

**MUNICIPAL WASTEWATER  
CHARACTERIZATION**

*Application of denitrification batch tests*

by

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**(MSc.)**

Submitting in fulfillment of the academic requirements for the degree of

**Doctor of Philosophy**

in the

Department of Chemical Engineering

University of Natal, Durban.

February 1999

## *Abstract*

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The biological treatment of wastewater has evolved significantly from simple single sludge systems practicing organic carbon removal to ones which now include either nitrification/denitrification (N/DN) and / or phosphorus (P) removal. The inclusion of more biological processes have increased the complexity of current wastewater systems which has subsequently led to the development of more complex mathematical models. The operation of plants can be assessed and improved by the use of mathematical modelling tools which require accurate input data. Thus, knowledge of the wastewater characteristics is an important step towards the optimum modelling, design and operation of present and future plants. However, for these tools to be effective, the input data needs to be accurate which is dependent on the current methods used to determine them.

Wastewater is a complex substrate consisting of compounds of differing biodegradability. Biokinetically, these compounds have been divided into readily biodegradable (RBCOD), slowly biodegradable (SBCOD) and unbiodegradable substrate groups. Compounds with intermediate biodegradability i.e. compounds which fall between the RBCOD and SBCOD groups, have been termed readily hydrolyzable organic substrates (RHCOD). The organic matter is discussed in terms of chemical oxygen demand (COD). The readily biodegradable and readily hydrolyzable COD fractions of wastewater can be determined by respirometric tests such as the oxygen utilization rate (OUR) and nitrate-N utilization rate (NUR) tests.

The principal aim of this project was to investigate the NUR test as a tool for wastewater characterization and to study denitrification kinetics in batch reactors. In addition, an experimental readily biodegradable substrate, acetate, was used to determine the reliability of the NUR tests. Acetate was also used to ascertain utilization profiles and rates of a typical readily biodegradable substrate during denitrification. Biodegradable COD characterizations with enhanced biological phosphorus removal (EBPR) sludges were also investigated to determine the impact of anoxic phosphorus removal on NUR tests. The results obtained from the numerous NUR tests added to the understanding of the NUR test.

Samples from 22 wastewater treatment plants were tested, most of which were located in France. Four South African plants were also tested. Data obtained from the NUR tests were used to calculate the RBCOD and RHCOD fractions. The SBCOD, however, could not be determined directly from the 6 h NUR batch tests. The readily biodegradable COD (RBCOD)

fractions ranged between 7 and 25 % of the total COD concentration of raw wastewater, with majority of those results falling within the 10-20 % (of the total COD) range. The results also showed that the initial rapid rate associated with readily biodegradable COD utilization was sometimes followed by a short intermediate phase (*i.e.* short duration, 2 to 3 h). The intermediate fraction was found to range between 5 and 29 % of the total COD concentration and was classed as a readily hydrolyzable COD component of raw wastewater since the magnitude of the RHCOD fraction was too small to be classed as slowly biodegradable COD which comprises approximately 30 to 60 % of the total COD found in raw wastewaters. The variability of the RHCOD fractions suggests that this fraction is either very variable or that the NUR test does adequately or accurately characterize it. Another possibility is that the RHCOD (or second biodegradable fraction) calculated from the NUR test is a component of the RBCOD of the influent wastewater. In this case, the bacteria may have used some of the RBCOD directly for energy and accumulated or stored the rest as part of a survival mechanism which allows them to be more competitive under dynamic operating conditions. Once the readily biodegradable COD becomes limiting, the bacteria will use the accumulated or stored compounds. This hypothesis is substantiated by tests done with acetate as substrate.

An intermediate phase was also observed when acetate was the sole substrate. Thus, it was possible with the 3-phase profiles to calculate a second biodegradable fraction. Results suggest that a significant part of the added acetate (as COD) was stored and the second phase is in fact an 'apparent or residual' phase brought about by the consumption of the stored or accumulated acetate products. This is suggested in two ways : (1) the calculation of the yield coefficient is lower and closer to the 0.5 mg/l values, cited in the literature, when the COD calculated from phases 1 and 2 are considered, and (2) the acetate mass balances were found to be approximately 100 % when phases 1 and 2 were used to calculate the amount of acetate utilized under anoxic conditions.

Several of the NO<sub>x</sub> profiles revealed either 2 or 3 rates due to the control of the substrate to biomass ratio ( $S/X : \leq 0.1 \text{ mgO}_2 / \text{mgO}_2$ ). Majority of the samples (*i.e.* 85%) tested produced initial maximum specific denitrification rates ( $k_1$ ) between 3 and 6 mgN/gVSS.h. The intermediate denitrification rate ( $k_2$ ) was found to vary between 2 and 3 mgN/gVSS.h. Denitrification rates ( $k_3$ ) obtained from utilization of influent and endogenous slowly biodegradable COD (SBCOD) varied between 1.0 and 1.5 mgN/gVSS.h. This latter rate is significantly higher than the endogenous denitrification rates cited in the literature. One of the reasons for these higher rates could be linked to the reuse of stored or accumulated products by the microorganisms.

An experimental readily biodegradable organic substrate, sodium acetate, was tested under anoxic conditions. The results were used to formulate several conclusions on acetate utilization during denitrification. Firstly, from acetate mass balances it was found that acetate may be used exclusively for denitrification (100 % acetate was accounted for). In this case, the sludge contains a significant proportion of denitrifiers and little or no polyphosphate accumulating organisms. This observation was made only when non-EBPR (enhanced biological phosphorus removal) sludges were used. Secondly, acetate mass balances which were found to be < 100 % suggest that acetate could be used for denitrification and the production of storage products like polyhydroxyalkanoates (PHA's). These sludges probably contained a higher proportion of polyphosphate accumulating organisms which competed for the available acetate in the bulk liquid. This observation was made for both EBPR and non-EBPR sludges. Thirdly, acetate could be used for denitrification by denitrifiers and for polyhydroxyalkanoate synthesis by denitrifying polyphosphate accumulating organisms. The stored PHA's in the denitrifying polyphosphate accumulating organisms are subsequently utilized during denitrification. This secondary utilization is manifested in the second denitrification phase and is supported by the observation of phosphorus uptake. These results showed that wastewaters high in volatile fatty acids (VFA's) were also subject to denitrifying polyphosphate accumulating organism activity even though the sludge was sampled from non enhanced biological phosphorus removal systems (non EBPR).

In addition, a comparative study on RBCOD determination of wastewaters with enhanced biological phosphorus removal and non-EBPR sludges. It was found that the RBCOD values derived by NUR tests with EBPR sludge were consistently lower (4 to 5 %) than those with non-EBPR sludge. Thus, the NUR tests with EBPR sludge resulted in a 4 to 5 % underestimation of the RBCOD fraction of raw wastewaters. This loss in RBCOD to polyphosphate accumulating organisms appears to be linked to the influent raw wastewater acetate concentration.

These tests showed that the RBCOD fraction could be adequately characterized using the NUR method. The accuracy of the tests appears to be compromised when enhanced biological phosphorus removal sludges are used in the NUR tests. Moreover, it was found that non-EBPR sludges can also consume some of the acetate that is present in the system for the production and replenishment of storage compounds. Fortunately, for the wastewaters tested, the acetate component of the RBCOD fraction was small and therefore, did not significantly affect the results. Mechanisms such as substrate accumulation and storage may also impact on substrate removal and hence, the determination of the readily biodegradable COD concentration of

municipal wastewaters. Thus, while the results showed that the NUR is a useful characterization tool for wastewaters, it will continue to be a more tedious characterization tool than the oxygen utilization rate test, until a suitable nitrate/nitrite electrode is developed to automate the test.

## *Dedication*

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*'Success is something in your heart,  
its an inner strength thats born  
from the ability to carry on,  
to finish everything you start,  
to push towards your ultimate goal.'*

*.....Charlotte*

*This dissertation is dedicated to my family and friends for their  
unwavering support, understanding, and belief.*

## *Preface*

---

I hereby declare that this dissertation is my own work, unless stated to the contrary in the text, and that it has not been submitted for a degree to any other University or Institution.

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Valerie Naidoo

February 1999

## *Acknowledgements*

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*I wish to express my sincerest gratitude to the following people for their contribution towards this dissertation.*

The **Water Research Commission** of South Africa for their financial assistance and the efforts made in facilitating liasons between CIRSEE-Suez-lyonnaise-des-eaux, France, and the University of Natal, South Africa.

**CIRSEE-Suez-Lyonnaise-des-Eaux**, France, for providing me with the financial and technical support while completing my research in France (first 2 years - 1996/1997) and South Africa (final year - 1998).

**Dr Vincent Urbain**, my co-supervisor at CIRSEE (in 1996 and 1997), for his guidance, assistance and hospitality under some trying circumstances. *‘Merci beaucoup, Vincent’*

**Dr Philippe Ginestet**, my co-supervisor in 1998, for his assistance, guidance and some interesting conversations in the lab.

**Bruno Levine**, my office pal, for the entertaining and stimulating discussions *version anglais* and the creation of a relaxed work environment.

**Mon. Herve Harduin, Mlle Monique Allain et Mlle Danielle Bellachen**, the technical staff at CIRSEE, *merci beaucoup pour l’asistance.*

**My colleagues at the Department of Chemical Engineering, University of Natal**, for the creation of a fun work atmosphere.

**Prof. Chris Buckley**, my co-supervisor in the Department of Chemical Engineering, for his guidance, assistance and encouragement during the course of this project.



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## *Abbreviations*

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ATP	adenosine triphosphate
BNR	biological nutrient removal
BEPR	biologically enriched phosphorus removal
Bio-P	biological phosphorus removing sludge
COD	chemical oxygen demand (mgO <sub>2</sub> /l)
CV	coefficient of variation
DO	dissolved oxygen
DPAO	denitrifying poly-accumulating organism
FAD	flavin adenine dinucleotide
FADH <sub>2</sub>	flavin adenine dinucleotide (reduced)
GAM	glycogen accumulating metabolism
g	gaseous
h	hour
K	Kelvin
k <sub>1</sub>	first rate (mgN/gVSS.h)
k <sub>2</sub>	second rate (mgN/gVSS.h)
k <sub>3</sub>	third rate (mgN/gVSS.h)
min	minute
mV	millivolts
µm	micrometer
N	Nitrogen
N/ND	Nitrification/denitrification
N/A	not applicable
n.d.	not determined
n.o.	not observable
NO <sub>x</sub>	nitrates and nitrites as N (mg/l)
NUR	Nitrate utilization rate
OUR	Oxygen utilization rate
P	Phosphorus (mg/l)
PAO	poly-accumulating organism
PAM	poly-accumulating metabolism
p.e.	population equivalents
PHB	polyhydroxybutyrate
PHA	polyhydroxyalkanoate
RBCOD	readily biodegradable COD (mg/l)
RHCOD	readily hydrolyzable COD (mg/l)
rw	raw wastewater
S	substrate
S <sub>s</sub>	truly soluble fraction
SBCOD	slowly biodegradable COD

S-ce	COD of supernatant after centrifugation
S-f <sub>0.45</sub>	COD of supernatant after 0.45 $\mu\text{m}$ filtration
S-co	COD fraction after coagulation
S-p	particulate COD (after filtration)
S-t	total COD
S-uns.	COD of supernatant after 2h settling
T	temperature in degrees Celsius
t	time
TSS	total suspended solids
V	volume
V <sub>t</sub>	total volume
V <sub>ww</sub>	volume of raw wastewater
V <sub>x</sub>	volume of sludge
VFA	volatile fatty acid
VSS	volatile suspended solids
WTP	wastewater treatment plant
X <sub>t</sub>	biomass
X <sub>f</sub>	filtered fraction of biomass
Y <sub>HD</sub>	yield coefficient (anoxic)
Y <sub>H</sub>	yield coefficient (aerobic)

## *Glossary*

---

anabolism	the biosynthesis of new cellular material
anoxic	bacteria use NO <sub>3</sub> as the terminal electron acceptor
aerobic	bacteria use O <sub>2</sub> as the terminal electron acceptor
anaerobic	Bacteria use terminal electron acceptors other than O <sub>2</sub> or NO <sub>3</sub>
active mass	active biomass
adenosine triphosphate	energy rich molecule
biodegradation	breakdown of compounds by biologically mediated reactions
biosorption	
bioadsorption	
biomass	bacterial cells
culture	
catabolism	breakdown of complex molecules for metabolic processes
combined sewers	sewers that collect municipal wastewater and storm waters
coagulation	
denitrifiers	microorganisms that use NO <sub>3</sub> as a final electron acceptor
denitrifying poly- accumulating organism	phosphorus removing bacteria that are capable of using NO <sub>3</sub> as a terminal electron acceptor
dissimilatory denitrification	
effluent	
facultative anaerobes	
fermentation	
guanosine triphosphate	energy rich molecule
gram negative	
glycogen accumulating metabolism	
hydraulic retention time	
hydrolysis	
hydrolysate	
inert	
influent	
mixed culture	
poly-accumulating	

metabolism

poly-accumulating  
organism

readily biodegradable

rapidly hydrolyzable

soluble

soluble microbial product

sequester

solids retention time

substrate

separate sewer

slowly biodegradable

unbiodegradable

compounds that cannot be biodegraded any further in the  
treatment system

# Chapter One

## *INTRODUCTION*

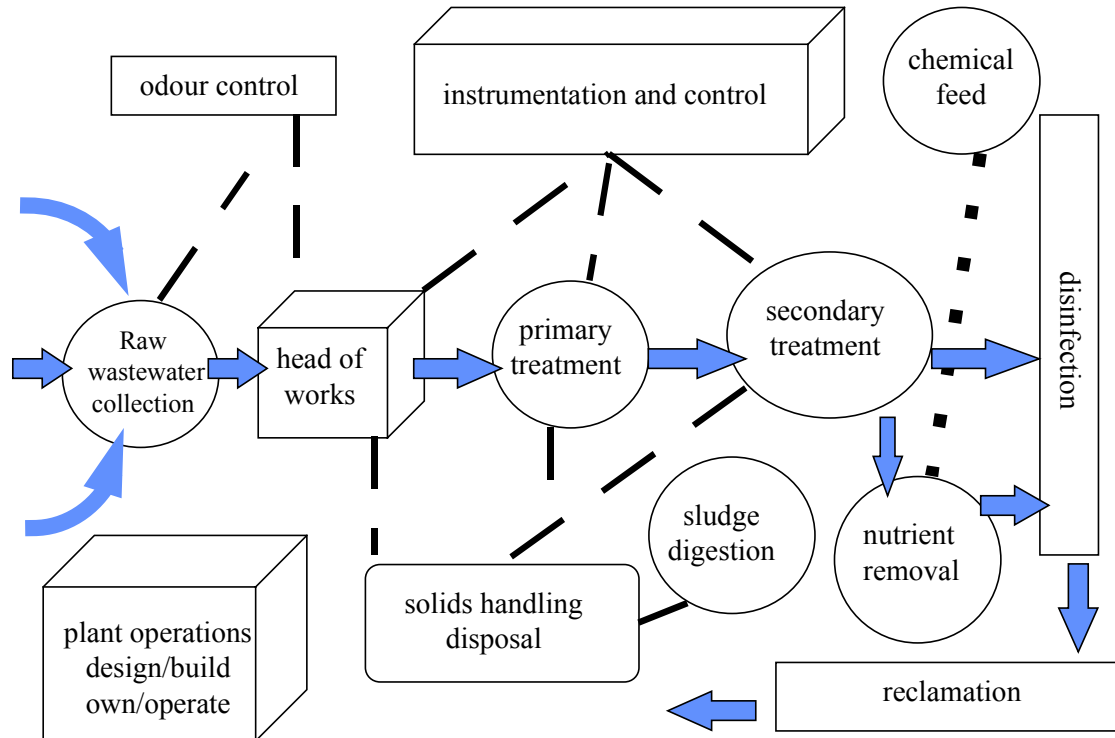
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### *1.1. BACKGROUND*

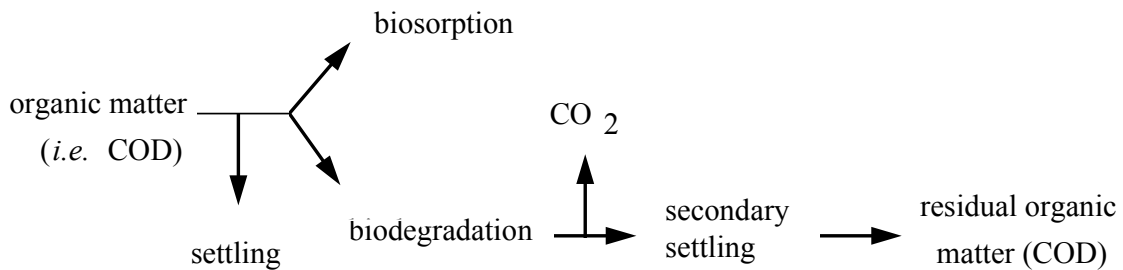
Wastewaters are high in organic compounds, phosphorus (P) and nitrogen (N). The dumping of wastes rich in these compounds is one of the factors which promotes eutrophication. Eutrophication results in excessive growth of algae which results in the depletion of oxygen (O<sub>2</sub>) and sunlight in the water systems, particularly still water systems. This adversely affects the life in these ecosystems. In addition, eutrophication leads to turbidity and odour problems which impacts on the drinking water and recreational quality of the rivers. Thus, the deterioration of water systems due to release of wastes rich in nutrients has led to more stringent standards which regulate the concentration of organics and nutrients discharged into water systems. The implementation of these standards has led to the emergence of wastewater treatment plants which may combine biological, physical and chemical processes to achieve favourable effluent concentrations (Figure 1-1).

