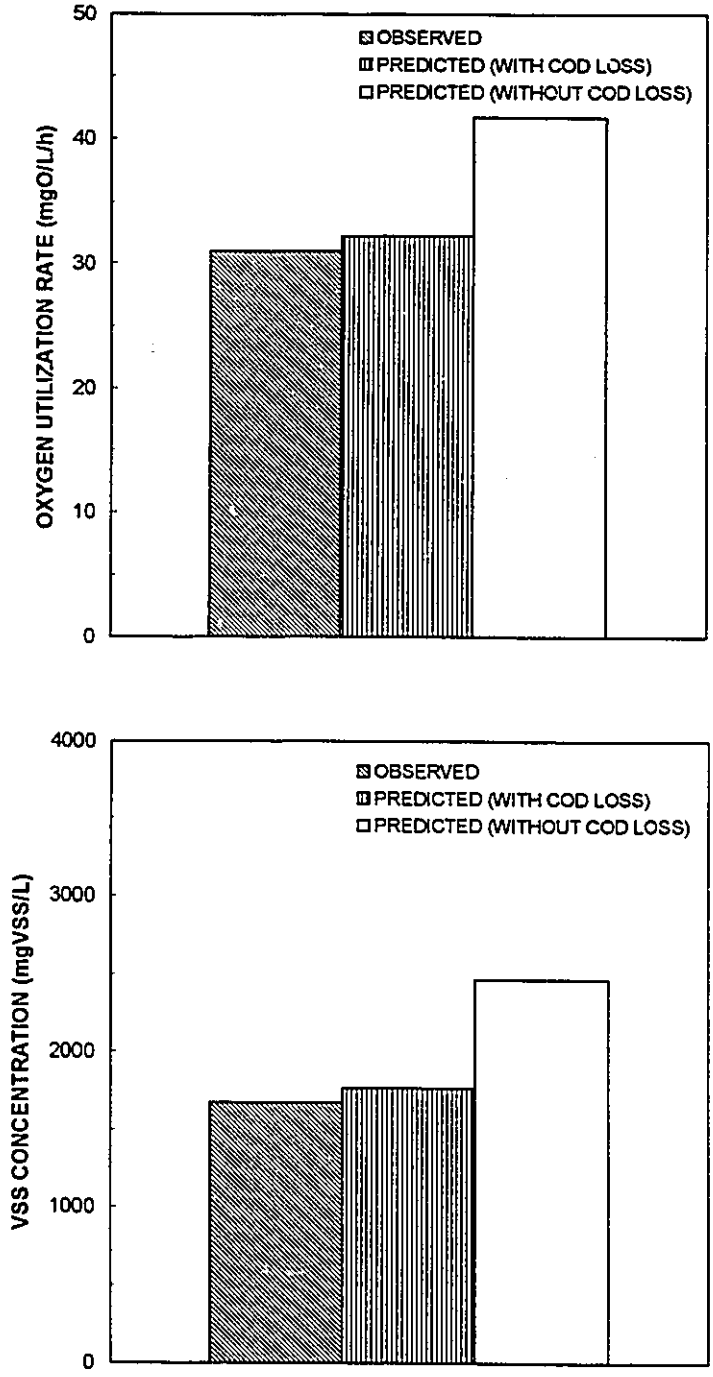

Figure 8.5 **Predicted *versus* observed values for oxygen utilization rates and VSS concentration for anoxic-aerobic system of Power *et al.* (1992) with and without assuming COD loss after re-calibration for N and P removal.**

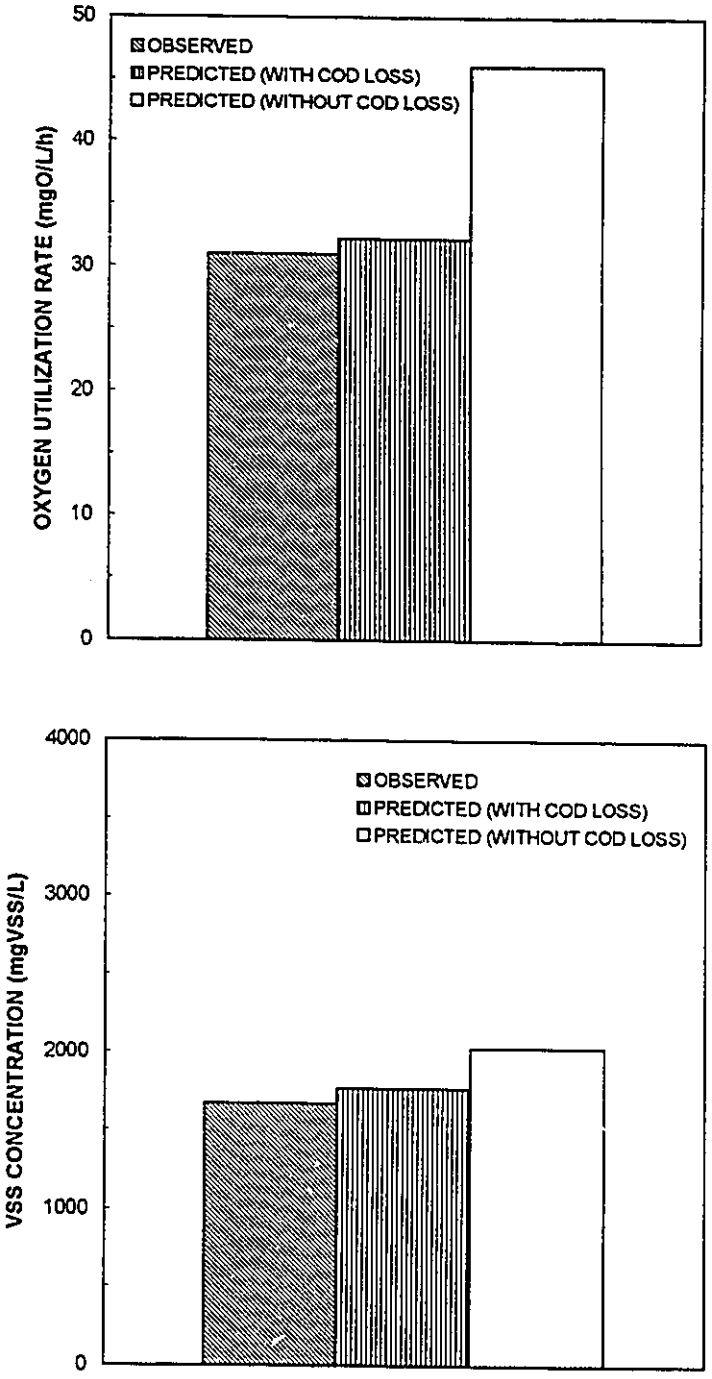

Figure 8.6 **Predicted *versus* observed values for oxygen utilization rates and VSS concentration for anoxic-aerobic system of Power *et al.* (1992) with and without assuming COD loss after re-calibration for N and P removal (f_{UP} reduced).**

ANAEROBIC-ANOXIC-AEROBIC SYSTEMS RECEIVING DOMESTIC WASTEWATER

The model was applied to eighteen NDBEPR systems of Wentzel *et al.* (1990). Model predictions of oxygen consumption and VSS production with and without assuming COD loss are compared to observed data in Fig. 8.7. The predictions in Fig. 8.7 were obtained by using the f_{US} and f_{UP} values estimated using the model incorporating COD loss. Adjustment of f_{UP} did not improve predictions, as was the case for the anoxic-aerobic systems.

One of the above systems was a laboratory scale 5-reactor UCT system receiving domestic wastewater at a rate of 15 L/d, and operated at a sludge age of 15 days. Additional information on operating parameters is given by Wentzel *et al.* (1990). Model predictions of oxygen utilization rates and VSS concentrations with and without assuming COD loss are shown in Fig. 8.8. When no COD loss was incorporated in the model predictions of nitrogen and phosphorus profiles from reactor to reactor were poor. Re-calibration of a number of model parameters to improve N and P removal predictions (as described in the previous section) did not improve the predicted VSS concentration, but resulted in a significantly worse prediction for the OUR in the second aerobic reactor.

ANAEROBIC-ANOXIC-AEROBIC SYSTEMS RECEIVING ACETATE ONLY

The model was applied to the four enhanced culture BEPR systems of Wentzel *et al.* (1989a). These systems received a short chain fatty acid (acetate) as the only organic carbon source, and therefore were not significantly affected by the assumptions regarding hydrolysis or fermentation. However, the model assumption that COD loss also occurs in the sequestration process (i.e. conversion of SCFA to PHB), has an impact on model predictions. Fig. 8.9 shows results of model application to these enhanced culture systems, with and without assuming COD loss. Clearly the assumptions regarding COD loss do have a significant effect on model predictions, as both oxygen consumption and VSS production are over-estimated for the no loss case.

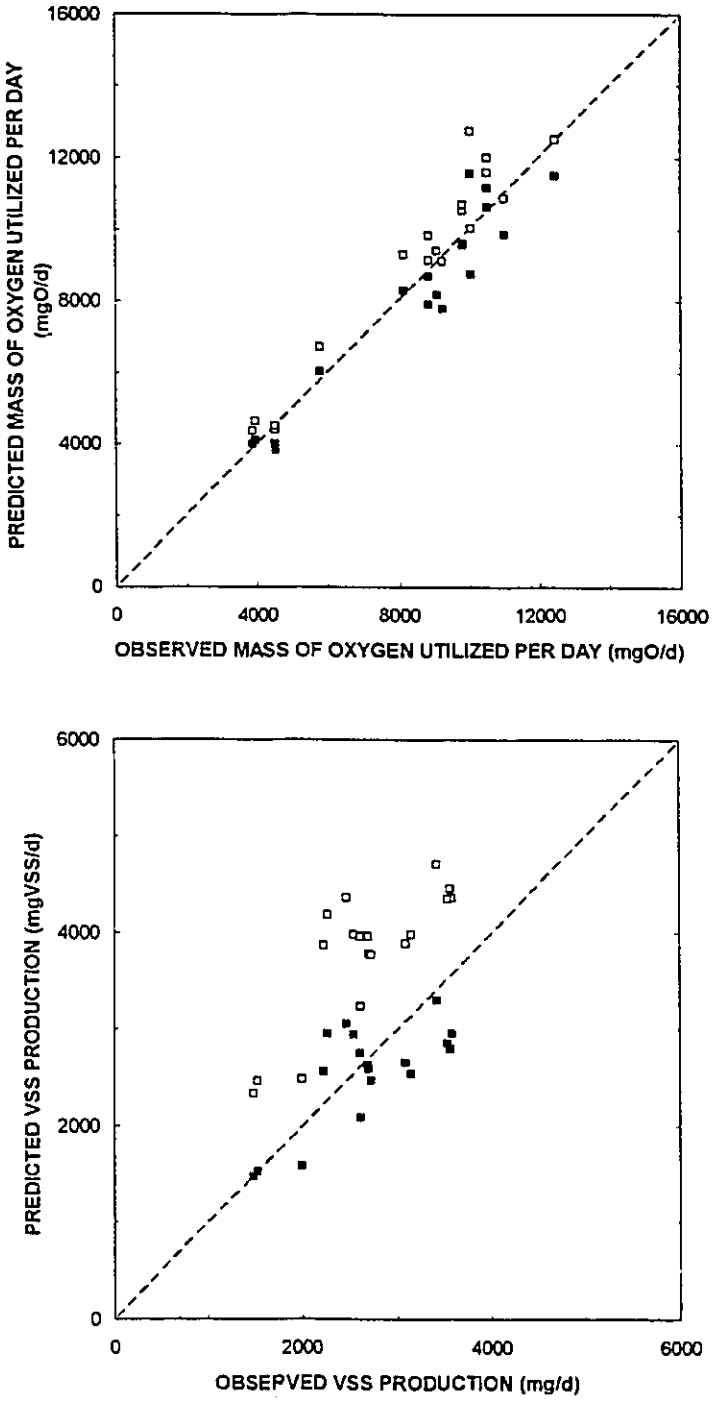

Figure 8.7 Predicted *versus* observed values for oxygen consumption and VSS production for NDBEPR systems (receiving domestic wastewater) of Wentzel *et al.* (1990). [■ assuming COD loss, □ assuming no COD loss].

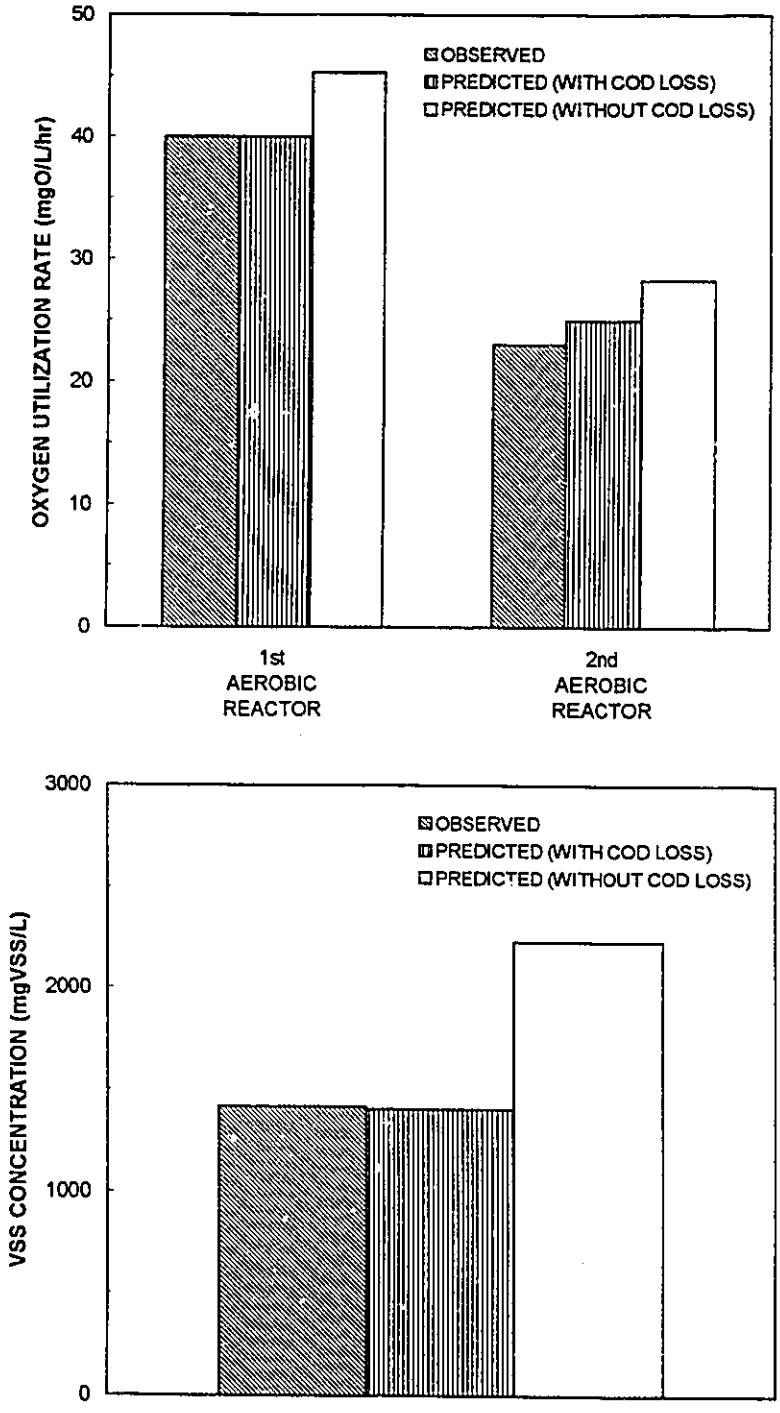

Figure 8.8 **Observed and predicted oxygen utilization rates and VSS concentrations for NDBEPR system 11a of Wentzel *et al.* (1990) with and without assuming COD loss.**

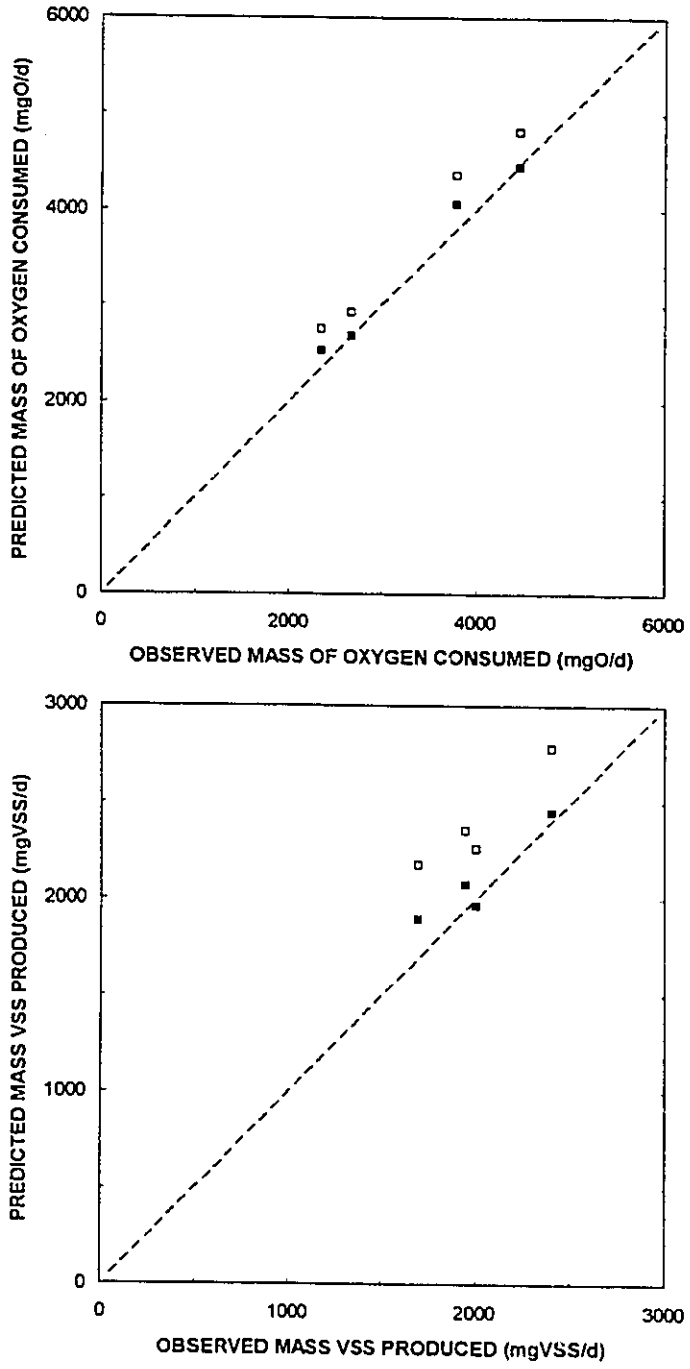

Figure 8.9 Predicted *versus* observed values for oxygen consumption and VSS production for enhanced culture BEPR systems of Wentzel *et al.* (1989a). [■ assuming COD loss, □ assuming no COD loss].

CLOSURE

Results of model simulations indicate that without the assumption of COD loss, predictions of oxygen consumption and volatile suspended solids production significantly over-estimate observed data for nutrient removal activated sludge systems. This loss of COD has a significant impact on the oxygen utilization and solids production observed in both BEPR systems, and to a lesser extent, anoxic-aerobic systems. As implications of this for both plant design and operation are very significant, it is important that the model used for plant simulation be capable of predicting the expected oxygen requirements and sludge production with reasonable accuracy.