One of the principle aims of present day wastewater treatment plants is the removal of organic carbon (COD) from wastewaters (Henze *et al.*, 1997). This has been achieved by effecting several steps in the treatment process such as primary settling, bioadsorption, biodegradation, followed by a secondary settling step to remove the sludge flocs (Figure 1-2). This eventually results in the production of residual organic carbon which can be released into the river systems.

Furthermore, the activated sludge process has shown that under certain selector conditions (aerobic, anaerobic and / or anoxic) it is also able to efficiently remove nitrogen and phosphorus. Nitrogen can be transformed and removed by biologically mediated nitrification (aerobic process) and denitrification (anoxic process). Nitrification is a process which converts ammonia to nitrites and then to nitrates while denitrification results in the transformation of nitrates and nitrites to nitrogen gas. Biological phosphorus removal is enhanced by the presence of anaerobic and aerobic zones, and polyphosphate accumulating organisms. Both denitrification and phosphorus removal efficiency are dependent on the biodegradability of the available organic carbon substrate (COD). This aspect will be discussed in more detail in **Chapter 2 and Chapter 3**.



**Figure 1-1: The biological and physical processes implemented to manage and treat municipal wastewater effectively.**



**Figure 1-2: Basic outline of organic matter (COD) removal mechanisms in municipal wastewater treatment systems.**

### **Process configuration**

In 1962 Ludzack and Ettinger (in Van Haandel *et al.*, 1981) were the first to recognize the importance of the influent organic carbon source for nitrogen removal. Accordingly, they proposed a system configuration with an anoxic reactor connected to an aerobic reactor but without complete separation (Figure 1-3). However, the incomplete separation of the two reactors led to less efficient process operation (Van Haandel *et al.*, 1981 ; Randall *et al.*, 1992). The Ludzig-Ettinger configuration was later improved by separating the anoxic zone from the aerobic zone and adding a recycle (A) line from the aerobic reactor to the anoxic reactor. This configuration was named the Modified Ludzig-Ettinger system (Fig 1-3). In 1973, Barnard proposed the Bardenpho process, which separated the anoxic and aerobic zones and included a post-denitrification reactor. A controlled recycle (A) line from the aerobic to the anoxic zone



was introduced and the underflow recycle (S) was discharged to the anoxic reactor (Figure 1-3). These changes in the process configuration improved the consistency and efficiency of the nitrogen removal processes (Van Haandel *et al.*, 1981).

Phosphorus removal has been achieved as a modification of the nitrogen removal systems. Some system configurations that are currently in use include the Phoredox, Johannesburg, UCT and MUCT systems. The Phoredox process can achieve optimal nitrogen removal through maximum use of the anoxic volume (Figure 1-4). However, the effectiveness of the anaerobic reactor is reduced since the sludge recycle which may contain nitrates discharges directly into the anaerobic zone. The negative effect of nitrates in phosphorus removal processes led to a modification in the Phoredox process which eliminated the recycle of nitrates in the return activated sludge to the anaerobic zone. This process was named the University of Cape Town (UCT) process. It was later modified to provide better protection of the anaerobic zone from nitrate recycle and termed the modified UCT (MUCT) process (Figure 1-4). Thus, the major difference between the UCT and MUCT systems is that the primary anoxic reactor is split into two reactors, one receiving the underflow recycle and recycling to the anaerobic, and the other receiving the aerobic recycle. (Randall *et al.*, 1992 and Wentzel *et al.*, 1992).

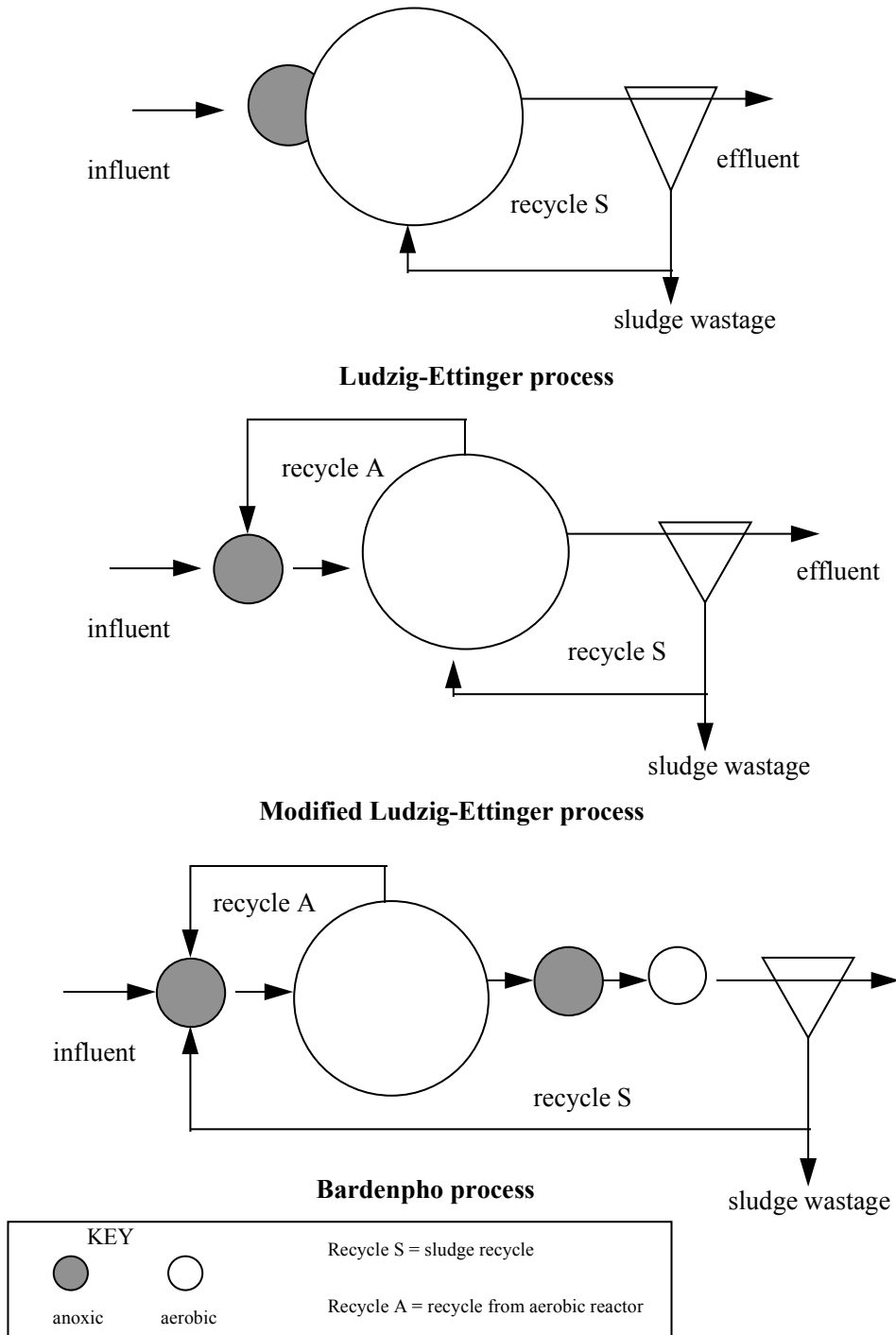
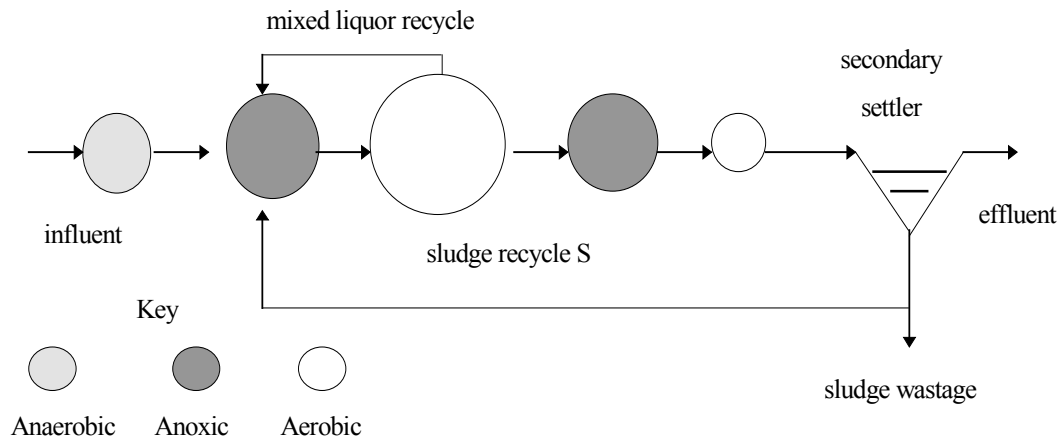
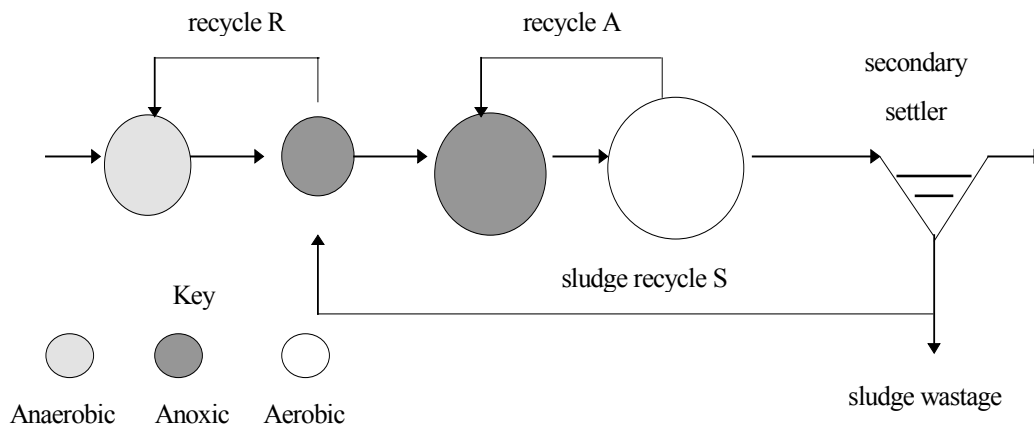


Figure 1-3: Some of the earlier nitrogen removal processes (Van Haandel et al. 1981)



The Phoredox process for biological nitrogen and phosphorus removal



The modified UCT process for biological nitrogen and phosphorus removal

**Figure 1-4: Configuration of the Phoredox and MUCT systems used for biological nitrogen and phosphorus removal (from Randall et al., 1992)**

### ***Biodegradability of organic carbon of raw wastewaters***

Studies on full-scale activated sludge plants showed that denitrification in a plug-flow primary anoxic reactor occurred in two linear phases. The rapid initial rate was followed by a slower denitrification rate which was hypothesized to arise from the utilization of two different biodegradable COD fractions (Ekama *et al.*, 1979). The first phase, which was a rapid, short phase, was linked to the utilization of a readily biodegradable COD fraction (RBCOD). This fraction consisted of small molecules that could pass directly through the cell wall of the organisms for metabolism.

The second phase was longer and produced a slower rate. This phase was attributed to the slowly biodegradable COD fraction (SBCOD) which consists of larger complex molecules that cannot pass directly through the cell wall of the microorganism. The compounds which belong to the SBCOD division

requires several hydrolytic steps before they can be taken up and utilized by the heterotrophic bacteria in activated sludge. Hydrolysis is facilitated by extracellular enzymes which break down the larger complex molecules into smaller simpler compounds. The second slower denitrification rate is limited by the rate of hydrolysis rather than the rate of metabolism (Wentzel *et al.*, 1992 ; Henze *et al.*, 1994).

Once the slowly biodegradable COD of the wastewater has been exhausted the bacteria will utilize endogenous respiration products. The latter occurs when the organic carbon substrate concentration is low. Consequently, the bacterial cells die and through lysis release cell material, which consists of unbiodegradable and biodegradable components. The biodegradable fraction is first adsorbed and hydrolyzed, before being utilized by the bacteria (Randall *et al.*, 1992 ; Wentzel *et al.*, 1992). These observations have led to greater interest in the characteristics of wastewaters and the methods employed to characterize them.

### ***Wastewater characteristics***

Organic matter in municipal wastewater has a very complex composition. Acetate may account for 2 to 10 % of the COD and all the other organic compounds occur in concentrations that are small. As a totality however, these compounds are important for overall reaction rates and removal capacities (Henze *et al.*, 1994 ; Henze *et al.*, 1995). Optimal and efficient use of municipal wastewaters as organic carbon sources in biological nutrient removal (BNR) systems requires a knowledge of the biodegradability of wastewater. This has led to a need to separate and to define wastewater fractions for the purposes of studying, understanding and optimizing organic carbon utilization in biological processes.

Wastewater can be characterized by physical and chemical methods into its soluble and particulate fraction. However, the division of wastewater into soluble and particulate components does not provide sufficient information to base process simulations on for biological processes, as the observed biokinetic responses are linked to the biodegradability of the substrate present (Ekama *et al.*, 1979; Isaacs and Henze, 1995; Skrinde and Bhagat, 1982; McCarty *et al.*, 1969). The influent wastewater has been classed biologically as biodegradable, unbiodegradable, and active biomass (as COD) by the IAWQ Task Group on modelling of activated sludge processes (Wentzel *et al.*, 1995; Henze *et al.*, 1995). The biodegradable fraction is divided into the readily biodegradable (RBCOD) and slowly biodegradable (SBCOD) fractions. The readily biodegradable COD fraction is further sub-divided into an acetate fraction and fermentable COD fraction. In addition, there have been suggestions that the SBCOD be divided into the rapidly hydrolyzable (RHCOD) and slowly hydrolyzable fractions (Orhon *et al.*, 1997). The division of the RBCOD and SBCOD are made entirely on the biokinetic response of bacteria to fractions of different biodegradability in the wastewater.

Since physico-chemical methods are more rapid and easier to conduct, several studies have been done with the objective of finding a physical and/or chemical method which is comparable to the biokinetic response of activated sludge to the RBCOD and SBCOD fractions (Wentzel *et al.*, 1995; Torrijos *et al.*,

1994; Bortone *et al.*, 1994; Mamais *et al.*, 1993). Different chemical and physical separation methods affect the size distribution of organics in a given wastewater. Therefore, care must be taken in choosing a fractionation method (Henze and Harremoes, 1990; Mamais *et al.*, 1993; Pouet and Grasmick, 1994). Dold *et al.* (1986) found that membranes with a molecular weight threshold of < 10 000 daltons gave RBCOD values comparable to that derived from biological methods. However, Bortone *et al.* (1994) showed that this comparability did not apply to industrial wastewater. Mamais *et al.* (1993) showed that the application of a coagulation method combined with filtration gave comparable results to biologically determined RBCOD fractions if the readily biodegradable fraction is considered to consist of a truly soluble fraction and a truly soluble inert fraction. However, this approach does not consider the possibility of soluble readily hydrolyzable COD (RHCOD) *i.e.* this method does not distinguish between the state of biodegradability (readily biodegradable or rapidly hydrolyzable) (Orhon and Østergaard, 1997).

To date several biological methods such as oxygen utilization rate (OUR) and nitrate-N utilization rate (NUR) (continuous and batch) tests have been employed successfully to determine the readily biodegradable fractions. Although the potential of the NUR method is recognized, the use of the method in studies has been largely neglected since it is more time-consuming and tedious than the OUR method. The NUR test is also often referred to as the anoxic batch test and is similar to that of the aerobic batch test (oxygen utilization rate-OUR) method. In the anoxic batch test, the nitrate concentration will initially decrease at a constant rapid rate reflecting the utilization of the readily biodegradable fraction (RBCOD) from the wastewater. This initial rapid rate is analogous to the initial high OUR in aerobic batch systems. The decrease in nitrate is linear when the substrate is in excess. Once the RBCOD from the influent is depleted, the denitrification rate is reduced to the rate of utilization of RBCOD generated by hydrolysis of complex molecules and particulate material. This second rate is analogous to the second OUR plateau in the aerobic batch test.