ACKNOWLEDGEMENT

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CHAPTER NINE

CONCLUSIONS AND RECOMMENDATIONS

9.1 OVERVIEW

The objective of this research was to develop and calibrate a dynamic mechanistic model for biological nutrient (nitrogen and phosphorus) removal activated sludge systems treating municipal wastewater. The approach used in model development involved several stages:

- The IAWPRC (ASM1) model for non-polyP heterotrophic organisms and autotrophic organisms (Henze *et al.*, 1987a,b) and the Wentzel *et al.* (1989b) model for polyP organisms were merged to form a general activated sludge model for biological nutrient removal activated sludge systems.

- After a number of initial modifications the model was tested against literature data from laboratory-scale nitrification denitrification biological excess phosphorus removal (NDBEPR) systems. Based on the preliminary results, specific areas were identified which required further study. These included: (1) accounting for sludge production and oxygen utilization in BEPR systems (*i.e.*, the COD "loss" phenomenon); (2) denitrification behaviour in BEPR systems; (3) other issues such as hydrolysis under unaerated conditions.

- A review of the literature was conducted, focusing mainly on the specific problem areas indentified in the initial model application.

- Further modifications were made to the general model. This included incorporating a number of new parameters, as well as making changes to process rate equations.

- The predictive capacity of the model was tested using literature data for a variety of activated sludge system types (i.e. aerobic, anoxic-aerobic, anaerobic- anoxic-aerobic) with differing configurations, operating parameters, and influent wastewater characteristics.

- Model parameters were calibrated to give the best overall predictions for the range of systems to which the model was applied (i.e. a single set of model parameters was identified which can be used for application of the model to any of the system types mentioned above). The calibration exercise also included an evaluation of the sensitivity of the model to various parameters.

The general model has been applied to a wide range of systems operated over a range of conditions (sludge age, recycle rates, etc.); for example, aerobic systems (with and without nitrification), ND systems, BEPR systems, NDBEPR systems (under steady state and dynamic conditions). The model simulates the organism mass distribution and satisfactorily tracks the changes in a range of key parameters such as soluble phosphorus and nitrate concentrations. What is most important is that the volatile suspended solids concentration and the oxygen utilization rates in the aerated reactors also are predicted reasonably. This is of particular significance given the model assumptions on COD loss.

An important feature of the model calibration exercise is that a single set of kinetic and stoichiometric model parameters produced quite accurate predictions for all systems. (with the exception of the nitrifier maximum specific growth rate - discussed in Chapter 6). This provides a degree of support for the model structure and integrity.

9.2 COMMENT ON DATA VARIABILITY

Due to the nature of the biological systems studied in this thesis, there is a certain amount of natural variability in the observed data, *i.e.* even at "steady state" conditions, the concentrations of measured parameters vary somewhat from day to day. The majority of systems considered in this thesis were laboratory-scale systems which generally can be controlled more closely than full-scale systems, and therefore less variation is expected in

measured parameters than would be observed in a full-scale system. Nevertheless, a certain amount of variation in the data is expected.

The thesis incorporates many plots of predicted *versus* observed parameters in which the observed data are shown as single points. No attempt has been made to show the variability in experimental data. This may be a basis for criticism of this research. However, the reason for not quantifying or showing experimental data variability in the plots was that the data were not available. That is, experimental data used in this thesis were obtained from literature sources which reported only averaged values for system parameters at different operating conditions. In most cases the data were values obtained by averaging daily measured values over an extended period (usually several system sludge ages).

One exception to the above was the data from Power *et al.* (1992) where the tabulated daily data were available. However, to maintain consistency in the thesis, only the averaged values were used in the plots. In an effort to demonstrate the potential significance of experimental variability, Fig. 8.3 has been regenerated here with error bars (using one standard deviation in the observed data). From Fig. 9.1 it is evident that the variations in experimental data are not a major factor, and do not compromise model results or the interpretation of data in the thesis.

9.3 LIMITATIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

This thesis has outlined a general activated sludge model with the capacity for modelling the biological processes of carbonaceous energy removal, nitrification, denitrification and biological excess phosphorus removal. The satisfactory results from use of the model provide a basis for further model evaluation and refinement. Improvements to the model no doubt will come about as the understanding of the complex interactions occurring within biological nutrient removal systems is expanded. Many aspects require further investigation; for example:

- The mechanisms, kinetics and temperature dependency of enzymatic hydrolysis of slowly biodegradable colloidal and particulate organic substrate. Current

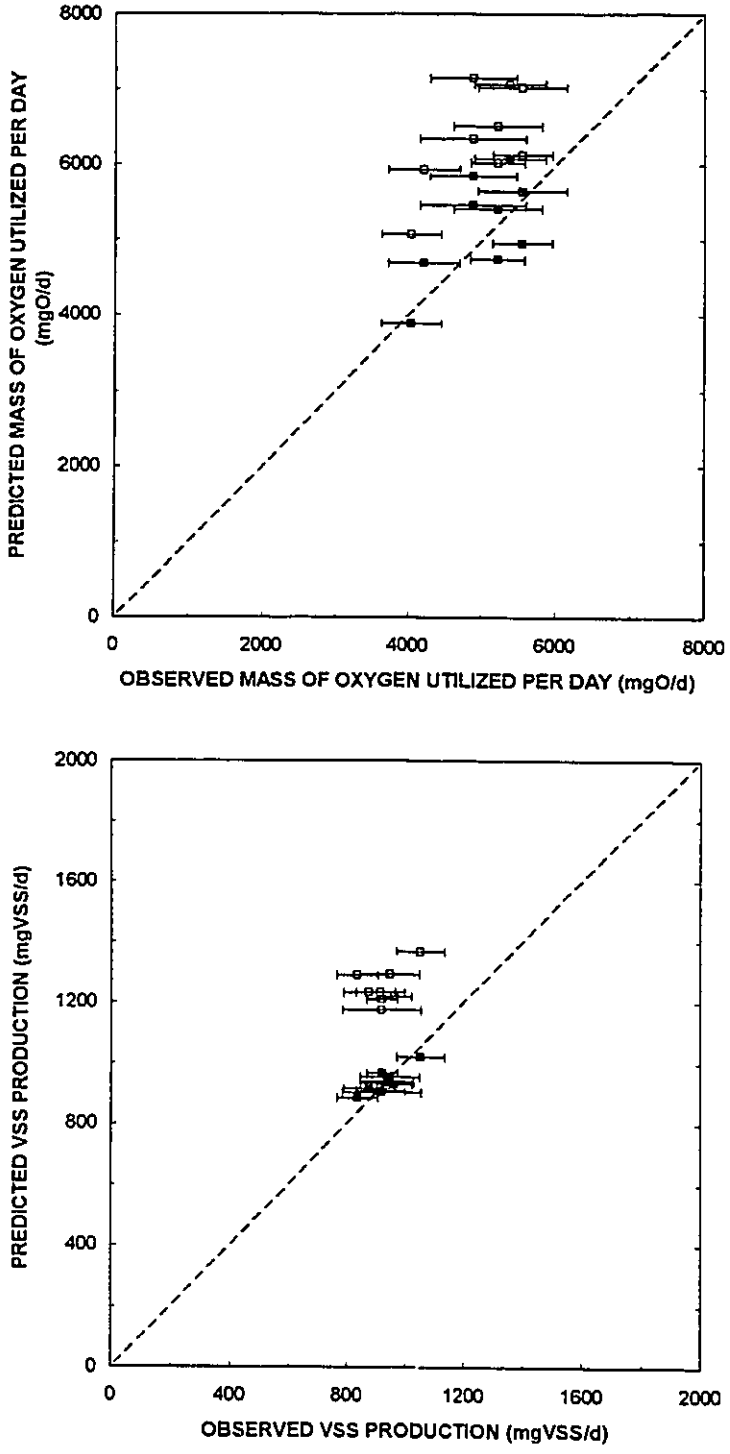

Figure 9.1 Predicted *versus* observed values for oxygen consumption and VSS production for anoxic-aerobic systems of Power *et al.* (1992) with f_{UP} reduced for the no loss case. [■ assuming COD loss, □ assuming no COD loss].

understanding of this behaviour is limited, particularly for anoxic and anaerobic conditions important to nutrient removal systems.

- Fermentation behaviour under anaerobic (and possibly anoxic) conditions.

- How the above two aspects impact denitrification behaviour, and the competition between polyP and non-polyP denitrifiers.

- The temperature dependency of the polyP organism kinetic behaviour.

- The fate of "unbiodegradable" COD generated by the endogenous processes of polyP organisms.

The most important unresolved aspect of NDBEPR modelling is the COD loss phenomenon. In the model COD loss is assumed to occur through three different biological processes: fermentation, sequestration, and hydrolysis under anoxic/anaerobic conditions. Empirical parameters have been incorporated which allow the model to predict the COD loss observed in a range of systems. While these empirical relationships appear to give reasonable results, an understanding of the underlying mechanisms is required in order to optimize system performance.

The behaviour of NDBEPR systems under dynamic conditions also needs to be further explored. As it was only possible to obtain sufficient data for modelling purposes for one system receiving a time-varying input, it is unknown whether results of model simulations are indicative of the model performance under dynamic conditions, or characteristic of this system in particular.

There is no doubt that modelling and simulation are assuming a prominent role in nutrient removal system design, operation and control. It should be recognized that the model described here considers only the activated sludge system. This is only one part of the wastewater treatment cycle. Other unit operations within the treatment plant (and operating procedures) are very important to overall system performance. A comprehensive treatment plant simulator should incorporate all of these aspects; for example, settling tanks, sludge fermenters, digesters, and handling of supernatant streams.

As many biological nutrient removal systems incorporate chemical addition (both as a coagulant and for the purpose of precipitating excess phosphorus), a complete system model should therefore include chemical addition as well. In addition some wastewaters (mainly in Europe) may contain active heterotrophic organisms in sufficient quantities to influence the mass of organisms in the system. In order to account for this, the influent wastewater composition would have to be characterized further into biodegradable COD (slowly degradable and readily degradable), unbiodegradable COD (soluble and particulate), and active organisms.

9.4 CONTRIBUTION TO KNOWLEDGE

The objective of this research was to develop and calibrate a dynamic mechanistic model for biological nutrient removal activated sludge systems treating municipal wastewater. In addressing this objective the research contained in this thesis makes a contribution to knowledge through an increased understanding of issues relating to biological phosphorus removal, in particular:

- The COD loss phenomenon, which leads to lower oxygen requirements and decreased sludge production in systems incorporating unaerated zones;

- Denitrification behaviour in BEPR systems.

In addition, results of model simulation and analysis of literature data have lead to an increased understanding of other processes occurring in a biological nutrient removal process, for example: hydrolysis of slowly biodegradable material under anaerobic conditions, anoxic decay of polyP organisms, and accumulation of "fixed" polyphosphate.

This research also provided a practical contribution to the field of Environmental Engineering through the concurrent development of the software *BioWin* (by EnviroSim Associates Ltd.) which utilizes the model developed in this thesis. This simulation program has been used for design and optimization of full-scale nutrient removal activated sludge systems.

ADDITIONAL REFERENCES

(For Chapters 1, 2 ,3, 9 & Appendix)

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APPENDIX

MODEL SENSITIVITY

INTRODUCTION

The sensitivity of the general model (presented in Chapter 6) to a number of model parameters is demonstrated for a UCT system (system 11a from Wentzel *et al.*, 1990). A schematic diagram of this system is given in Fig. A.1 below. The influent wastewater characteristics are listed in Table A.1, along with the model predictions obtained using the parameter values listed in Chapter 6. Due to the large total number of model parameters it is impractical to demonstrate the sensitivity of the model to every parameter and combination of parameters. Therefore the analysis has been limited to those parameters for which there is the most uncertainty. In many cases the parameters are empirical, and the values listed in Chapter 6 were obtained from model simulations for a range of activated sludge systems. Other parameter values were calibrated using a range of values obtained from a number of experimental studies. This analysis is divided into two sections: stoichiometric parameters and kinetic parameters (switching function parameters are discussed briefly in Chapter 7).

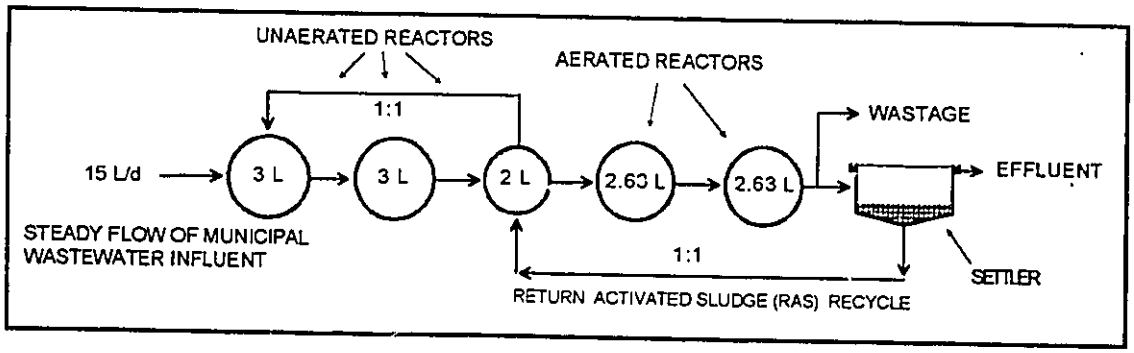

Figure A.1 **UCT/VIP Process NDBEPR system 11a (from Wentzel *et al.*, 1990). [Sludge age = 10 days; Feed volume = 15 L d^{-1}; Temperature = 20°C; Influent: unsettled municipal wastewater].**

Table A.1: Influent wastewater characteristics and observed and predicted response of selected parameters for the NDBEPR system shown in Fig. A.1 (system 11a from Wentzel *et al.*, 1990) using the parameter values tabulated in Chapter 6.

PARAMETER	VALUE	
	Observed	**Predicted**
Influent:		
Total COD (g COD m^{-3})	506	-
Readily biodegradable complex COD (S_{BSC}) (g COD m^{-3})	108	-
Readily biodegradable SCFA COD (S_{BSA}) (g COD m^{-3})	0	-
Unbiodegradable soluble COD (S_{US}) (g COD m^{-3})	53	
Unbiodegradable particulate COD (S_{UP}) (g COD m^{-3})	46	-
TKN (g N m^{-3})	51	-
Ammonia (g N m^{-3})	38.3	-
P (g P m^{-3})	22.6	-
Soluble phosphorus (g P m^{-3}):		
Reactor 1	43.4	38.9
Reactor 2	47.2	47.2
Reactor 3	37.6	32.7
Reactor 4	19.5	17.5
Reactor 5	10.8	9.4
Effluent	10.1	9.4
Overall P removal	12.5	13.2
Nitrate (g N m^{-3}):		
Reactor 1	0.0	0.0
Reactor 2	0.0	0.0
Reactor 3	2.4	3.3
Reactor 4	18.3	15.1
Reactor 5	20.1	21.7
Oxygen Utilization rate (g O_2 m^{-3} h^{-1}):		
Reactor 4	40	40
Reactor 5	23	25
Volatile Suspended Solids (g VSS m^{-3}):		
Reactor 5	1418	1405
Effluent:		
COD (g COD m^{-3})	61	60
TKN (g N m^{-3})	4.7	4.7

STOICHIOMETRIC PARAMETERS

Yield of Fermentation Products (Y_{AC})

The model assumes that the complex readily biodegradable COD is converted to short chain fatty acids (SCFA) through an anaerobic fermentation process mediated by facultative heterotrophs. This process is assumed to yield a small number of non-polyP heterotrophs ($Y_{H,ANA}$), as well as produce a yield of fermentation products (1 - $Y_{H,ANA}$). Only a portion (Y_{AC}) of the fermentation products is assumed to be SCFA, the remainder is assumed to be COD lost from the system. Fig. A.2 shows the variation in the predicted soluble phosphorus profile for system 11a for a range of Y_{AC} values. The model predictions for soluble P exhibit considerable sensitivity to this parameter; as the SCFA yield is increased, both anaerobic P release and aerobic P uptake are increased. Predictions of other parameters such as oxygen utilization rates (OUR), and volatile suspended solids (VSS) and nitrate concentrations, are relatively insensitive to this parameter.

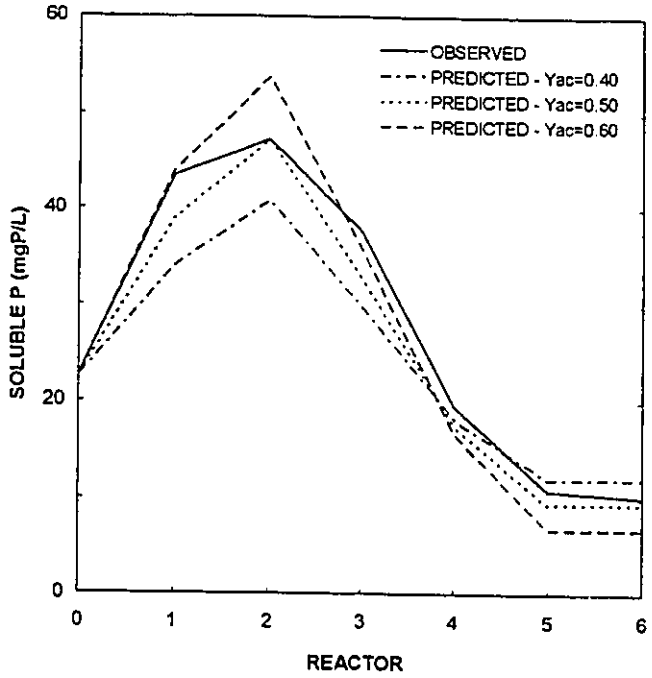

Figure A.2 **Observed and predicted soluble phosphorus profiles with varying acetate yields. ['0' indicates influent concentration; '1' and '2' represent anaerobic reactor concentrations; '3' indicates anoxic concentration; '4' and '5' represent aerobic concentrations; '6' indicates effluent concentration].**

Hydrolysis Efficiency Under Anoxic and Anaerobic Conditions

The solubilization of slowly biodegradable material enmeshed in the sludge mass is modelled on the basis of Levenspiel's surface reaction kinetics. The rate of hydrolysis under anoxic and anaerobic conditions is assumed to be a fraction of that under aerobic conditions. In addition the efficiency of hydrolysis is assumed to decrease under anoxic and anaerobic conditions to a fraction of that under aerobic conditions (E_{ANOX} and E_{ANA}, respectively). That is, the model assumes that under anoxic and anaerobic conditions a fraction (1-E) of the hydrolysis products is lost from the system.

Model predictions of oxygen utilization rates and aerobic volatile suspended solids concentrations with varying anoxic hydrolysis efficiencies are shown in Fig. A.3. The sensitivity of model predictions of OUR and VSS to this parameter is minimal for this system. However for systems with large anoxic zones such as that utilized by Power *et al.* (1992), this parameter will have a more substantial effect on VSS and OUR predictions (refer to Chapter 8). Fig. A.4 shows soluble P and nitrate profiles for a range of E_{ANOX} values. As E_{ANOX} approaches unity anaerobic P release is increased (as a result of an increase in the availability of complex readily biodegradable COD for fermentation to SCFA). In addition aerobic P uptake is increased as a result of increased storage of SCFA as PHB.

Fig. A.5 shows the soluble P profile for system 11a for a range of anaerobic hydrolysis efficiencies. As E_{ANA} is increased both anaerobic P release and aerobic P uptake are increased as a result of increased storage of SCFA as PHB. As E_{ANA} approaches unity the P concentration in the second anaerobic reactor is significantly over-predicted. Both oxygen consumption and volatile suspended solids production increased slightly with increasing E_{ANA} (not shown), due to the decrease in predicted COD "loss". Nitrate predictions were only affected minimally. The assumptions regarding COD loss and hydrolysis are discussed further in Chapter 8.