One of the major points of contention of the NUR method is the choice of yield coefficient,  $Y_H$  (mg COD / mg biomass as COD). Currently, the aerobic yield coefficient of 0.63 (mgO<sub>2</sub>/mgO<sub>2</sub>) is also used for anoxic conditions. However, recent work by Sozen *et al.* (1998), Sperandio *et al.* (1997) and Østergaard *et al.* (1998) have highlighted the need to use a lower yield coefficient for anoxic reactions. An anoxic yield coefficient of 0.5 (mgO<sub>2</sub>/mgO<sub>2</sub>) has been cited for acetate while a range of values from 0.5 to 0.61 (mgO<sub>2</sub>/mgO<sub>2</sub>) have been cited for domestic wastewater. Another factor which influences the biological characterization of wastewater by the NUR method is the presence of polyphosphate accumulating (Poly-P / bio-P) bacteria. The role of these organisms in enhanced biologically phosphorus removal (EBPR) systems has been well discussed (Wentzel *et al.*, 1992 ; Mino *et al.*, 1998). These organisms are known to take up volatile fatty acids (VFA's) for polyhydroxyalkanoates (PHA) synthesis with simultaneous phosphorus release (Hascoet and Florentz, 1985; Mostert *et al.*, 1988; Gerber *et al.*, 1986 and Wentzel *et al.*, 1992). Anoxic polyphosphate accumulating organism activity is an important factor to consider when characterizing the wastewater according to the NUR method. This aspect will be discussed further in Chapter 2, section 2.4.4.3.

Finally, the treatment of wastewater has evolved significantly from simple systems removing carbon to more complex systems for carbon and biological nutrient removal. The inclusion of more biological processes for wastewater treatment have increased the complexity of current wastewater treatment systems which has subsequently led to the development of more complex mathematical models. The accurate simulation of these processes requires accurate input data. Thus, the knowledge of the wastewater characteristics is an important step towards the successful modelling, design and operation of present and future plants.

## ***1.2 . OBJECTIVES***

The primary aims of this project were as follows :

- Study the protocol of NUR batch tests and apply it to a range of wastewaters and sludges with the aim to : (1) assess, (2) understand, and (3) make recommendations which could improve the procedure and make it easily applicable on-site.
- Characterize a variety of municipal wastewaters by the :
  - ◆ *nitrate-N utilization rate test - biological respirometry*
  - ◆ *physico-chemical methods*
- Study the utilization of an experimental readily biodegradable COD substrate, acetate, under anoxic conditions.
- Perform exploratory investigations to :
  - ◆ *Clarify the impact of EBPR sludges on wastewater characterization*
  - ◆ *Determine the influence of storage on wastewater characteristics*
  - ◆ *Assess the influence of sludge acclimatization on the accuracy of the NUR tests*

## ***1.3 . THESIS OUTLINE***

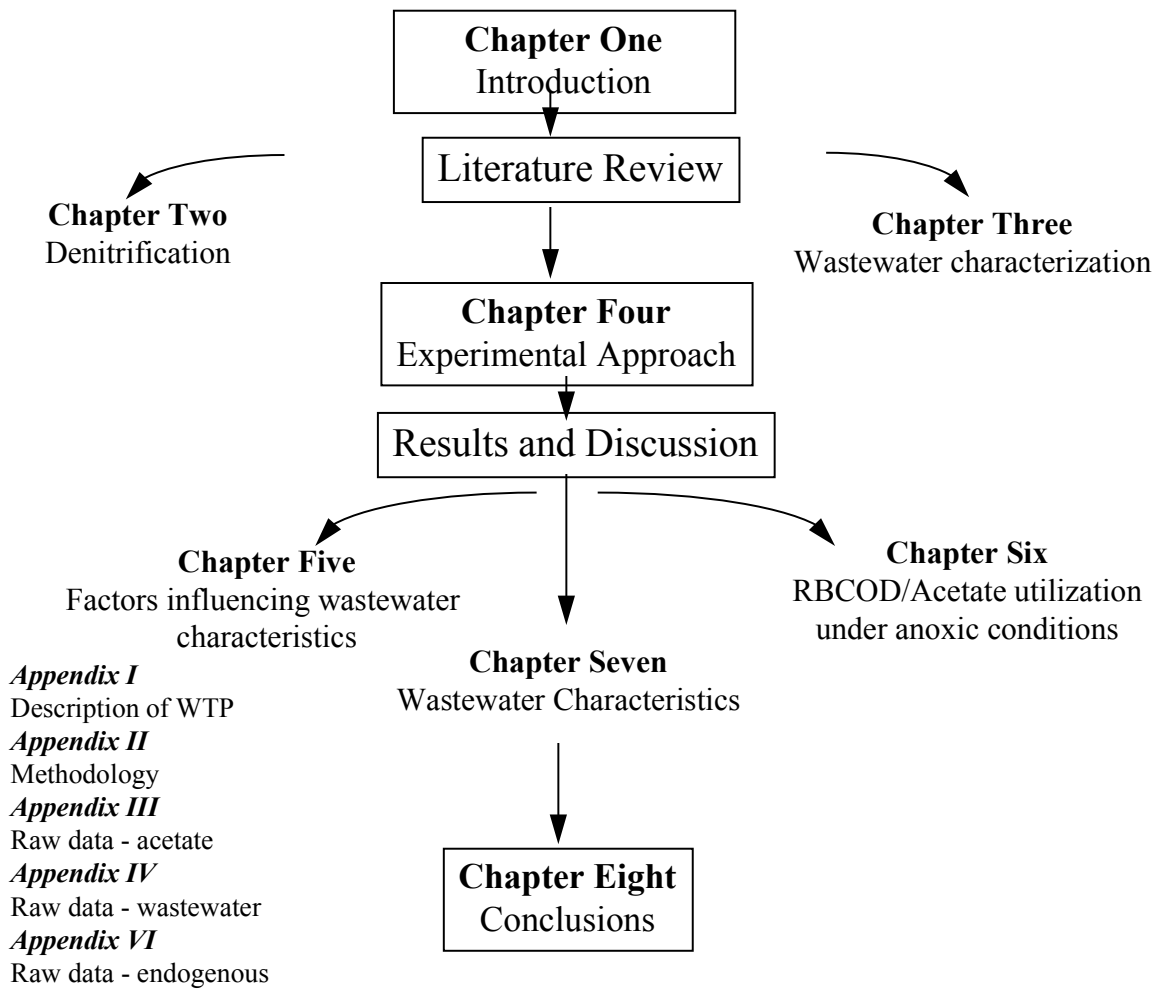
This thesis entitled *Municipal Wastewater Characterization : Application of denitrification batch tests* is divided into 9 chapters. A schematic representation is provided in Figure 1-5.

**Chapter 1** gives a brief introduction to the field of wastewater treatment, its importance and history, followed by brief summary of denitrification, wastewater characterization and the method that was applied to characterize the wastewaters sampled for this study. The major objectives of this study have also been outlined.

*Chapter 2* and *Chapter 3* focuses on the literature of wastewater characterization and denitrification. *Chapter 2* reviews the biological process of denitrification. The review endeavours to understand the mechanisms, the process and some of the factors which may influence the organisms capable of denitrification. *Chapter 3* deals largely with wastewater characteristics and the divisions as well as the methods which may be used to determine the wastewater fractions. Since the objective of this project was to use the NUR method to study the biological fractions, a more comprehensive review of the NUR method is provided.

The experimental approach and methodology are discussed in *Chapter 4*. This chapter can loosely be divided into two sections. The first one deals with the material and methods and describes the analytical, technical and experimental conditions used in these studies. The second section deals with the NUR protocol, assessing the method and the changes made to the original method outlined by Ekama *et al.* (1986).

The results from the NUR tests are presented and discussed in *Chapter 5*, *Chapter 6*, and *Chapter 7*. *Chapter 5* deals with secondary experiments that were done to investigate the influence of several factors on wastewater characteristics using the NUR method. These include storage time, the use of unacclimatized sludges for characterization tests and the range of the annual and weekly variations in wastewater characteristics. *Chapter 6* deals with the RBCOD component of wastewater. The first part of this chapter investigates the utilization of an experimental substrate, acetate, under anoxic conditions, while the second part of this chapter investigates the inaccuracy of the NUR method for determining the RBCOD fraction when using enhanced biological phosphorus removal (EBPR) sludge. *Chapter 7* presents and discusses the results and trends in the wastewater characteristics of numerous different wastewater treatment plants. The trends and correlations of the maximum, second and third specific denitrification rates ( $k$ ) are also discussed. The conclusions and recommendations are discussed in *Chapter 8*.



*Figure 1-5: Schematic representation of thesis outline.*



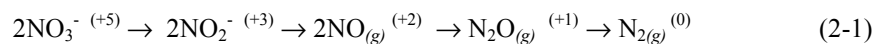
# Chapter Two

## ***A REVIEW OF DENITRIFICATION PROCESSES***

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This chapter deals with the process of denitrification (also referred to as anoxic respiration). It contains a generalized description of denitrification and the biochemical reactions involved when nitrate or nitrites act as the final electron acceptor. Since this project investigates the utilization of organic carbon under anoxic conditions, it will concentrate mainly on the heterotrophic denitrifying biomass found in activated sludge systems of wastewater treatment plants.

Denitrification is just one pathway in the nitrogen cycle. It is a biochemical reaction (equation 2-1) effected by microorganisms which transform nitrates/nitrites to the gaseous form, nitrogen. This reaction couples the transport of electrons by the respiratory chain to energy production via oxidative phosphorylation (Knowles, 1972 ; Payne, 1981).



where : (#) the values in the brackets refer to the oxidation states of the nitrogen atom for each nitrogenous compound.

(g) denotes gaseous species.

### ***2.1 MICROBIOLOGY***

Heterotrophs obtain their energy and carbon requirements from the transformation or breakdown of organic carbon substrates. This is termed metabolism which can be divided into anabolism and catabolism. The former is the enzymatic biosynthesis of complex cellular materials of the organism. Catabolism is the enzymatic degradation of complex organic molecules to smaller ones. The organic

molecules serve as electron donors and the electrons removed are transferred through a sequence of processes to the terminal electron acceptor. During this process chemical energy is released in the form of the energy rich molecule called adenosine triphosphate (ATP). This chemical energy is used by the organism for the growth part of metabolism (*i.e.* synthesis of new cell material, anabolism) and maintenance of, for example, cellular functions (*i.e.* catabolism). Catabolism includes both respiration (aerobic and anoxic) and fermentation. This review will concentrate largely on anoxic respiration (denitrifying) processes.

Although the population dynamics within wastewater may vary, the majority of bacteria are capable of respiratory nitrate reduction. The majority of the bacteria in raw sewage are facultative anaerobes and are gram negative rods (Randall *et al.*, 1992 ; Payne, 1981) (Table 2-1). Some of the bacterial genera that are capable of denitrification include *Achromobacter*, *Aerobacter*, *Bacillus*, *Flavobacterium*, *Micrococcus*, and *Proteus* (Christensen and Harremoes, 1977). Heterotrophic micro-organisms are capable of using a wide range of organic carbon compounds. Certain flavobacteria use only simple carbohydrates, while *Bacillus* and *Pseudomonas* species are capable of using a wide range of compounds such as methanol, organic acids, alcohols and aromatic compounds. *Moraxella* use only aromatic compounds as an organic carbon source (Payne, 1981). The nutrient requirements for denitrifying bacteria corresponds to those of aerobic heterotrophic micro-organisms. In municipal wastewater there are usually sufficient nutrients. However, treatment plants receiving high loads of industrial waste may find phosphorus to be limiting (Henze *et. al.*, 1997).

The denitrifiers can be subdivided into those organisms that are capable of the complete dissimilatory nitrate reduction process (*i.e.* nitrate to nitrogen gas) and those microorganisms that can carry out one or more of the reaction steps (*i.e.* nitrate to nitrite or nitrite to nitrous oxide) (Henze, 1992). For example, some *Bacillus* species are capable of nitrate and nitric oxide reduction but are unable to reduce nitrites or nitrous oxide, while some species of *Pseudomonas* have been shown to accumulate nitrous oxide as a terminal product instead of dinitrogen and initiate denitrification with nitrites rather than nitrate (Payne, 1981 ; Randall *et al.*, 1992). These microorganisms are termed partial denitrifiers. Those microorganisms that are only able to reduce nitrates to nitrites are termed nitrate reducers. Thus, within the heterotrophic biomass in activated sludge system there are different fractions of these microorganisms present (Table 2-1). This may explain the accumulation of the intermediate nitrite in some instances since if a bacteria *e.g.* *Comamonas testosteroni* is only able to reduce nitrates then nitrites will accumulate. It was also shown that some species that are capable of both nitrate and nitrite reduction still accumulate nitrites since the nitrate reduction rate is faster than the nitrite reduction rate (Betlach and Tiedje, 1981).

**Table 2-1: Some examples of facultative anaerobic bacteria capable of complete and partial denitrification, and nitrate reduction (Fass, 1994).**

Microorganism	Gram stain	Characteristics
<i>Agrobacterium radiobacter</i>	negative	Reduction of NO <sub>3</sub> <sup>-</sup> and NO <sub>2</sub> <sup>-</sup> to N <sub>2</sub>
<i>Agrobacterium tumefaciens</i>	negative	Reduction of NO <sub>3</sub> <sup>-</sup> and NO <sub>2</sub> <sup>-</sup> to N <sub>2</sub>
<i>Comamonas testoteroni</i>	negative	Reduction of NO <sub>3</sub> <sup>-</sup> to NO <sub>2</sub> <sup>-</sup> only
<i>Alcaligenes faecalis</i>	negative	Uses NO <sub>2</sub> <sup>-</sup> only and not NO <sub>3</sub> <sup>-</sup>
<i>Cytophage johnsonae</i>	negative	Uses NO <sub>2</sub> <sup>-</sup> only and not NO <sub>3</sub> <sup>-</sup>
<i>Aquaspirillum itersonii</i>	negative	Denitrification stops at N <sub>2</sub> O
<i>Chromobacterium violaceum</i>	negative	Denitrification stops at N <sub>2</sub> O
<i>Roseobacter denitrificans</i>	negative	Denitrification stops at N <sub>2</sub> O
<i>Pseudomonas fluorescens</i>	negative	Denitrification stops at N <sub>2</sub> O

## 2.2 BIOCHEMISTRY

Aerobic and anoxic respiration by heterotrophic bacteria involves the oxidation of organic substrates like carbohydrates, proteins and lipids to end products CO<sub>2</sub> and H<sub>2</sub>O. By the process of respiration the bacteria are able to produce energy. Energy becomes available to the micro-organism through a series of internally mediated oxidation-reduction reactions. This involves electron and proton transfers from an organic substrate through a number of intermediate enzyme complexes to the final electron acceptor (nitrates in this study). Two types of molecules, energy transport molecules and electron and proton transport molecules, are coupled to redox reactions to produce energy. The energy transport molecules of interest are adenosine triphosphate (ATP) and guanosine triphosphate (GTP) while the electron and proton transport molecules include nicotinamide adenine dinucleotide (NADH<sub>2</sub>) and flavin adenine dinucleotide (FADH<sub>2</sub>) (Lehninger, 1975 ; Casey *et al.*, 1993)

Respiratory metabolism can be divided into 4 stages (Figure 2-1):