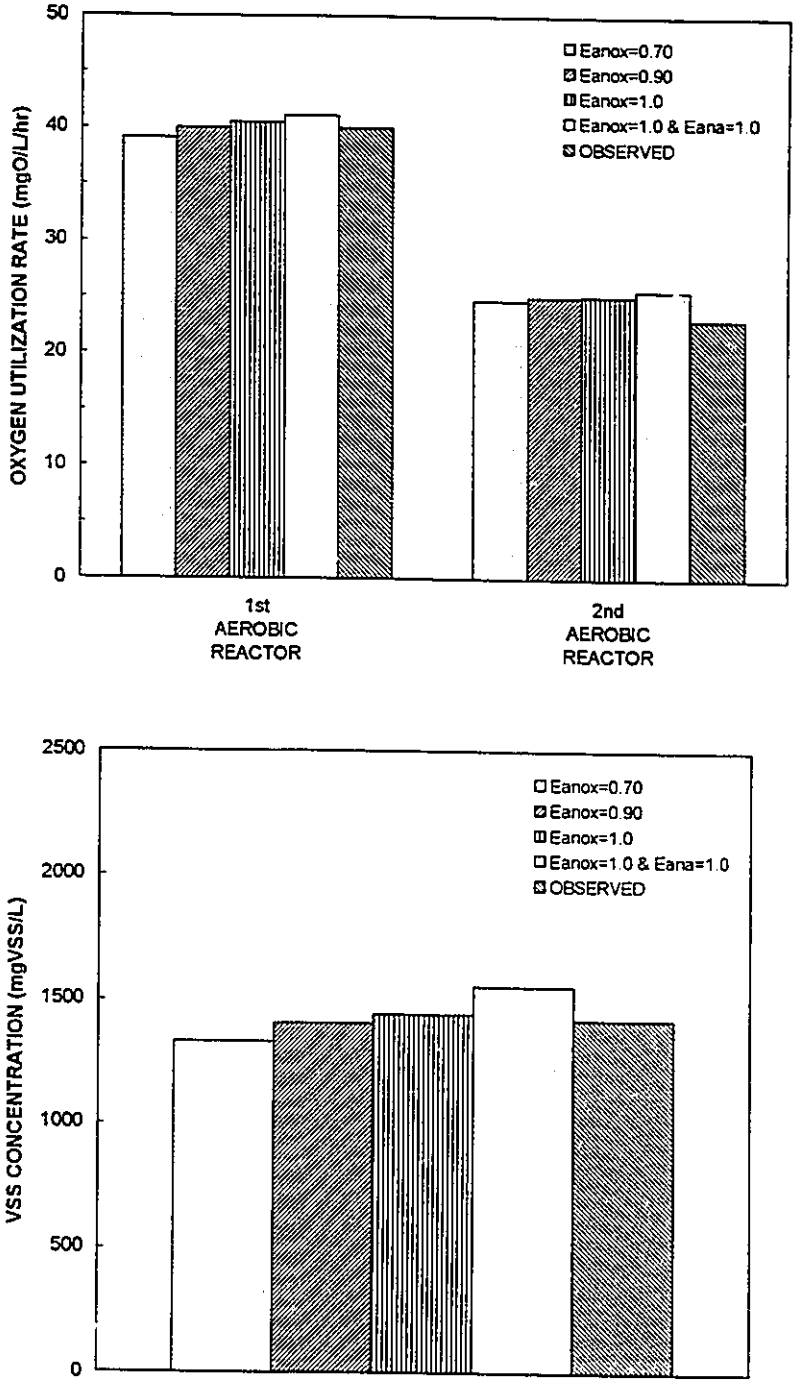

Figure A.3 Observed and predicted values with varying anoxic hydrolysis efficiencies for: (a) oxygen utilization rates; and (b) volatile suspended solids concentrations.

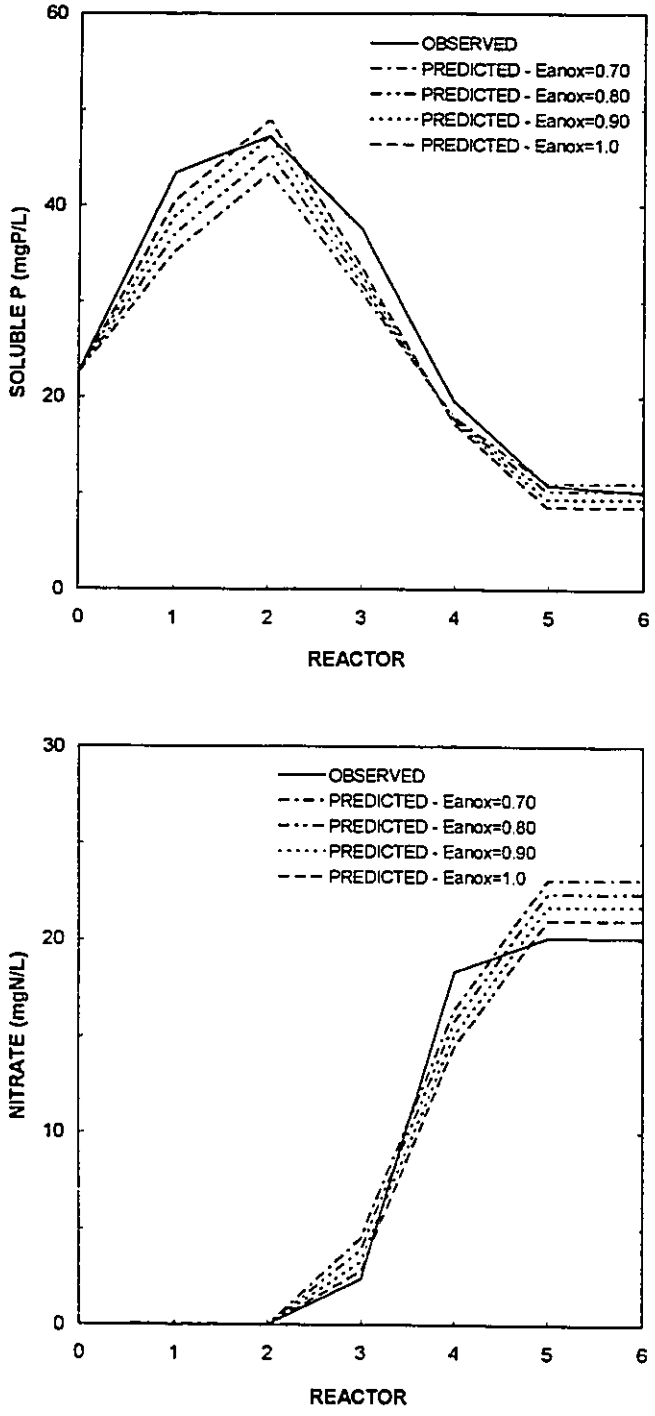

Figure A.4 Observed and predicted values with varying anoxic hydrolysis efficiencies for: (a) soluble phosphorus profiles; and (b) nitrate profiles.

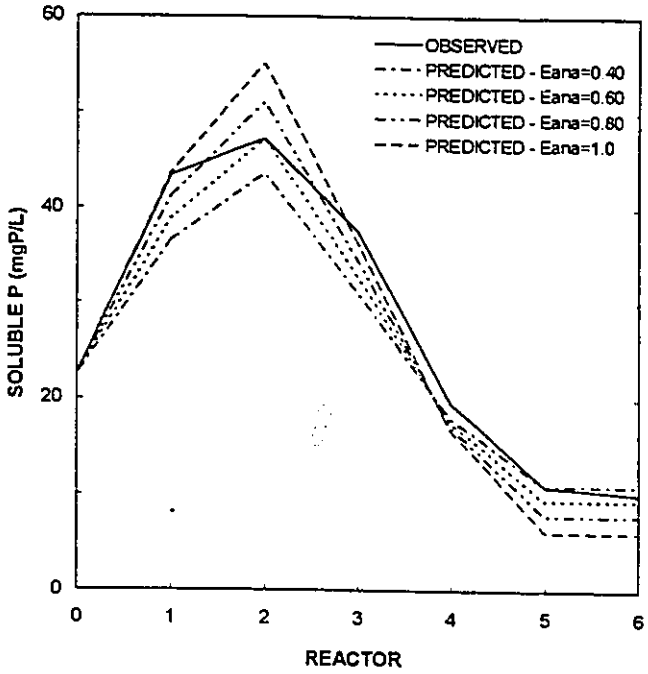

Figure A.5 Observed and predicted soluble phosphorus profiles with varying anaerobic hydrolysis efficiencies.

Aerobic P Uptake Ratio

The ratio of P taken up to COD utilized in aerobic growth of polyP organisms ($f_{P,UPT1}$) was determined from batch experiments to be approximately 0.9 - 1.1 $gP(gCOD)^{-1}$ (Wentzel *et al.*, 1989b). Fig. A.6 shows the variability in the P profile of system 11a for a number of $f_{P,UPT1}$ values close to this range. As $f_{P,UPT1}$ is increased from 0.80 to 1.0 the predicted aerobic soluble P concentration is reduced. Once $f_{P,UPT1}$ exceeds 0.95 the effluent soluble P prediction becomes under-predicted; for $f_{P,UPT1}$ values below 0.75 the polyP organisms washed out.

Anoxic P Uptake Ratio

The ratio of P taken up to COD utilized in anoxic growth of polyP organisms ($f_{P,UPT2}$) was estimated from model simulation of a number of systems to be approximately 0.55 $gP(gCOD)^{-1}$. This value is close to the range of values determined experimentally (refer to chapter 6 for more details). Fig. A.7 shows the variability in the P profile of system 11a for a number of $f_{P,UPT2}$ values in this range. As $f_{P,UPT2}$ is increased from 0.35 to 0.75 the predicted anoxic and aerobic soluble P concentrations are reduced. Other model predictions are not significantly affected by either $f_{P,UPT1}$ or $f_{P,UPT2}$.