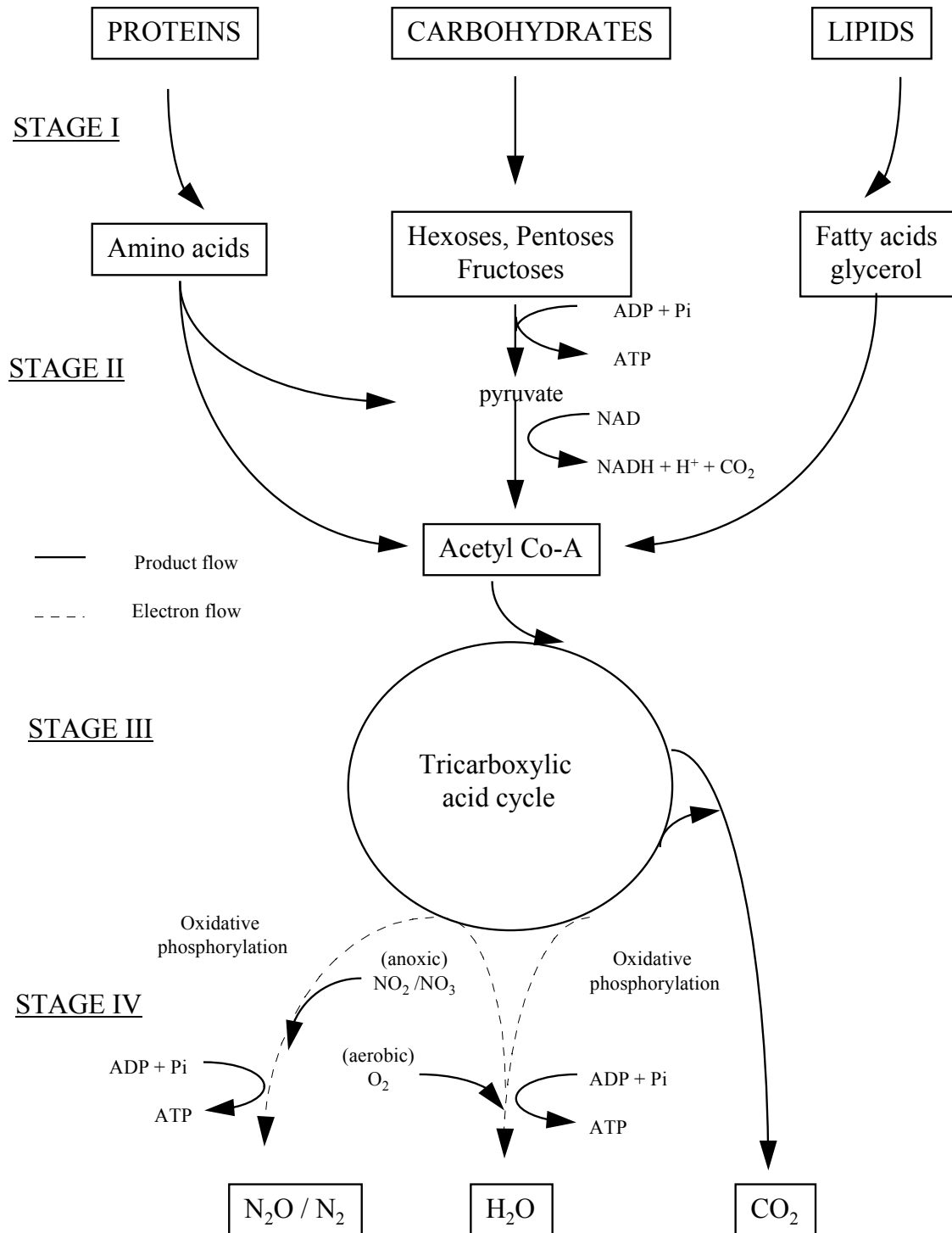
### 2.2.1 Stages in anoxic respiration

During the first stage complex organic molecules are hydrolyzed to simpler ones. Carbohydrates are degraded to sugars, proteins to amino acids, and lipids to fatty acids (Figure 2-1). In stage 2, the end products of stage 1 are degraded further to form acetyl-Coenzyme A (acetyl Co-A) and carbon dioxide. This step involves different biochemical pathways. For example, amino acid breakdown can result in the formation of Acetyl Co-A either with or without pyruvate formation. Some amino acids are not converted to acetyl Co-A but enter the third stage *i.e.* the tricarboxylic acid (TCA) cycle directly. Carbohydrate degradation can occur via a number of different pathways. The most common of which is the Embden-Meyerhof pathway which can be divided into 2 stages. The first stage (activation stage) involves the phosphorylation of simple sugars to glyceraldehyde-3-phosphate at the expense of ATP. In the second

stage glyceraldehyde-3-phosphate is converted to pyruvate via a series of dehydrogenations. NADH and ATP are formed via substrate phosphorylation during this stage (Lehninger, 1975 and Casey *et al.*, 1993).

Long chain fatty acids are hydrolyzed by  $\beta$ -oxidation to VFA's which are further degraded to acetyl Co-A, NADH, and FADH<sub>2</sub> at the expense of ATP (Figure 2-2). Acetate passes through the cell membrane via active transport. Once in the cell, acetate enters into the TCA cycle as acetyl Co-A. Propionate, butyrate and valerate undergo several reactions before forming acetyl Co-A. During the transformation of propionate to acetyl Co-A several intermediates such as succinate, fumarate, malate and pyruvate are formed. Butyrate is transformed to 2 moles of acetyl Co-A by  $\beta$ -oxidation while valerate is transformed to acetyl Co-A and propionyl Co-A. The latter product is further degraded via the same mechanism described for propionate (Fass, 1994).

Acetyl Co-A which is the final end-product of stage 2 enters the tri-carboxylic (TCA) cycle where acetyl Co-A is oxidized to form 2 molecules of CO<sub>2</sub>, eight protons, 4 pairs of electrons and 1 guanine tri-phosphate (GTP) (Figure 2-3). In the final stage (stage 4) the electrons and protons produced in stages 2 and 3 pass via electron and proton carrier enzymes to a final electron acceptor (*i.e.* NO<sub>3</sub><sup>-</sup> in anoxic respiration). During this process adenosine tri-phosphate (ATP) is formed via oxidative phosphorylation. The complexes of the electron transport pathway are arranged within the membrane (Figure 2-4) (Lehninger, 1975 and Casey *et al.*, 1993).



*Figure 2-1: Illustration of anoxic respiratory stages showing the substrate degradation and metabolic pathways (Casey et al., 1993, adapted from Lehninger, 1975).*

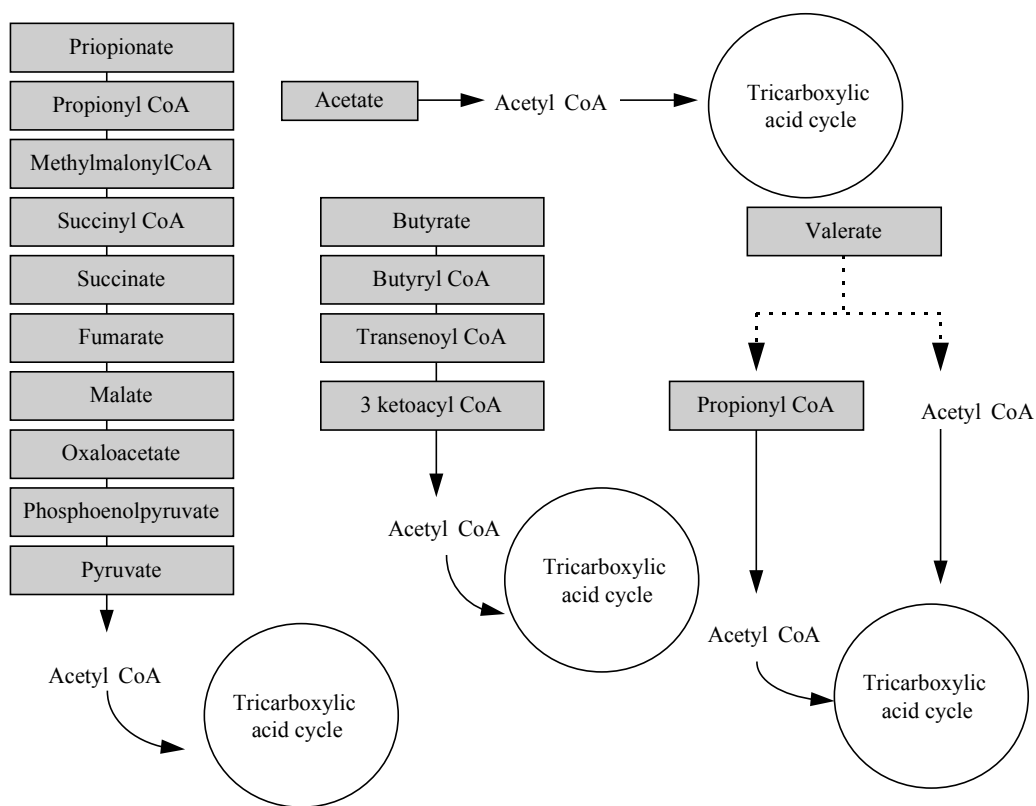


Figure 2-2: Metabolic pathways for the degradation of volatile fatty acids, acetate, propionate, butyrate and valerate to acetyl Co-A (from Fass, 1994).

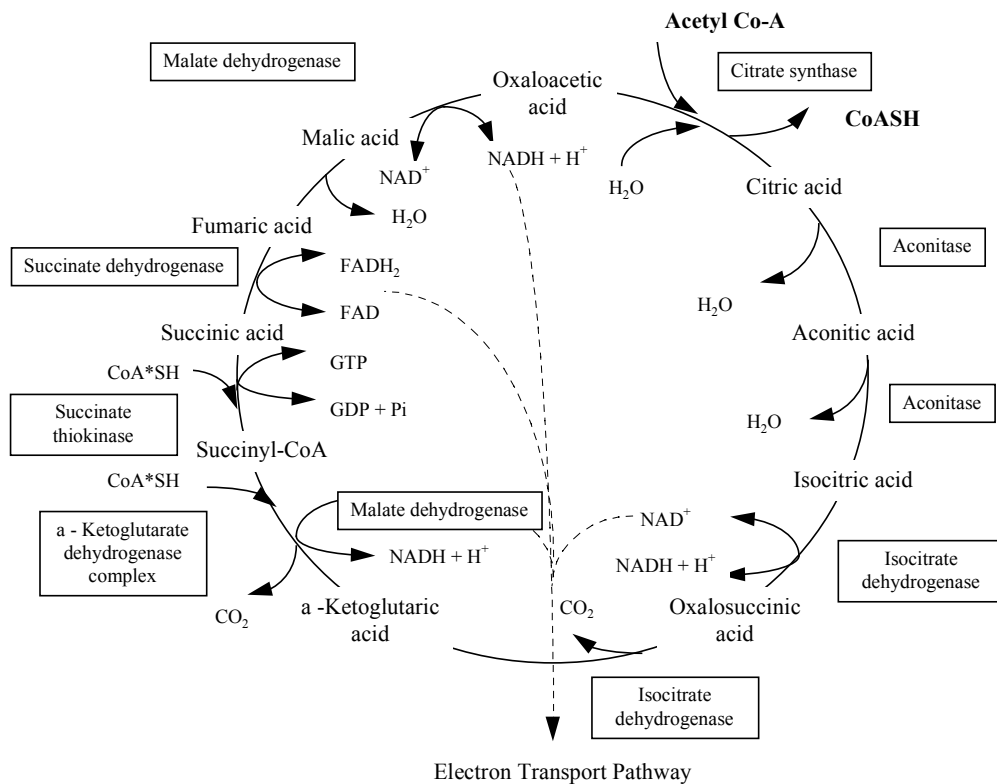
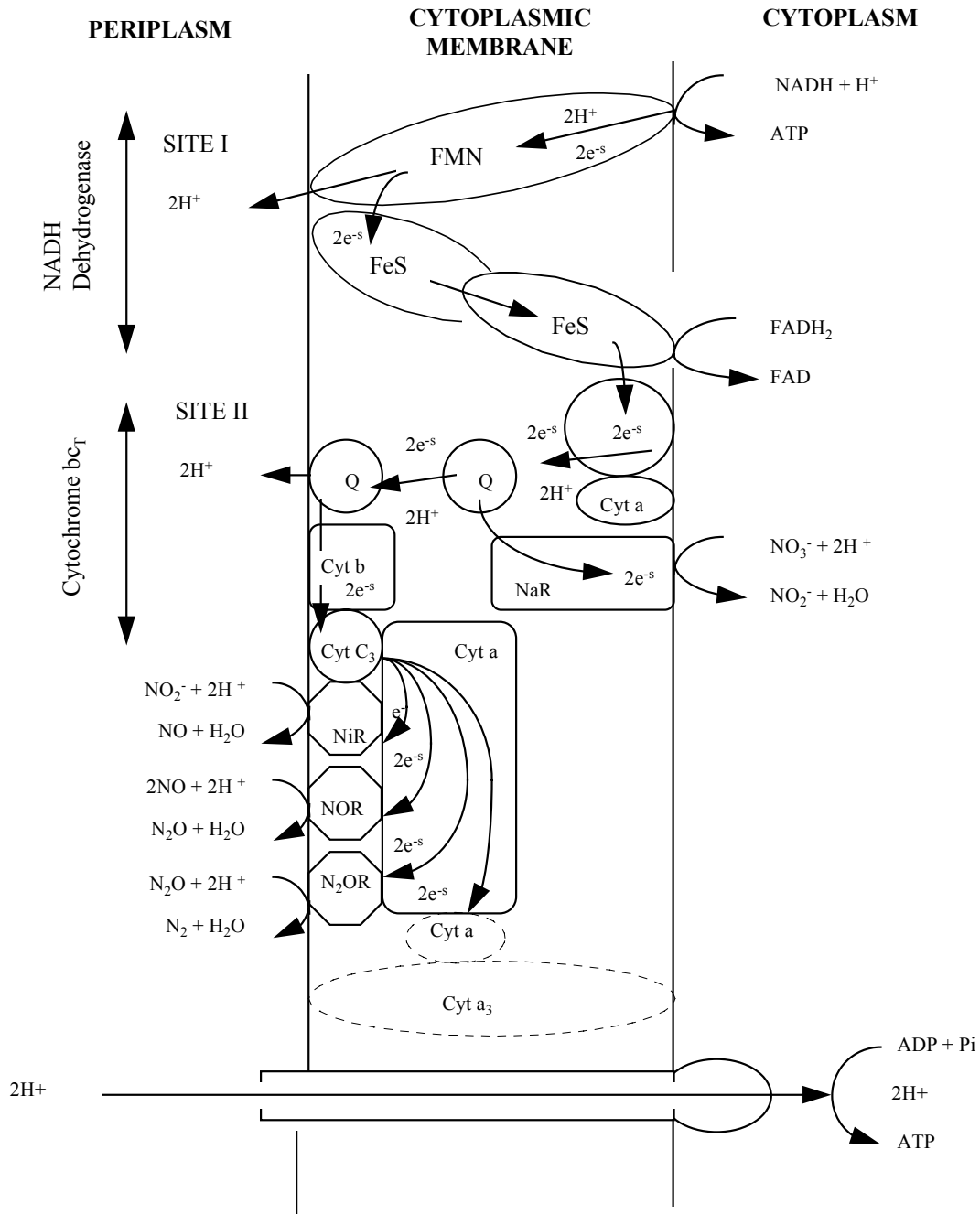


Figure 2-3: The tricarboxylic acid (TCA) cycle (from Casey et al., 1993).



**Figure 2-4: The electron transport pathway (ETP) for anoxic micro-organisms ( key : NaR - nitrate reductase; N<sub>2</sub>OR - nitrous oxide reductase; NiR - nitrite reductase; NoR - nitric oxide reductase; ADP - adenosine diphosphate; ATP - adenosine triphosphate; NAD - nicotinamide dehydrogenase; NADH - nicotinamide dehydrogenase reduced; cyt - cytochrome complexes; FMN - ; FeS - iron sulphur complex ; Q - quinone) (from Casey et al., 1993).**

## 2.2.2 Enzymes involved in denitrification

Denitrification is catalyzed by 4 enzymes which reduce nitrates to dinitrogen. Table 2-2 lists the main characteristics of the 4 reductase enzymes discussed below (Hochstein and Tomlinson, 1988 ; Casey *et al.*, 1993, and Fass, 1994).

### 2.2.2.1 Nitrate reductases

Nitrate reductases catalyze the reduction of nitrates to nitrites and couple this reduction to the translocation of protons. The nitrate reductase associated with denitrification and respiration are, with one exception, membrane bound enzymes. In the case of *Staphylococcus aureus* the enzymes appear to be bound to the cytoplasmic membrane. These enzymes contain molybdenum, heme and non-heme iron and labile sulphur (Alefounder and Ferguson, 1980; Hochstein and Tomlinson, 1988; and Fass, 1994). Nitrate reductases consists of the subunits,  $\alpha$  and  $\beta$ , but sometimes a third subunit,  $\gamma$  is observed containing a b-type cytochrome. The  $\alpha$  subunit has a molecular mass ranging between 104 and 150 kd and is involved in catalysis. The  $\beta$  subunit has a molecular weight of 52 to 63 kd and is thought to be involved in membrane attachment. The  $\gamma$  subunit is the smallest subunit, 19 to 20 kd and links the nitrate reductase to electron transport chain at the level of ubiquinone. The synthesis of these enzymes is repressed by oxygen. Furthermore, these enzymes are inhibited by azide (competitive inhibition) as well as thiocyanate and toluene-3,4-dithiol, reagents that chelate molybdenum and cyanide (Hochstein and Tomlinson, 1988; and Casey *et al.*, 1993).