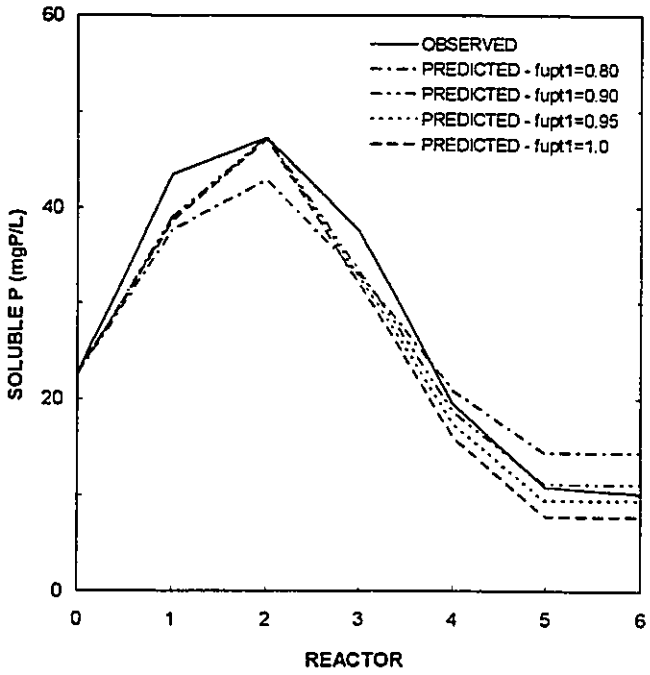

Figure A.6 Observed and predicted soluble phosphorus profiles with varying aerobic P uptake ratios.

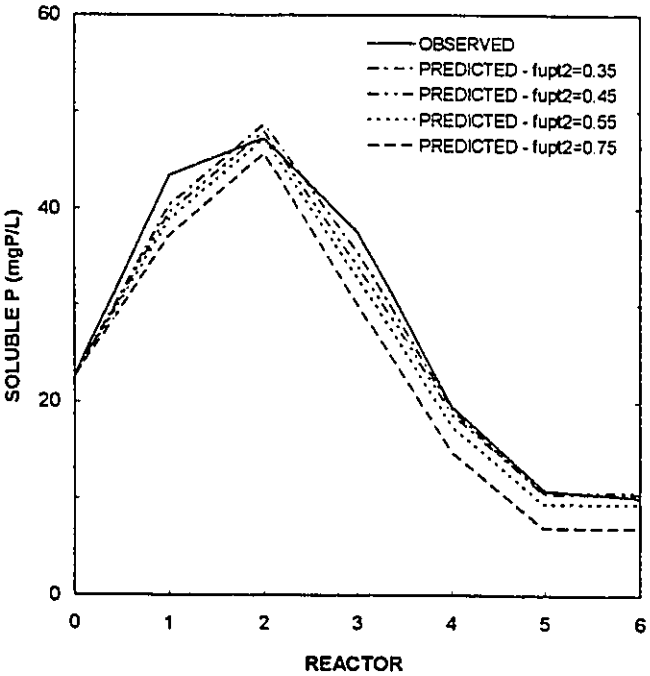

Figure A.7 Observed and predicted soluble phosphorus profiles with varying anoxic P uptake ratios.

Anaerobic P Release Ratio

The ratio of soluble P released to SCFA COD taken up (for sequestration by polyP organisms, $f_{P,REL}$) has been estimated from model simulation to be approximately 0.52 gP(gSCFA COD)$^{-1}$. This value is close to the values determined experimentally by Wentzel *et al.* (1989), and concurs with the Comeau/Wentzel biochemical model described in Chapter 2 (equivalent to approximately 1:1 on a molar basis). However there has been a considerable range of values determined experimentally by other researchers, suggesting that perhaps this value is too high (see Wentzel *et al.*, 1991). Fig. A.8 shows the soluble P profile for system 11a for a range of $f_{P,REL}$ values. As $f_{P,REL}$ is increased from 0.45 to 0.60 gP(gSCFA COD)$^{-1}$ the predicted soluble P profile is shifted upwards. It should be noted that there is an interactive effect in the soluble P predictions between $f_{P,REL}$, and $f_{P,UPT1}$ and $f_{P,UPT2}$. For example, increasing the aerobic P uptake ratio and decreasing the anaerobic P release ratio have similar (but not identical) effects, as both result in a reduction in reactor soluble P concentrations. However, increasing the aerobic P uptake ratio primarily affects the aerobic zone concentrations, while decreasing the anaerobic release ratio has the affect of lowering the entire P profile across the system.

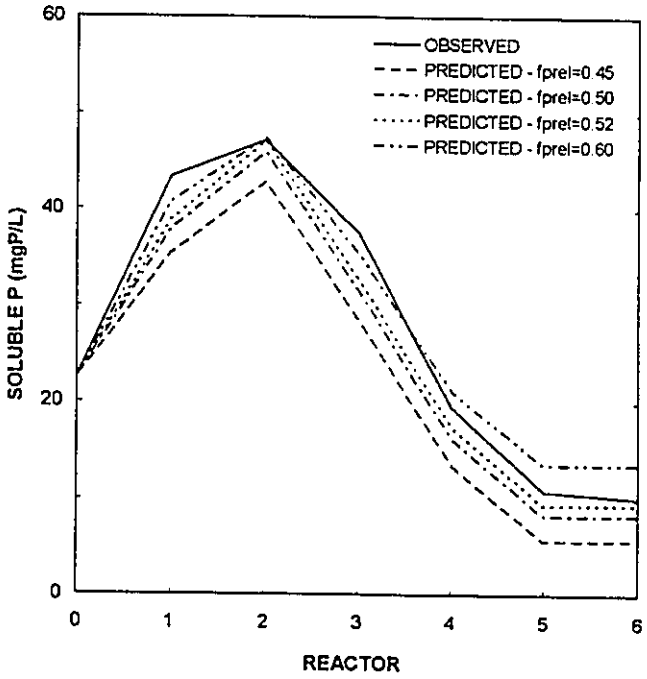

Figure A.8 Observed and predicted soluble phosphorus profiles with varying anaerobic P release ratios.

Yield of PHB

In the anaerobic sequestration of SCFA by polyP organisms (for PHB storage, with associated phosphate release) it is assumed that the yield of PHB is Y_{PHB} units of PHB (as COD) per unit SCFA COD taken up. A value of 0.89 gCOD.(gCOD)$^{-1}$ is suggested for Y_{PHB} based on the assumption that for an initial amount of 2.25 moles acetate, 2 moles enter the PHB formation pathway directly (refer to Wentzel *et al.*, 1986), this assumes the remaining COD is lost from the system. [It should be noted that the biochemical model of Wentzel *et al.* (1986) assumes that the available electrons from the 0.25 moles acetate are returned to the PHB formation pathway from the TCA cycle, and there is no COD loss]. Fig. A.9 shows soluble P profiles for a range of Y_{PHB} values. This parameter primarily affects the aerobic soluble P concentration, reducing it as Y_{PHB} is increased (below a value of 0.70 washout of polyP organisms ocurred). OUR and VSS predictions were increased only slightly as Y_{PHB} is increased (as the COD loss is reduced). In a system comprised mainly of polyP organisms the effect would be expected to be greater.

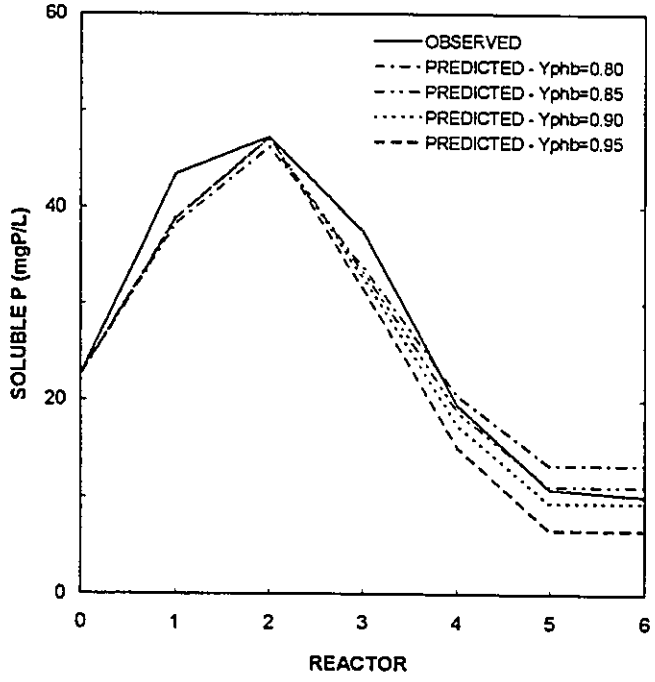

Figure A.9 Observed and predicted soluble phosphorus profiles with varying PHB yields.

KINETIC PARAMETERS

Maximum Specific Hydrolysis Rate

The maximum specific hydrolysis rate constant is listed in Chapter 6 as 2.81 d^{-1}. This value is similar to the value suggested for the ASM1 model (Dold and Marais, 1986). Fig. A.10 shows the predicted oxygen utilization rates and volatile suspended solids concentrations for system 11a for a range of K_H values. For K_H values below 2, hydrolysis is under-predicted, resulting in an under-prediction of OUR's and an over-prediction of VSS concentrations. For K_H values greater than 2, the sensitivity of model predictions is reduced. However the OUR in the second aerobic reactor still show some sensitivity to this parameter, perhaps due to the fact that the rate of carbon oxidation is limited by the hydrolysis rate in this zone. [It should be noted that the half-saturation coefficient for hydrolysis (K_X) could also be adjusted to reduce hydrolysis, *i.e.* increasing the value for K_X would reduce the amount of hydrolysis occurring, as the concentration at which the maximum specific hydrolysis rate is reached would be greater.] Soluble P predictions were also affected by varying K_H (not shown); nitrate concentrations were only affected minimally.