Due to the location of this enzyme (*i.e.* inside the cytoplasmic membrane) nitrate has to be translocated across the membrane. Several mechanisms have been suggested. In *Paracoccus denitrificans* nitrate uptake is thought to occur by facilitated diffusion. Two other nitrate uptake systems have been proposed : one operates in symport with protons ; while the other operates as a  $\text{NO}_3^- / \text{NO}_2^-$  antiport (Figure 2-5). The former initiates nitrate uptake in the absence of nitrite when the antiporter system is inoperative while the latter serves to maintain a low intracellular concentration of nitrite. In addition, the antiporter system provides a mechanism for export of nitrite to the location of the nitrite reductase which appears to be a periplasmic enzyme in *Paracoccus denitrificans*. It has also been suggested that the nitrate reductase complex forms a nitrate-specific channel which provides access to the active site of nitrate reductase (Boogerd *et al.*, 1983 ; Hochstein and Tomlinson, 1988; and Casey *et al.*, 1993).

### 2.2.2.2 Nitrite reductase

Nitrite reductase reduces nitrite which originates from the bulk solution or from the reduction of nitrate to nitric oxide. The reduction of nitrite on the periplasmic side of the cytoplasmic membrane necessitates the transport of nitrite from the cytoplasm where it is formed, to the periplasm where it is reduced. This transport occurs as part of the  $\text{NO}_3^- / \text{NO}_2^-$  antiport mechanism described for the translocation of nitrate across the cytoplasmic membrane. Nitrite reduction is carried out by 2 distinct reductases, each present in



different denitrifiers (Alefounder and Ferguson, 1982; Boogerd et al., 1981; and Hochstein and Tomlinson, 1988):

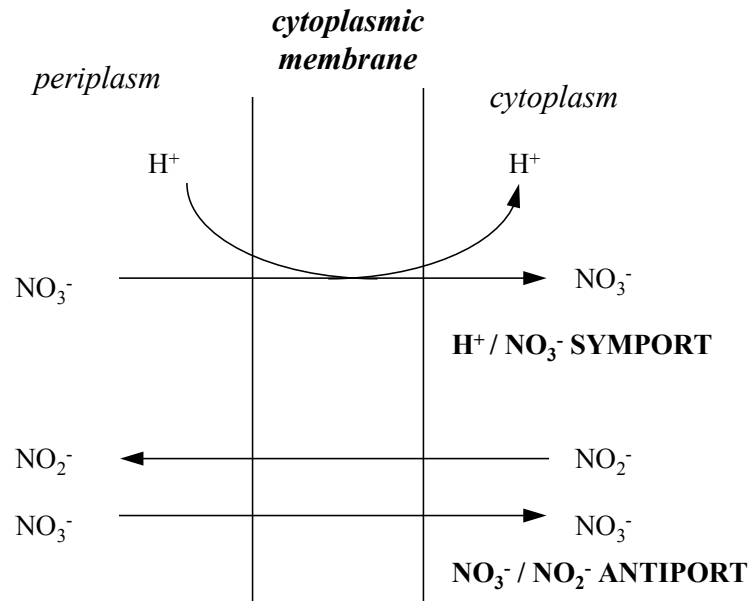
- One is a metalloprotein containing copper (the copper nitrite reductase). This enzyme is about 70 to 150 kd and has 2 types of copper containing proteins. Type I copper proteins are involved in electron transfer reactions and are not catalysts while Type II copper proteins occurs as a periplasmic enzyme and is thought to act as an electron acceptor (Hochstein and Tomlinson, 1988).
- The second is a heme protein that contains c- and d- type cytochromes (the  $cd_1$  cytochrome nitrite reductase). These enzymes are composed of 2 identical subunits each containing a c- and d- type cytochrome (90 to 140 kd). The location of the enzyme is debatable with some species revealing a cytoplasmically associated enzyme while for others the enzyme is reported in the cytoplasmic fraction, periplasmic space, the periplasmic aspect of the cytoplasmic membrane or the cytoplasmic aspect of the cytoplasmic membrane. The nature of the reducing system and the cellular location of the enzyme appears to determine the end products of the  $cd_1$ -cytochrome nitrite reductase activity ((Hochstein and Tomlinson, 1988; and Casey *et al.*, 1993).

### ***2.2.2.3 Nitric Oxide reductase***

The function of nitric oxide reductase is to reduce nitric oxide (NO) to nitrous oxide (N<sub>2</sub>O). However, this is the least characterized of the enzymatic steps of denitrification since nitric oxide is rarely detected during denitrification. Although this enzyme is said to occur on the periplasmic side of the membrane, there are varying opinions. The transfer of electrons from nitric oxide reductase occurs via the reactive centre of the reductase, a bc-type heme. The formation of nitrous oxide results in the formation of a dinitrogen bond which is necessary for the final step *i.e.* the production of N<sub>2</sub>. The molecular weight of this enzyme is less than 55 kd (Stouthamer, 1988; and Casey *et al.*, 1993).

### ***2.2.2.4 Nitrous Oxide reductase***

This enzyme reduces nitrous oxide (N<sub>2</sub>O) to dinitrogen (N<sub>2</sub>) which is released from the cell. This enzyme is associated with the periplasmic side of the membrane and is a soluble copper containing enzyme which is considered to be between 80 and 145 kd (Boogerd *et al.*, 1981, Casey *et al.*, 1993; and Fass, 1994).



*Figure 2-5: Mechanism of nitrate transport systems across the cytoplasmic membrane (Casey et al., 1993, redrawn from Stouthamer, 1988).*

*Table 2-2: Important characteristics of the four reductase enzymes involved in transforming nitrates to nitrogen gas (Fass, 1994).*

Enzyme	Nitrate reductase	Nitrite reductase	Nitric reductase	Nitrous reductase
Reaction	$\text{NO}_3^- \rightarrow \text{NO}_2^-$	$\text{NO}_2^- \rightarrow \text{NO}$	$\text{NO} \rightarrow 0.5\text{N}_2\text{O}$	$0.5\text{N}_2\text{O} \rightarrow 0.5\text{N}_2$
e <sup>-s</sup> transferred	2	1	1	1
Location	cytoplasm	periplasm	periplasm	periplasm
Composition	Mo, Fe, S	protein + Cu heme protein + cyt c-d	Cytochrome b+c	Soluble + Cu
Molecular Mass (kd)	100 to 200	70 to 150 90 to 140	< 55	80 to 145

(Mo - molybdenum ; Fe - iron ; S - sulphur ; Cu - copper ; e<sup>-s</sup> - electrons ; kd - kilodaltons)

### 2.3 STOICHIOMETRY

Balanced stoichiometric equations are important to describe the material inputs as well as outputs in a biological system. As discussed earlier, all bacterial mediated reactions consist of a synthesis (anabolism) and an energy (catabolism) component. These reactions are oxidation-reduction reactions and thus, involve the transfer of electrons. They involve an electron donor and an electron acceptor. With heterotrophic micro-organisms the electron donor for the synthesis reaction is the same as the electron donor for the energy reaction (McCarty, 1969). Table 2-3 shows some of the stoichiometric equations derived for denitrification reactions with wastewater, propionate and acetate as organic carbon substrates.

These equations allow for the calculation of the average state of oxidation of carbon for each substrate with the theoretical production of biomass. It also allows for the calculation of the C/N stoichiometric ratio (*i.e.* carbon required to reduce all nitrates to nitrogen). However, these theoretical equations do not take into account the experimental conditions such as pH, temperature and bacterial species.

**Table 2-3 : Example of stoichiometric equations for denitrification (from McCarty, 1969).**

Substrates	Stoichiometric equations
Acetate	$\text{CH}_3\text{COO}^- + 1.01 \text{NO}_3^- + 1.01 \text{H}^+ \rightarrow 0.13 \text{C}_5\text{H}_7\text{O}_2\text{N} + 0.36 \text{CO}_2 + \text{HCO}_3^- + 1.06 \text{H}_2\text{O} + 0.44 \text{N}_2$
Propionate	$\text{CH}_3 \text{CH}_2\text{COO}^- + 1.77 \text{NO}_3^- + 1.77 \text{H}^+ \rightarrow 0.22 \text{C}_5\text{H}_7\text{O}_2\text{N} + 0.82 \text{CO}_2 + \text{HCO}_3^- + 2.1 \text{H}_2\text{O} + 0.77 \text{N}_2$
Wastewater	$\text{C}_{10}\text{H}_{19}\text{O}_3\text{N} + 6.05 \text{NO}_3^- + 6.05 \text{H}^+ \rightarrow 0.85 \text{C}_5\text{H}_7\text{O}_2\text{N} + \text{NH}_4^+ + 4.71 \text{CO}_2 + \text{HCO}_3^- + 7.03 \text{H}_2\text{O} + 2.6 \text{N}_2$

( $\text{C}_5\text{H}_7\text{O}_2\text{N}$  is the molecular formula for biomass ;  $\text{C}_{10}\text{H}_{19}\text{O}_3\text{N}$  is the molecular formula for wastewater)

## 2.4 FACTORS INFLUENCING DENITRIFICATION

This section deals with four factors that influence heterotrophic denitrification. These include oxygen, temperature, pH and organic carbon availability and type.

### 2.4.1 Oxygen

The presence of dissolved oxygen (DO) acts as a strong inhibitor on denitrification as it prevents the expression of the necessary enzymes for the electron transfer (Van Haandel *et al.*, 1981; Karnaros and Lyberatos, 1998). It was shown for *Pseudomonas denitrificans* that nitrate reduction was the least sensitive while the reduction of  $\text{N}_2\text{O}$  and / or  $\text{NO}$  was almost completely inhibited by dissolved oxygen (Karnaros and Lyberatos, 1998). The inhibition is reversible once the oxygen concentration decreases (Fass, 1994). Skrinde *et al.* (1982) obtained high nitrogen removal using sewage sludge as carbon source in a controlled environment operating at dissolved oxygen concentrations below 0.2 mg/l. It has also been observed that denitrification is possible at DO concentrations as high as 6 mg/l. However, studies have shown that an increase in DO from 0.2 to 2.0 mg/l results in a decrease in denitrification rates from 50 to 10 % of the anoxic values. Thus, although denitrification is possible in the presence of low concentrations of dissolved oxygen, it is not beneficial to the denitrification process. It is suggested that in suspended cultures the dissolved oxygen concentration should be below 0.5 mg/l to prevent the preferential utilization of dissolved oxygen as an electron acceptor. This difference in dissolved oxygen levels for denitrification could be due to varying techniques for measurement of DO, and by the fact that the measured bulk liquid dissolved oxygen concentration does not represent the actual DO concentration within the sludge floc. Most researchers agree, however, that if the micro-environment is anoxic then denitrification will proceed even if the bulk solution (*i.e.* the macro-environment) contains detectable dissolved oxygen concentrations (Abufayed, 1983 ; Randall *et al.*, 1992).

### 2.4.2 Temperature

The denitrification rate is a function of temperature and is described by a bell-shaped curve, *i.e.* the denitrification rate increases with an increase in temperature, reaches a maximum and then drops when the temperature is increased further. An Arrhenius type relationship between temperature and unit denitrification rate between 3°C (276 K) and 27°C (300 K) has been suggested (equation 2-3) (Abufayed, 1983) :

$$k = k_0 \cdot e^{-E/RT} \quad (2-3)$$

k = rate of denitrification, 1/time

k<sub>0</sub> = frequency factor

E = activation energy

R = ideal gas constant

T = absolute temperature (K)

Since reaction rate is usually evaluated at 20°C, Lewandowski (1982) and Metcalf and Eddy (1991) expressed the relationship between measured values and the reaction rate at 20°C with equation 2-4. The temperature coefficient,  $\theta$  varies from about 1.04 to 1.20 for activated sludge systems with domestic wastewater as a carbon source (Metcalf and Eddy, 1991). The denitrification process can also occur thermophilically at 50 to 60 °C. In this case the nitrate removal rate is approximately 50 % greater than at the mesophilic range of 35 °C (Henze *et al.*, 1997).

$$R_T = R_{20} \theta^{T-20} \quad (2-4)$$

R<sub>T</sub> = denitrification rate at temperature T

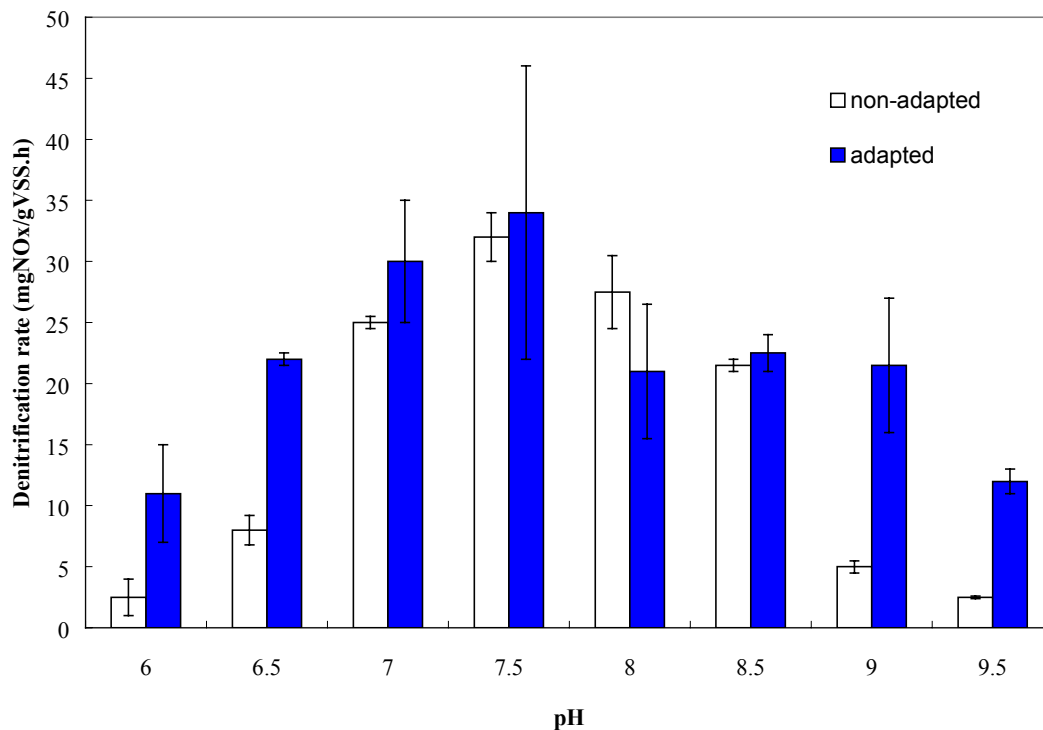
R<sub>20</sub> = denitrification rate at temperature 20°C

$\theta$  = temperature coefficient

### 2.4.3 pH

The same general dependency is exhibited by pH as was discussed for temperature *i.e.* bell shape. Various pH optima (7.0, 7.4, 7.5, 7.6) and pH ranges have been cited in the literature (Dodd and Bone, 1975 ; Christensen and Harremoës, 1977 ; Wang *et al.*, 1995 ; and Urbain *et al.*, 1997). Batch studies conducted by Dodd and Bone in 1975 at pH values of 7.0 ; 7.5 ; 8.0 and 8.5 showed that denitrification occurred

optimally at pH 7.5. They also reported that the activity of nitrite reductase diminishes quicker when the pH value rises above the optimum. Thus, at a pH of 8.5, nitrite was found to accumulate. A similar observation was made by Urbain *et al.* (1997). Wang *et al.* (1995) showed that cultures of *Ps. denitrificans*, grown at 30°C reduced nitrate optimally at a pH between 7.4 and 7.6 and nitrite at a pH between 7.2 and 7.3. A pH of 7.5 is generally used for denitrification studies since it has been shown that for a pH above 7.3, N<sub>2</sub> gas is the end product. At a pH below 7.3 nitrous oxide occurs as an end product while for a pH below 5.0 nitric oxide can account for approximately 20 % of the total gas produced (Christensen and Harremoes, 1977). Furthermore, Urbain *et al.* (1997) found that biomass adapted to non optimum pH's (*i.e.* 7 > pH > 8.5) gave better denitrification rates than the non-adapted biomass (Figure 2-6). These results showed that bacteria have the ability to adapt to a non-optimum pH with time. Table 2-4 shows the differing pH maximum obtained for various bacterial species. The differences in the optimum pH values and the pH ranges could be due to the difference in the cultures tested by the different researchers.



**Figure 2-6: Influence of pH on specific maximum denitrification rates for adapted and non-adapted biomass (Urbain *et al.*, 1997).**

**Table 2-4 : The pH optima for specific denitrifying bacteria (Fass, 1994).**

Bacterial species	Gram stain	pH optima
<i>Thiobacillus denitrificans</i>	negative	6.8 to 7.4
<i>Thiobacillus novellus</i>	negative	7.0
<i>Thiobacillus versutus</i>	negative	7.5 to 7.9
<i>Bradyrhizobium japonicum</i>	negative	6.0 to 7.0

During denitrification a pH increase is expected. However, the magnitude of the increase is dependent on the buffering capacity of the wastewater (Christensen and Harremoes, 1977). The control of pH is also important if complete denitrification is to occur. Therefore, optimization of the denitrification kinetics should require pH regulation between 7.0 and 9.0 (Figure 2-7) (Henze *et al.*, 1997).

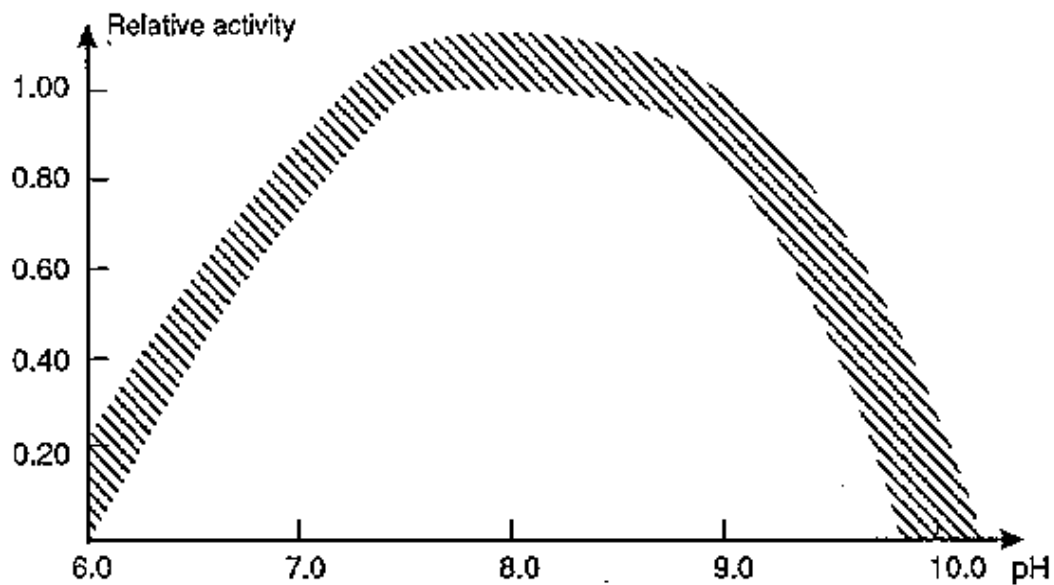


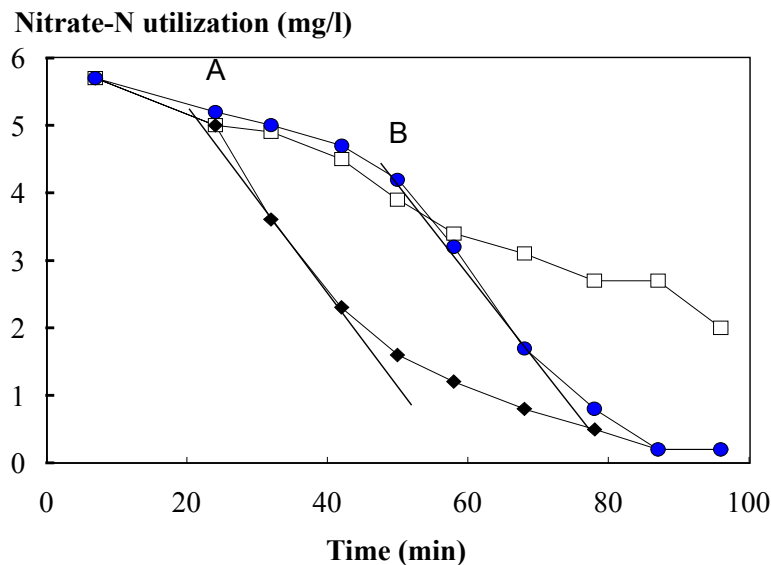
Figure 2-7 : Denitrification as a function of pH (Henze *et al.*, 1997).

#### 2.4.4 Organic carbon substrates

Several studies have highlighted that the biodegradability of substrates strongly influences denitrification rates (McCarty *et al.*, 1969 ; Monteith *et al.*, 1980 ; Isaacs and Henze, 1995 ; Henze and Harremoes, 1990). Studies on full-scale denitrification and phosphorus removal plants have shown that denitrification in a plug-flow primary anoxic reactor occurred in two linear phases, a rapid initial rate followed by a slower denitrification rate. Ekama *et al.* (1979) hypothesized that the two linear phases arose from the utilization of two different biodegradable COD fractions, a readily biodegradable and a slowly biodegradable COD fraction. The second slower denitrification rate appears to be limited by the hydrolysis rate rather than the rate of metabolism (Wentzel *et al.*, 1992). Henze *et al.* (1994) stated that the dominating rate limiting factor in nutrient removal processes is the organic carbon source. The rate of hydrolysis of higher molecular weight compounds to readily biodegradable compounds will limit the denitrification rate. The addition of readily biodegradable carbon to a carbon limited sludge will speed up the denitrification rate as seen in Figure 2-8. However, once the readily biodegradable carbon material

(hydrolyzate) is utilized the denitrification rate falls back to the rate limited by the rate of utilization of the endogenous respiration products.

As mentioned in Chapter 1, endogenous respiration occurs when the organic carbon substrate concentration is low. The bacterial cells die and lyse, releasing cell material which are subsequently adsorbed, hydrolyzed and utilized by the bacteria in the sludge floc (Randall *et al.*, 1992 ; Wentzel *et al.*, 1992). This type of energy source for denitrification in which cell death and lysis occurs was first proposed by Wuhrmann in 1964. The Wuhrmann process contained an aerobic reactor at the start of the process followed by an anoxic reactor (post denitrification). Thus, by the time the influent carbon source reached the anoxic zone all the readily biodegradable substrate had been exhausted. The remaining carbon source available to the anoxic reactor consisted of slowly biodegradable organic carbon. The rate of utilization of this substrate is dictated by the rate of hydrolysis of the slowly biologically biodegradable organic carbon substrate. Thus, the denitrification rates are relatively low (Van Haandel *et al.*, 1981).



**Figure 2-8:** Controlled addition of a readily biodegradable substrate (hydrolyzate) at points A and B in a carbon-limited batch denitrification system. (□) refers to the endogenous denitrification profile ; (◆) hydrolyzate addition at point A ; (●) hydrolyzate addition at point B. (from Isaacs and Henze, 1995).

It has been observed that the endogenous denitrification rate is dependent on the respiration rate of the bacteria using stored food reserves or substrate released from endogenous decay. It was also observed that variation in the endogenous denitrification rates could be related to the different respiration rates of the sludge which is a function of the system operating solids retention time. This was verified in studies which found that equivalent oxygen respiration utilization rate under anoxic respiration was approximately equal to one-half the OUR under aerobic respiration conditions (Randall *et al.*, 1992).

#### 2.4.4.1 *Internal Carbon Sources*

Initially the trend was to use industrial or agricultural wastes as external carbon sources for denitrification (McCarty *et al.*, 1969 ; Skrinde and Bhagat, 1982). The cost involved in such schemes, however, has led to more studies being conducted on the potential of internal carbon sources within wastewater treatment works for enhancement of denitrification rates. An organic carbon source is defined as internal when present or derived from the influent wastewater.

The concept of introducing hydrolyzed sludge (hydrolyzate) to denitrifying systems was studied by Abufayed and Schroeder (1986). Primary sludge was used as a carbon source in denitrification studies and was hydrolysed for 24 h before being introduced into a SBR system. Under non-carbon limiting conditions (*i.e.* at COD/N ratios greater than 6.3) complete nitrogen removal was obtained. The same concept was applied in the HYPRO (hydrolysis process) project which was developed through the collaboration between research institutions and companies from Denmark, Sweden and Norway to attempt to solve the problem of carbon limitation in denitrification systems. The objective of this project was to solubilize the particulate organic matter in the wastewater as carbon source in the nutrient removal process. It is based on pre-precipitation of the organic matter, sludge hydrolysis and biological nutrient removal. Biological, chemical and physical (thermal) hydrolysis techniques were investigated as a means of improving the bioavailability of the organic carbon (Henze and Harremoes, 1990 ; Smith and Goransson, 1992 ; Soy and Degaard, 1994). Even though the hydrolyzate yield from biological hydrolysis was inferior to the yield from some chemical methods, it was considered to be the best method for solubilization since it produced substances which were more biodegradable and therefore, effective in enhancing denitrification rates.

A comparative study between the organic carbon sources, acetate and hydrolyzate, obtained in the HYPRO project was conducted by Isaacs and Henze (1995). They investigated the controlled addition of these carbon sources to batch reactors, under carbon limiting and non-carbon limiting conditions. At COD/N ratios less than 1.86 the denitrification rate was dependent on the COD (acetate) concentration. At a COD/N ratio of 7.5, however, acetate was well in excess of that required to denitrify all the nitrate present. Under carbon limiting conditions denitrification rates of 1.8-1.9 mgN/gVSS.h were obtained and a rate of 3.4 mgN/gVSS.h was obtained when carbon was in excess.

Hydrolyzate as a carbon source gave similar results to those observed for acetate. At COD/N ratios greater than 5.4 fast initial denitrification rates of ca. 2.4 mgN/gVSS.h were produced. These rates were followed by slow rates of ca. 0.6 mgN/gVSS.h, respectively, which compared favourably with the rate of 0.7 mgN/gVSS.h for endogenous denitrification. Two distinct phases were observed when acetate was limiting while non-limiting conditions produced a single linear phase. For hydrolyzate, however, return to the original denitrification rate occurred more gradually (Figure 2-8). It was suggested that the latter effect was owing to the fact that hydrolyzate is more complex than acetate and is composed of carbon



compounds of varying degrees of biodegradability. Similar trends were reported for acetate and hydrolyzate in an alternating nitrification-denitrification pilot-scale system (Isaacs and Henze, 1995).

Table 2-5 compares the different denitrification rates at 20°C obtained under varying operating conditions. The literature cites several more examples of denitrification rates. However, the conditions under which they were calculated are either not listed or not fully described. Hoffman and Klute (1990) found that hydrolyzate derived from various methods produced higher rates than raw wastewater. They concluded that, although, biological hydrolysis produced lower yields of hydrolyzate, the denitrification rates were higher than that for chemically derived hydrolyzate. Isaacs and Henze (1995) showed that hydrolyzate as a carbon source gave similar results to those observed for acetate. Carucci *et al.* (1996) showed that RBCOD fed batch reactors produced rates of about 10 mgN/gVSS.h at 20°C. This value is almost three times the value given by Isaacs and Henze using hydrolyzate. Table 2-5 also shows that there is a variation in denitrification rates even if the substrates are the same which is probably due to differences in biomass activity and operating conditions of the various reactors. These differences may be due to the method used to calculate specific denitrification rates, which is a function of the total volatile suspended solids (VSS) concentration rather than the active biomass concentration.

#### 2.4.4.2 External Carbon Sources

Monteith *et al.* (1980) tested several industrial wastes as organic carbon sources. They found that some organic wastes such as formaldehyde and dextrose waste were less efficiently degraded than distillery oils or methanol. Tam *et al.* (1992) used three external carbon sources (methanol, glucose and acetate) in SBR systems. It was shown that at a COD/N ratio greater than 2, the amount of nitrate removed increased and the time required for complete denitrification decreased. In addition, of the three substrates tested acetate was the most effective (98% NO<sub>x</sub>-N removal), followed by methanol (86%) and glucose (78%) (Tam *et al.*, 1992). These results correlate with Gerber *et al.* (1986) who reported that compounds such as acetate, propionate, butyrate and lactate consistently produced higher denitrification rates than methanol, glucose or citrate. Tam *et al.* (1992) concluded that the results could be explained biochemically. The glycolytic pathway and tri-carboxylic acid (TCA) cycle are the two metabolic pathways for utilizing organic substrate as sources of energy and carbon in most organisms. Acetyl Co-A, which is easily formed from acetic acid or acetate is the key compound of these pathways. Therefore, sodium acetate is a directly utilisable substrate which is more readily metabolizable than methanol or glucose. Sodium acetate enters the pathways directly while methanol must undergo a condensation process to form 3-C or 4-C intermediates before entering the TCA cycle.

**Table 2-5 : Denitrification rates ( $k_1$ ) at 20 °C obtained with activated sludge fed with different organic carbon sources and at different COD/N ratios.**

carbon source	reactor type	COD/N	$k_1$ (mgN/gVSS.h)	Reference

Raw wastewater	continuous	2	1.50 to 2.10	Hoffmann and Klute (1990)
Carbon from BH	continuous	2	4.90 to 7.50	Hoffmann and Klute (1990)
Carbon from BH/PA	continuous	2	6.10 to 7.30	Hoffmann and Klute (1990)
Carbon from CH	continuous	2	3.90 to 5.70	Hoffmann and Klute (1990)
Hydrolyzate	continuous	4 to 5	2.65	Isaacs and Henze (1995)
Acetate	continuous	6 to 7	3.09 to 3.53	Isaacs and Henze (1995)
Acetate	continuous	5	3.20	Karlsson (1990)
Acetate	SBR	3	7.95	Tam <i>et al.</i> (1992)
Acetate	SBR	6	10.60	Tam <i>et al.</i> (1992)
RBCOD	batch	11	10.40	Carucci <i>et al.</i> (1996)
RBCOD	batch	3.7	4.20	Carucci <i>et al.</i> (1996)
Acetate	batch	0.8	2.20	Isaacs and Henze (1995)
Acetate	batch	1.9	2.08	Isaacs and Henze (1995)
Acetate	batch	7.5	3.94	Isaacs and Henze (1995)
Hydrolyzate	batch	1.3	0.67	Isaacs and Henze (1995)
Hydrolyzate	batch	2.6	2.78	Isaacs and Henze (1995)
Hydrolyzate	batch	5.2	1.97	Isaacs and Henze (1995)
Hydrolyzate	batch	10.4	3.09	Isaacs and Henze (1995)

BH - biological hydrolysis ; PA - post alkalization ; CH - chemical hydrolysis

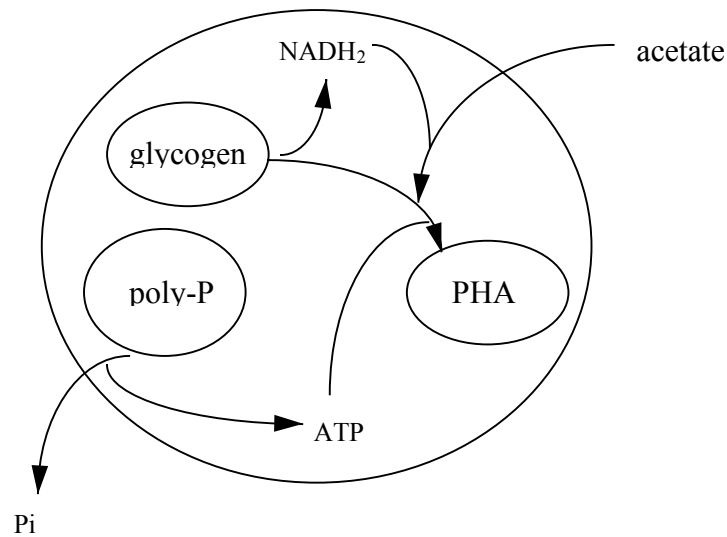
(Denitrification rates at 20°C are calculated from equation 2-4 using a  $\theta$  value of 1.04).