Anaerobic and Anoxic Solubilization Factors

In the ASM1 model the rate of solubilization under *anoxic* conditions is assumed to be reduced by a factor η_{SOL} compared to the rate under aerobic conditions. Under anaerobic conditions the rate is assumed zero. Recent research on enzymatic hydrolysis (Dold *et al.*, 1991, San Pedro *et al.*, 1994) indicates that hydrolysis does in fact occur under anaerobic conditions, and under anoxic conditions the rate of hydrolysis appears similar to that under aerobic conditions. This behavior requires further research. To provide flexibility in the model two η_{SOL} factors are incorporated: $\eta_{S,ANOX}$ and $\eta_{S,ANA}$. In Chapter 6 $\eta_{S,ANOX}$ is listed as 1.0, and $\eta_{S,ANA}$ as 0.50. These values were derived from model simulations for a range of systems. Fig. A.11 shows predicted oxygen utilization rates and volatile suspended solids concentrations for system 11a for a range of $\eta_{S,ANA}$ values. As $\eta_{S,ANA}$ is increased from 0.20 to 1.0 the OUR's in both aerobic reactors are reduced, presumably due to an increase in predicted COD loss. The sensitivity of the VSS predictions is minimal.

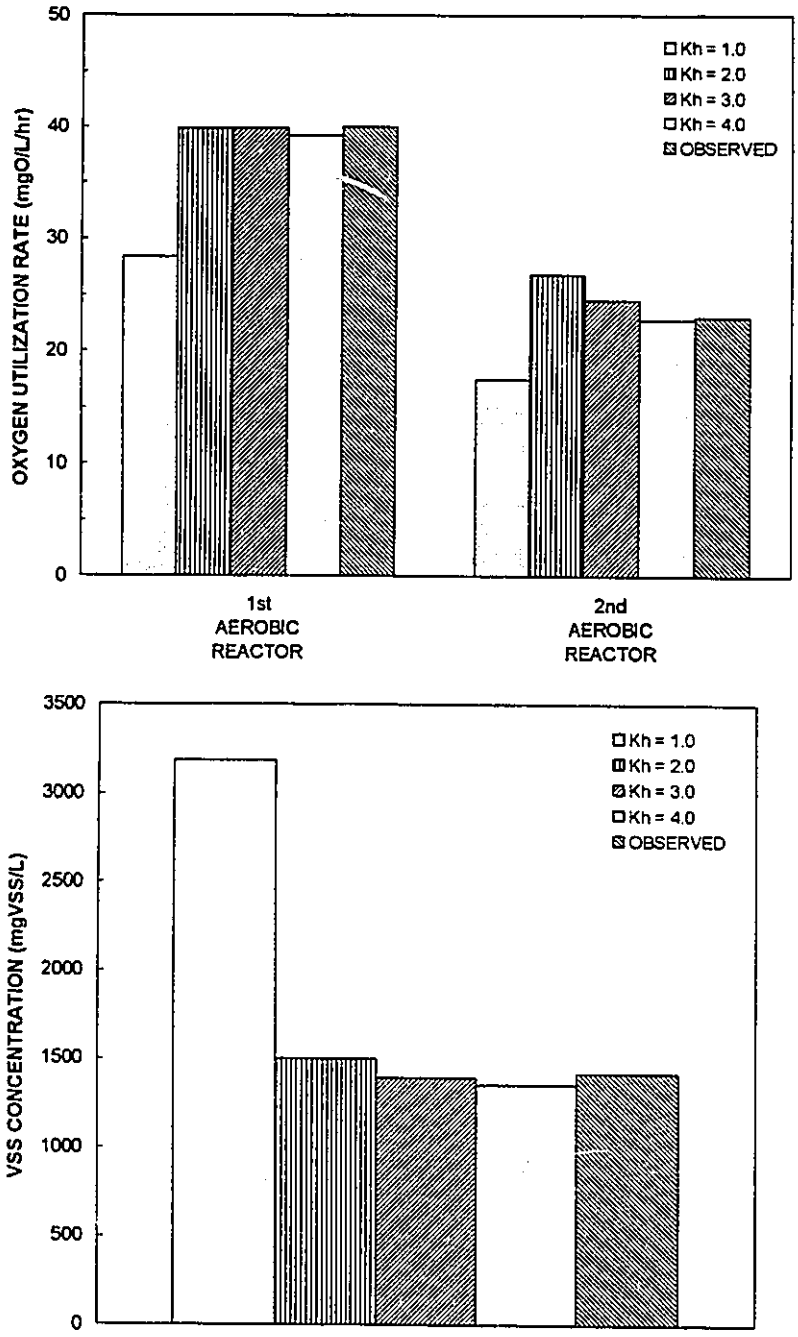

Figure A.10 Observed and predicted values with varying maximum specific hydrolysis rates for: (a) oxygen utilization rates; and (b) volatile suspended solids concentrations.

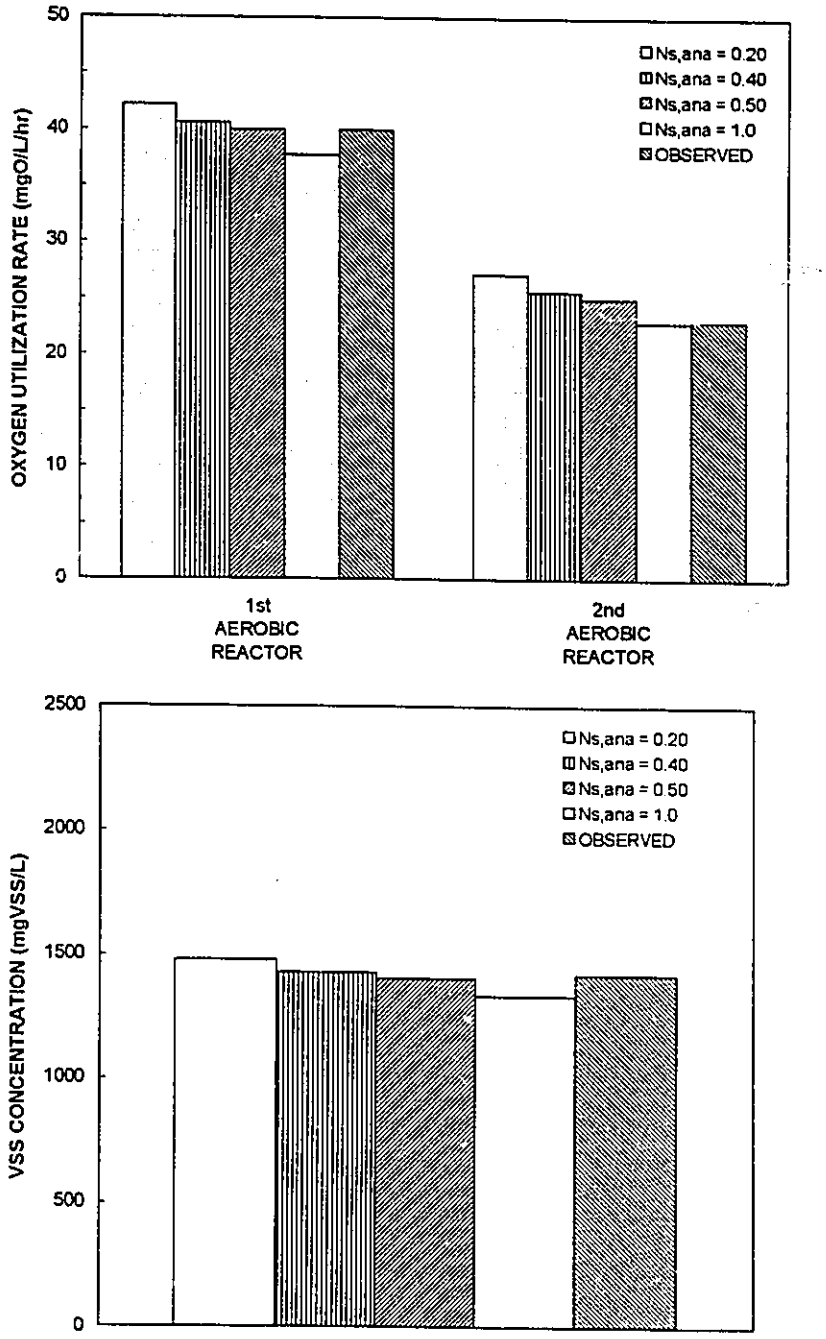

Figure A.11 Observed and predicted values with varying anaerobic solubilization factors for: (a) oxygen utilization rates; and (b) volatile suspended solids concentrations.

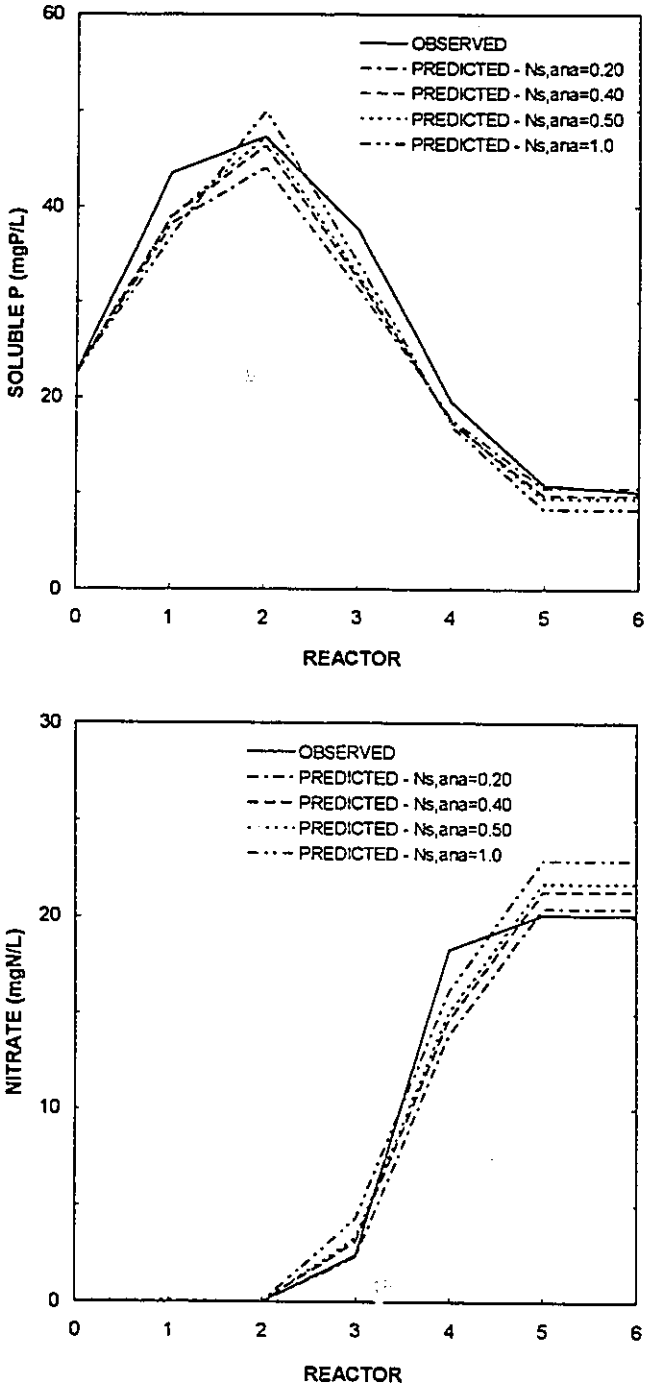

Figure A.12 Observed and predicted values with varying anaerobic solubilization factors for: (a) soluble phosphorus profiles; and (b) nitrate profiles.