### ***2.4.5 The P release/uptake phenomenon in activated sludge systems***

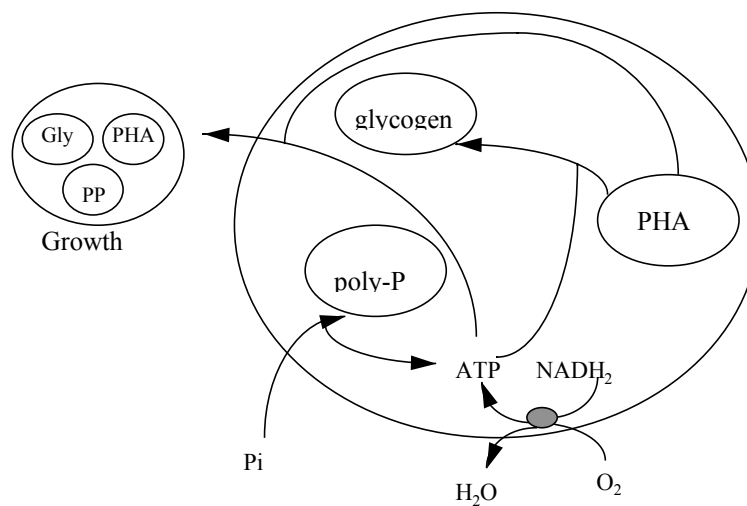
Rapid removal of nitrates from solution in wastewaters is governed to a large extent by the concentration and type of biodegradable organic carbon substrate that is made available to the denitrifying bacteria. Phosphorus removing bacteria in wastewater systems also rapidly take up readily biodegradable organic carbon substrates. Thus, phosphorus removing bacteria and denitrifiers will compete for the available readily biodegradable organic carbon present. If complete denitrification is the primary aim of a wastewater treatment system, then the presence of phosphorus removing bacteria can have a major impact on removal rates. The following sub-section will briefly discuss the process of biological phosphorus removal in activated sludge systems.

Biologically enriched phosphorus removal has been well documented in recent years (Wentzel *et al.*, 1985 ; Wentzel *et al.*, 1989a ; Wentzel *et al.*, 1989b and Wentzel *et al.*, 1992 ; Kern-Jespersen and Henze, 1993 ; Mino *et al.*, 1998 ; Brdjanovic *et al.*, 1998a,b,c,d ; Meinhold *et al.*, 1999). Biological phosphate

removal from wastewater can be achieved by stoichiometric coupling to microbial growth or enhanced storage in the biomass as polyphosphate (Van Loosdrecht *et al.*, 1997b). In the anaerobic phase, biological phosphorus removing bacteria take up carbon sources (short chained fatty acids) and store them in the form polyhydroxyalkanoates (PHA). The energy required is generated by the conversion of glycogen and polyphosphate. The degradation of polyphosphate results in its release into the bulk solution (Figure 2-9). In the subsequent aerobic or anoxic phase the internal pool of polyhydroxyalkanoates is oxidized and used for growth, phosphate uptake, glycogen synthesis and maintenance (Figure 2-10) (Van Loosdrecht *et al.*, 1997a ; Brdjanovic *et al.*, 1998a). Thus, in an enhanced biological phosphorus removal (EBPR) system the behaviour of the 3 storage pools viz: PHA, poly-P, and glycogen, in cells is highly dynamic and is determined by their conversion during the anaerobic and aerobic (or anoxic) phase (Brdjanovic *et al.*, 1998b).



**Figure 2-9 :** Metabolic processes of polyphosphate accumulating organisms involved in anaerobic phase of phosphorus removal systems (poly-P - polyphosphate ; PHA - polyhydroxyalkanoate) (from Van Loosdrecht et al., 1997).



**Figure 2-10 :** Metabolic processes of polyphosphate accumulating organisms involved in anaerobic/aerobic phosphorus removal (Gly - glycogen ; PP - polyphosphate ; PHA - polyhydroxyalkanoate) (from Van Loosdrecht et al., 1997).

#### 2.4.5.1 Polyhydroxyalkanoates (PHA)

Initially, polyhydroxybutyrate (PHB) was recognized as the storage polymer in the anaerobic phase (Clayton et al., 1991 ; Wentzel et al., 1995). It was later verified that the PHB-like polymer contains 3-

hydroxybutyrate (3HB) and 3-hydroxyvalerate (3HV) as monomeric building units. These polymers are now referred to as polyhydroxyalkanoates (PHA) in general. Polyhydroxyalkanoates have been verified to be co-polymers composed of these 4 units. When acetate is the sole substrate, then 3HB is the major unit in the PHA formed (Barker and Dold, 1997 ; Shuler and Jenkins, 1997 ; Mino *et al.*, 1998).

Polyhydroxyalkanoate is a more reduced compound than acetate, therefore the conversion of acetate, a favourable substrate for enhanced biological phosphorus removal, to PHA requires reducing power. Two possibilities exist for the generation of this reducing power in bacterial cells. In the Comeau-Wentzel model it is suggested that the required reducing power is produced by partial oxidation of acetyl CoA through the tri-carboxylic acid cycle. In the Mino model the reducing power is considered to be derived from degradation of intracellularly stored glycogen. (Van Loosdrecht *et al.*, 1997a ; Mino *et al.*, 1998). Several of the experimental results seem to support the Mino model :

- The theoretically developed stoichiometry for the Mino model adequately explains the experimentally observed stoichiometry of anaerobic acetate uptake, polyhydroxyalkanoate formation, glycogen utilization and carbon dioxide (CO<sub>2</sub>) production (Mino *et al.*, 1998).
- Bordacs and Chiesa (1989) used radioactively labelled acetate and showed that only a very small portion of the radioactivity was found in the CO<sub>2</sub> generated under anaerobic conditions. This indicated that the acetate taken up was not metabolized through the tri-carboxylic acid cycle.
- Satoh *et al.*, (1992) proposed that in anaerobic uptake of propionate the acetyl CoA necessary for polyhydroxyalkanoate production was not derived from the external substrate but from possibly the utilization of glycogen.
- Pereira *et al.*, (1996) demonstrated that acetate taken up anaerobically was converted to PHA which is subsequently converted to glycogen in the aerobic phase which further supplies the carbon source for PHA formation and CO<sub>2</sub> generation in the anaerobic phase.

However, it is also likely that there may be a partial functioning of the tricarboxylic acid cycle. Bordacs and Chiesa (1989) and Pereira *et al.*, (1996) found that a small fraction of the labelled carbon in acetate was released as CO<sub>2</sub>. Based on redox balance considerations, Pereira *et al.*, (1996) concluded that the reducing power generated in the observed degradation of glycogen was insufficient to account for the polyhydroxyalkanoate production. These are strong indications that a small fraction of acetate is metabolized through the tri-carboxylic acid cycle under anaerobic conditions supplying a minor part of the reducing power for polyhydroxyalkanoate formation.

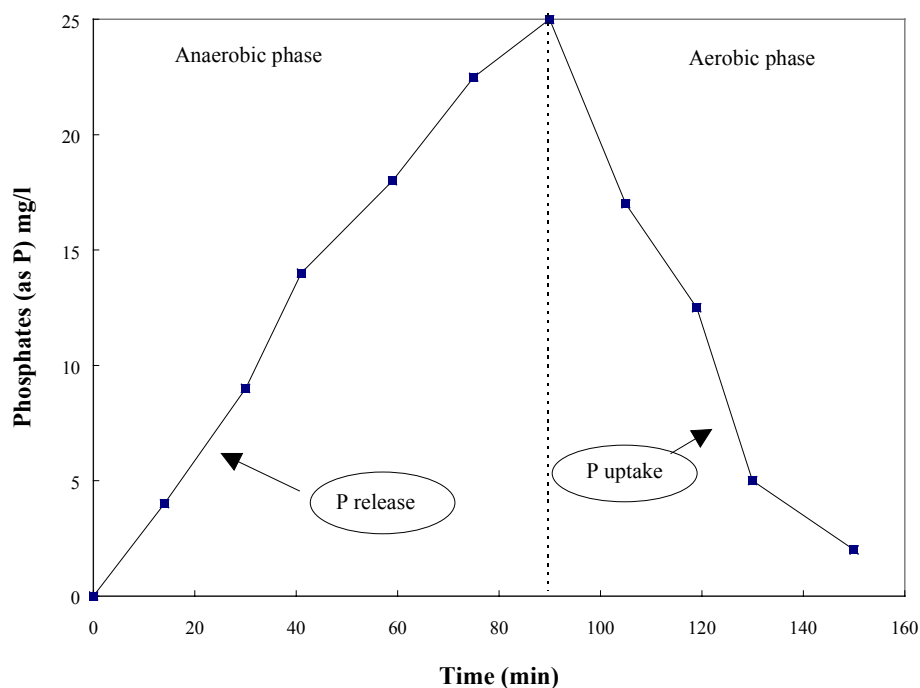
The anaerobic polyhydroxyalkanoate production is dependent on substrate loading while the aerobic polyhydroxyalkanoate consumption depends on the PHA level inside the biomass. The

polyhydroxyalkanoates that are not used will accumulate in the cell until a saturation level is reached. Once this level is reached no further acetate uptake will occur under anaerobic conditions (Brdjanovic *et al.*, 1998d ; Meinhold *et al.*, 1999). In biological phosphorus removal systems the aerobic solids retention time (SRT) should be long enough to oxidize the amount of polyhydroxyalkanoate stored in the cell during the anaerobic phase. Thus, the minimally required solids retention time depends on the polyhydroxyalkanoate conversion kinetics and the cell PHA storage capacity. It was also found that the doubling of the SRT from 8 to 16 d at 10 °C strongly increased the content of storage polymers in the biomass (Brdjanovic *et al.*, 1998c). Brdjanovic *et al.* (1998d) developed a model that was able to predict the minimally required SRT in a sequencing batch reactor system adequately.

It was also shown that the PHA consumption was strongly influenced by temperature during long term experiments *i.e.* microorganisms exposed to a change in temperature for a relatively long time (couple of weeks). It was concluded that temperature impact on the stoichiometry and phosphorus (P) uptake process rate was marginal. However, a strong temperature effect on metabolic processes such as PHA consumption and growth was observed *i.e.* it was observed that the conversion rate of storage polymers decreased with a decrease in temperature (Brdjanovic *et al.*, 1998c).

#### **2.4.5.2 Polyphosphate (Poly-P)**

Under anaerobic conditions energy is required for transport of external substrates into the cell, conversion of substrates to PHA and related metabolism, and maintenance. Poly-P is considered to be the energy storage polymer for anaerobic substrate uptake. As mentioned earlier in this sub-section, during the anaerobic phase short chained fatty acids (like acetate) are taken up by the bacterial cells with a concomitant release of phosphates into the bulk liquid (Figure 2-11). The appearance of phosphate in the bulk liquid is as a result of the degradation of internal reserves of polyphosphates to provide the energy necessary for production of storage compounds like polyhydroxyalkanoates. It should be noted that phosphorus release is not limited to the anaerobic phase and has also been observed in the aerobic phase when acetate was present. However, phosphorus release in the aerobic zone could lead to a deterioration in overall efficiency of the EBPR system (Brdjanovic *et al.*, (1998b). The cells internal poly-P supplies are replenished during the aerobic phase by taking up phosphates (*i.e.* phosphate uptake) from the bulk liquid (Figure 2-11) ( Sorm *et al.*, 1997 ; Mino *et al.*, 1998).



**Figure 2-11 : The course of ortho-phosphate concentration under anaerobic and aerobic conditions during experiments using the Dephanox process (adapted from Sorm *et al.*, 1997).**

It has been shown that the enzyme, AMP-phosphotransferase, correlated with the EBPR capabilities and catalyzes the reaction :  $(\text{Pi})_n + \text{AMP} \rightarrow (\text{Pi})_{n-1} + \text{ADP}$ . This enzyme appears to be responsible for the energy conservation in bacteria which are capable of phosphorus removal. One of the strange phenomena observed in enhanced biological phosphorus removal systems is the variation in the ratio of carbon source taken up to phosphorus released. It has been reported that a lower pH gave a lower P-release/acetate uptake ratio with a variation of 0.25 to 0.75 P-mol/C-mol (Mino *et al.*, 1998). Brdjanovic *et al.* (1997a) further suggested that polyP (energy source) would be limiting at high pH since more energy is required for acetate transport through the membrane at high pH. Moreover, this variation indicates that the dependency on poly-P as energy source can vary due to the balance between production and consumption of energy in the cell. Energy requirements for the PHA formation metabolism depends on the metabolic pathways used. (Mino *et al.*, 1998).

It was shown that excessive aeration leads to a quick full depletion of the already relatively low PHA content of the bio-P cells present at the end of the standard aerobic phase. After the system is returned to normal operation the phosphate uptake is strongly affected due to the dependence of phosphate uptake on the PHA content of the bacterial cells. The aerobic phosphate uptake depends not only on the polyhydroxyalkanoate concentration but also on polyphosphate content of the cells. Under aerobic starvation conditions glycogen cannot replace PHA's for phosphate uptake and is only used for maintenance. During this period no oxygen consumption due to decay processes has been observed (Brdjanovic *et al.*, 1998b). Since the phosphorus release is hardly affected the net result is a decreased phosphorus removal efficiency after a period of excessive aeration.

### 2.4.5.3 Glycogen

Glycogen according to the Mino model is a key substrate for the generation of the reducing power required for polyhydroxyalkanoate synthesis. Brdjanovic *et al.* (1997a) reported that when excess acetate is fed to biological phosphorus removing sludge, the anaerobic uptake of acetate stops not because of polyphosphate limitation or polyhydroxyalkanoate saturation but because of glycogen exhaustion. This suggests that glycogen can be the limiting substance in the anaerobic substrate uptake phase under shock loading conditions. Glycogen is metabolized via the Entner-Doudoroff (ED) pathway and is also known to be anaerobically metabolized via the succinate-propionate pathway (Mino *et al.*, 1998).

There are several different methods to measure the glycogen content of bacterial cells. However, these analytical methods measure not only glycogen but also total carbohydrates and glucose which could lead to possible overestimation of glycogen. Recently two methods have been proposed for the measurement of glycogen. Schulze *et al.*, (1995) used an enzymatic method for glycogen determination while Brdjanovic *et al.*, (1997a) proposed a batch experiment in which the sludge is exposed to excess acetate feeding under anaerobic conditions and the maximum acetate uptake rate is measured for glycogen determination, the stoichiometric relation between acetate uptake and glycogen consumption is applied assuming glycogen is limiting.

### 2.4.5.4 Microbiology

The biological phosphorus bacteria are collectively referred to as polyphosphate accumulating organisms (PAO's). PAO isolates should have the anaerobic acetate metabolisms (acetate uptake and its conversion to polyhydroxyalkanoates for storage coupled with hydrolysis of stored polyphosphate and consequently the release of ortho-phosphate under anaerobic conditions) (Mino *et al.*, 1998). Initially it was thought that *Acinetobacter spp.* was primarily responsible for enhanced biological phosphorus removal. However, it was later demonstrated by a fluorescent antibody staining technique and the application of 16s-rRNA targeted oligonucleotide probe techniques that the number of *Acinetobacter spp.* was significantly smaller (< 10 % of the total population) (Wagner *et al.*, 1994 ; Bond *et al.*, 1995). The reported predominance of *Acinetobacterspp.* in EBPR systems can be explained by the culture dependent methods that were initially used to identify these polyaccumulating organisms. The development and use of gene probe techniques showed that the classical culture dependent techniques for bacterial enumeration was and is strongly selective for *Acinetobacter spp.* Some of the polyphosphate organisms isolated were found to accumulate polyphosphates under aerobic conditions while taking up glucose and casamino acids. However, they did not take up acetate and were found to have quinone 9 (Q-9) which is different to the Q-8 or MK-8 normally found in polyphosphate removing sludge. Other organisms isolated from EBPR sludges were found to accumulate phosphates while taking up acetate but they differed morphologically to polyphosphate accumulating organisms (Mino *et al.*, 1998).



Conventionally, it has been assumed that enhanced biological phosphorus removal sludges with high phosphorus removal capabilities would be enriched with a single dominant group of microorganisms. However, there is evidence to suggest that the microbial community of the EBPR process is diverse (Bond *et al.*, 1995). It was shown by electron microscopy and genetic techniques that even under very selective conditions (i.e. one carbon source - acetate, controlled temperature and pH, and a long steady operation of the process) there was more than one type of organism present (Mino *et al.*, 1998 ; Brdjanovic *et al.*, 1998a).