Fig. A.12 shows the predicted soluble P and nitrate profiles for a range of $\eta_{S,ANA}$ values. Increasing $\eta_{S,ANA}$ increases both the anaerobic P release, and the aerobic P uptake (since more hydrolysis occurs anaerobically, more fermentation of complex readily biodegradable COD to SCFA also occurs, increasing the amount of stored PHB). The predicted nitrate profiles are shifted upwards with increasing $\eta_{S,ANA}$, perhaps as a result of increased nitrification resulting from the increased hydrolysis of particulate organic N (assumed to occur at the same rate as hydrolysis of carbonaceous slowly degradable material).

Fig. A.13 and A.14 show the predicted oxygen utilization rates and soluble P and nitrate profiles for a range of $\eta_{S,ANOX}$ values. The sensitivity of model predictions of OUR to $\eta_{S,ANOX}$ values is less than that for $\eta_{S,ANA}$, due to the fact that less COD loss is assumed to occur with anoxic solubilization than with anaerobic solubilization. The effects on model predictions of soluble P and nitrate are similar to that for $\eta_{S,ANA}$ described above.

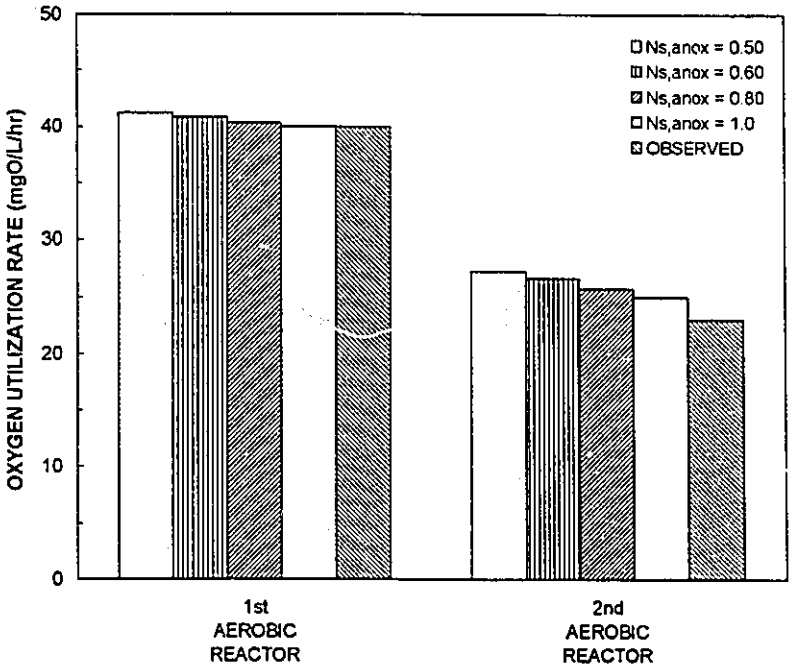

Figure A.13 Observed and predicted oxygen utilization rates with varying anoxic solubilization factors.

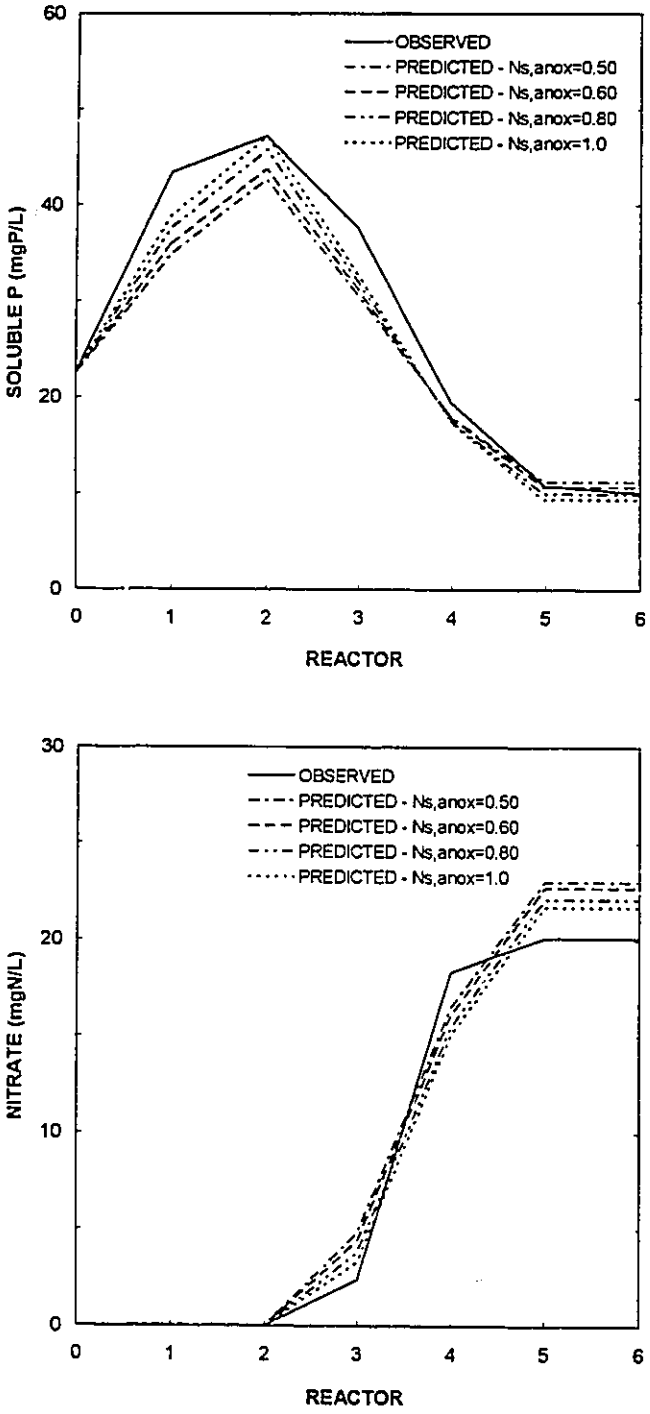

Figure A.14 Observed and predicted values with varying anoxic solubilization factors for: (a) soluble phosphorus profiles; and (b) nitrate profiles.

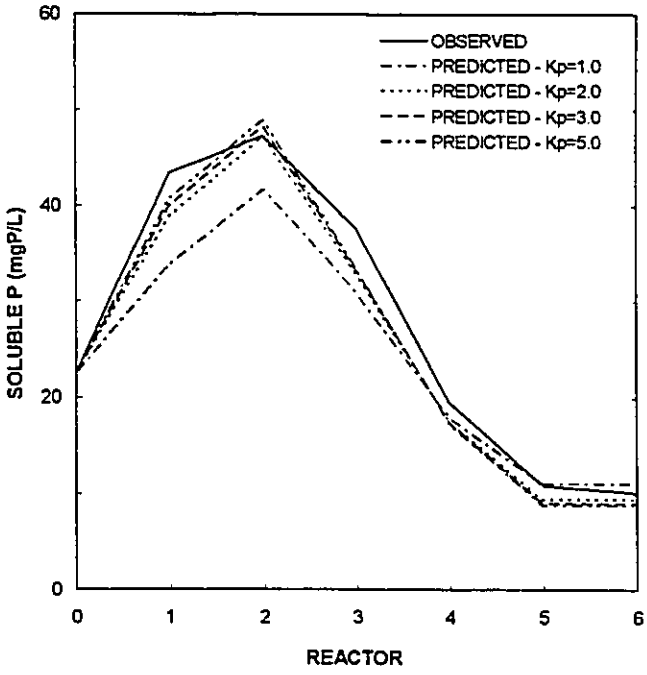

Figure A.15 Observed and predicted soluble phosphorus profiles with varying polyP specific SCFA sequestration rates.

Specific Rate of SCFA Sequestration

The specific SCFA sequestration rate constant (K_P) has been estimated from model simulations to be approximately 2.0 gCOD.(gCOD.d)$^{-1}$. Model predictions of soluble P for a range of K_P values are shown in Fig. A.15 for system 11a. As the sequestration rate constant is increased predictions of anaerobic P release and aerobic P uptake also increase. For K_P values greater than 2 the effect of sequestration rate on P predictions is minimal (below 1.0 washout of polyP organisms occurred).

CLOSURE

The sensitivity of model predictions to a number of model parameters has been demonstrated for a laboratory scale UCT system. It should be noted that the sensitivity the model exhibits for this system is not necessarily applicable to activated sludge systems in general. Additional factors not considered in this analysis will also determine the

sensitivity of model predictions to specific model parameters. A comprehensive sensitivity analysis would include analysis of model sensitivity for a number of systems with a range of design and operating parameters (including systems with a time-varying input), as well as varying wastewater characteristics, for each model parameter and combination of parameters.