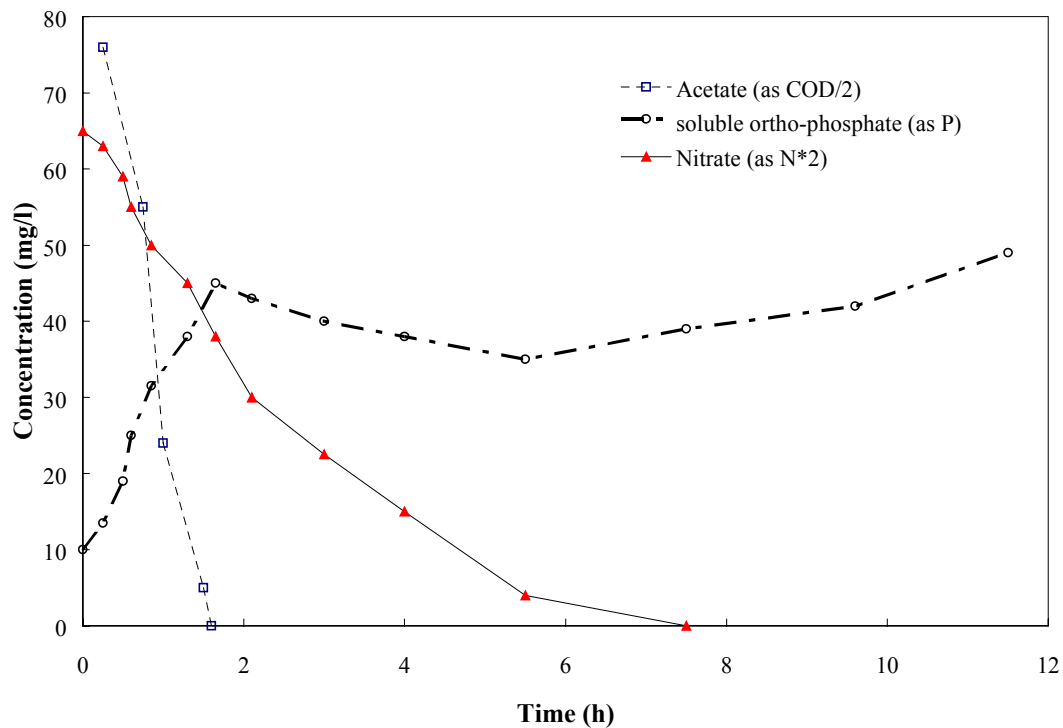
The enhanced biological phosphorus removal (EBPR) process is generally a relatively stable process in practice. However, factors such as excessive rainfall, too high loading, shortage of potassium, excessive aeration and high nitrate loading can affect the efficiency of the process. In some laboratory scale experiments where P removal efficiencies decreased, it was found that a different group of bacteria dominated and these were found in glucose fed reactors and named G-bacteria or glycogen accumulating organisms (GAO's). These organisms take up organic substrates in the anaerobic zone without P release. GAO proliferation is thought to be influenced by factors such as presence of glucose in the wastewater, long SRT and HRT, and improper seeding. Thus, two types of microbial populations are described in the literature as being responsible for anaerobic storage of acetic acid in activated sludge processes ; the polyphosphate accumulating organisms (PAO's) and glycogen accumulating non-polyphosphate organisms (GAO's) (Brdjanovic *et al.*, (1998a,b).

In polyphosphate accumulating organisms glycogen is only converted to deliver the reducing power (NADH) required for acetate reduction to polyhydroxybutyrate while in glycogen accumulating organisms internally stored glycogen would provide the energy as well as the reducing power necessary for anaerobic substrate uptake. Glycogen is therefore, the key storage compound. GAO's have the ability to produce energy through utilization of glycogen without disturbing the redox balance in the cell. The surplus in reducing equivalents obtained in this way is balanced by formation and polymerization of propionyl-CoA into polyhydroxybutyrate or polyhydroxyvalerate. Thus, the metabolism of GAO's is similar to PAO's except glycogen is thought to be the sole energy (ATP) source for the GAO's while PAO's release phosphorus via polyphosphate cleavage (Mino *et al.*, 1994 ; Liu *et al.*, 1997 ; Van Loosdrecht *et al.*, 1997 ; and Schuler and Jenkins, 1997). However, GAO's and PAO's are morphologically different and GAO's are Gram negative organisms. In addition, GAO's contain Neisser positive stains only on their cell walls while PAO's contain strongly Neisser positive granules inside the cell.

The next decisive step in BNR processes is probably going to come from understanding the population dynamics of the systems better. This will lead to the exclusive culturing of these organisms so that the biological phosphorus removal programme is optimized and made more efficient (Ekama and Wentzel, 1999).

### 2.4.5.5 Anoxic Phosphorus Removal

It was initially thought that PAO's could not grow or accumulate phosphorus under anoxic conditions, or that only a small percentage were capable of it. However, it has been shown that poly-accumulating organisms are able to grow and accumulate phosphorus anoxically (Hascoet and Florentz, 1985 ; Mostert *et al.*, 1988 ; Kuba *et al.*, 1993 ; Kern-Jespersen and Henze, 1993 ; Meinhold *et al.*, 1999). Gerber *et al.* (1986) clearly showed (albeit to argue the case against nitrates in the anaerobic reactor) that the phenomenon of P release from sludge acclimatized to enhanced P removal, is primarily dependent on the nature of the substrate and not the anaerobic state *per se*. They showed that the presence of acetate and propionate resulted in rapid phosphorus release under anoxic conditions and that the disappearance of these compounds coincided with a pronounced reduction in phosphorus release (Figure 2-12). It was also shown that during the anoxic phase P release was effectively prevented for substrates such as butyric acid, lactic acid, citric acid, succinic acid, glucose, ethanol, methanol, and settled aewage (Gerber *et al.*, 1986).



**Figure 2-12 : Sequential periods showing phosphorus release and uptake under anoxic conditions (presence of nitrate) followed by phosphorus release under anaerobic conditions (absence of nitrate) (adapted from Gerber *et al.*, 1996).**

In addition, Van Loosdrecht *et al.* (1997) postulated that in the presence of nitrates and acetate the substrate is converted to PHA's instead of being used for growth since the formation of storage materials seems to be a basic characteristic of microorganisms in systems with feast/famine conditions such as those that occur in wastewater treatment plants. When the readily biodegradable COD (acetate) is depleted,

PHA's are used as substrates to produce new biomass and restore polyphosphate and glycogen (Chuang *et al.*, 1996 ; and Van Loosdrecht *et al.*, 1997).

The energy production efficiency with nitrate expressed in terms of mol ATP/mol NADH is estimated to be 40 % lower than that with oxygen. Consequently a 20% lower cell yield value was reported for an anaerobic-anoxic EBPR process (Murnleitner *et al.*, 1997). Kern-Jespersen and Henze (1993) reported that anoxic P uptake appeared to occur at a slower rate than under aerobic conditions. They suggested that the PAO's consisted of 2 groups : (1) a portion which can utilize either oxygen or nitrate as an electron acceptor, and (2) a portion that is able to use only oxygen. This was corroborated recently by studies on anoxic phosphorus removal by Meinhold *et al.*, (1999) which pointed strongly to the existence of 2 populations of PAO's. While the division of the polyphosphate organisms into 2 groups explained the different P uptake rates under different electron acceptor conditions, it is by no means conclusive since other factors such as PHB concentration can also influence P uptake. Batch tests by Sorm *et al.* (1997) demonstrated that the occurrence of anoxic P uptake could be initiated and stimulated by process conditions *i.e.* populations acclimatized to anoxic conditions showed significantly higher anoxic phosphorus uptake than populations exposed to only aerobic conditions. This could be due to a difference in microbial populations or enzymatic induction.

The organisms capable of anoxic phosphorus removal have been termed denitrifying poly-accumulating organisms (DPAO's). Denitrifying capabilities of PAO's is important for 2 reasons:

- In mathematical modelling - behaviour of phosphate and nitrogenous compounds like nitrite, nitrate and ammonia can be predicted only by introducing denitrifying PAO's. In the activated sludge model II (ASM2) the denitrification capability of PAO's is not considered and glycogen is not introduced as a variable (Meinhold *et al.*, 1999).
- The available amount of COD in the wastewater is a crucial limiting factor for both EBPR and denitrification. Anoxic phosphorus removal can achieve enhanced biological phosphorus removal and denitrification at the same time and save significant amounts of COD (Filipe and Daigger, 1997 ; Meinhold *et al.*, 1999). However, it is thought that PAO's that denitrify do not accumulate in biological nutrient removal systems since they grow at a disadvantage due to their lower utilization efficiency for stored PHA's under anoxic conditions (Murnleitner *et al.*, 1997 ; Filipe and Daigger, 1997).

## 2.5 DENITRIFICATION KINETICS

### 2.5.1 Kinetic equation

Denitrification kinetics can be described by a Monod expression (equation 2-5).  $\mu_{\max}$  is the maximum growth rate achievable when  $S > K_s$  and the concentration of all other essential nutrients are available.  $K_s$  is the value of the limiting nutrient concentration at which the specific growth rate is half its maximum value.

$$\mu = (\mu_{\max} \cdot S) / (K_s + S) * S_{\text{NO}_3} / (K_s + S_{\text{NO}_3}) \quad (2-5)$$

However, when the substrates (organic carbon and nitrate) are not limiting, a zero order expression (equation 2-6) can be used (Van Haandel *et al.*, 1981 and Henze *et al.*, 1997). The kinetic reaction describing denitrification can be expressed by :

$$dN/dt = -rX_v \quad (2-6a)$$

$$dN/dt = -rX_a \quad (2-6b)$$

where

N = nitrate concentration (mgNO<sub>3</sub>-N/l)

dN/dt = denitrification rate (mgN/l/h)

t = time in hours

X<sub>v</sub> = volatile solids concentration (g/l)

X<sub>a</sub> = active biomass concentration (g/l)

r = specific denitrification rate (mgN/gVSS.h)

This equation indicates that the nitrate versus time relationship is linear (zero order reaction) and is independent of the nitrate concentration. The denitrification rate is only a function of the volatile solids concentration (Eqn 2-6a). The specific denitrification rate can be expressed more accurately as a function of the active biomass concentration (Eqn 2-6b).

### 2.5.2 Kinetic parameters

The major parameters affecting the denitrification process kinetics are nitrate (electron acceptor), organic carbon (electron donor) type and concentrations, cell residence time and physico-chemical conditions

such as pH, oxygen and temperature. Electron donor and nitrate removals are interdependent as the removal of one will result in the removal of the other. The type of electron donor will affect the nitrate reduction rate, cell yield (mass of organisms produced per unit mass of substrate utilized) and nitrite accumulation rates (in batch systems).

The saturation constant  $K_s$  for nitrate has a value of 0.1 mgNO<sub>3</sub>-N/l (Christensen and Harremoës, 1977 ; and Abufayed, 1983) for non-carbon limited systems. However, this value can range from 0.2 to 0.5 mgN/l. The Activated Sludge Model No.2 recommends a  $K_s$  value of 0.5 mgN/l (Henze *et al.*, 1995). It has been proposed that zero order kinetics are followed until the nitrate-nitrogen concentration reaches 1 mg/l and thereafter, the rates are thought to follow first order kinetics (Payne, 1981). Table 2-6 lists some of the denitrification kinetic constants that are used to model denitrification processes (Henze *et al.*, 1995 ; Metcalf and Eddy, 1991 and Henze *et al.*, 1997).

**Table 2-6 : Denitrification rate constants for denitrification (Henze *et al.*, 1995 ; Metcalf and Eddy, 1991 and Henze *et al.*, 1997).**

Reaction rate constants	Symbol	Unit	Constant
Maximum specific growth rate	$\mu_{max}$	d <sup>-1</sup>	3 to 6
Decay constant	<b>b</b>	d <sup>-1</sup>	0.05 to 0.4
Saturation constant, COD	$K_{s,COD}$	mgCOD/l	10 to 20
Saturation constant, nitrate*	$K_{s,NO_3}$	mgN/l	0.2 to 0.5
Hydrolysis constant	$k_{hX}$	mgCOD/mgCOD. d <sup>-1</sup>	0.15 to 0.4
Maximum yield constant	$Y_{max}$	mgCOD/mgCOD	0.4 to 0.66

\* Metcalf and Eddy lists this value as low as 0.06 mgN/l

**Yield coefficient** : The yield coefficient is defined as the ratio of the organic carbon used for synthesis over the total amount of organic carbon consumed. Of all the parameters liable to affect the wastewater characterization results using anoxic respiration, the yield coefficient is the most difficult to assess and control. This parameter can be measured in 3 ways :

- 1) Direct measurement *i.e.* directly measuring the amount of biomass produced and the amount of organic matter consumed. The imprecision of this method stems from the inability to accurately measure the active biomass growth during the test, especially when there are small variations.
- 2) Indirect measurement *i.e.* measure the total amount of electron acceptor consumed (NO<sub>3</sub>) and the total amount of organic carbon consumed. This method is reliable when specific carbon sources are used *i.e.* when the concentration of these carbon sources can be measured directly by specific analytical methods. However, this is no longer relevant when domestic wastewaters are tested since the measurements would accounts for only 50 to 70 % of the total RBCOD. The use of the global parameter, COD is suggested based on the hypothesis that the filtered COD is representative of the

organic matter consumed. However, the inaccuracies of this method is rooted in both the hypothesis and the COD analytical method itself (Nogueira *et al.*, 1998).

- 3) Sperandio *et al.* (1998) suggested the use of CO<sub>2</sub> evolution rate for determining the heterotrophic yield. They suggested that instead of defining the  $Y_H$  on the basis of energetic exchanges by COD balances, it was possible to express it in terms of carbon conversion ( $Y_H^c$ ), in mass of carbon produced per mass of carbon consumed ( $\Delta C_s$ ).

High observed yield coefficients (ratio between oxidized and removed substrate) suggests that storage may be a significant mechanism in substrate removal. However, accumulation and biosorption can also cause high observed yields. The observed yield is also likely to change during a dynamic response because of competition for substrate which will depend on the time scale and the substrate to biomass ratio. The observed yield shows a general trend to decrease as the sludge age decreases (Majone *et al.*, 1999).

Intermittently fed sludges typically exhibit faster substrate uptake and higher observed yields than continuously fed ones. This difference in yields has been explained by the presence of those microorganisms that are most able to store substrates quickly during imposed transient conditions (Majone *et al.*, 1996). Cech and Chudoba (1983) demonstrated that both the accumulation and storage mechanisms are acting when sludge is intermittently fed while only storage is possible for the continuously fed sludge. It is hypothesized that the stored products are initially produced at a constant rate and then at a decreasing rate when the saturation of the maximum storage capacity is approached. This can cause both the overall and observed storage yield to vary with time (Majone *et al.*, 1999).

***Substrate to biomass ratios*** : Grady *et al.* (1996) indicated that there is a greater variability in kinetic parameter estimates found in the literature which is due to differences in the ratio of the initial substrate and initial biomass (S/X) ratios which range from below 0.025 to higher than 20. S represents a carbon and energy source for biosynthesis while X represents a source of carbon and energy consumption. If the ratio is very large significant changes can occur in the culture during the assay which would not be reflective of the original culture. A large ratio will reflect the characteristics of the fastest growing species rather than the original culture. If the ratio is very small it is possible for the parameters to be representative of the kinetics manifested in the source environment. For all S/X values in between these two extremes, bacteria will achieve only a partial change in physiological state and the extent of the change depends on the ratio.

Chudoba *et al.* (1985) reported that when the S/X (theoretical oxygen demand / volatile suspended solids) ratio is sufficiently low (below 2) the substrates are removed linearly and no significant cell multiplication is observed. Under high S/X conditions more energy is spent for cell multiplication and a greater part of the substrate is oxidized. This results in a higher production of microbial polymers for mixed culture

organisms. Furthermore, low biomass concentrations are indicated by sigmoidal growth curves which are essentially growth and consumption curves with mixed substrates (Chudoba *et al.*, 1985). Therefore, for biodegradation with the aim to obtain kinetic constants it is necessary to work at low S/X ratios to prevent mixed culture organisms from substantial cell multiplication.

Recent studies by Majone *et al.* (1996) using activated sludge fed continuously, and intermittently, showed the the S/X ratio did not play a major role in determining the type and extent of the response. They reported that both cultures showed that storage of polyhydroxybutyrate was in general the main mechanism of substrate removal. The biomass dominated by floc-forming bacteria showed a very fast response to the substrate spike with a high observed yield. they showed that storage of PHB is the main part of the observed yield when starvation is low and is a minor part when starvation is high. When the yield decreases, growth becomes the main mechanism of substrate removal.

# Chapter Three

## ***A REVIEW OF MUNICIPAL WASTEWATER CHARACTERIZATION***

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Global analytical parameters such as biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are used routinely to assess the organic content of wastewaters. In this investigation, the chemical oxygen demand (COD) measurement was chosen as the parameter which adequately represents the organic carbon material found in raw wastewater and mixed liquor. COD measurements allows for the calculation of mass and electron balances which is not possible with BOD or total organic carbon (TOC) measurements. The organic carbon in the influent can be divided into biodegradable COD, non-biodegradable COD (particulate and soluble) and active biomass (also referred to as the active mass fraction). The mixed liquor can also be divided into the above but a distinction needs to be made between the active, endogenous, and inert sludge fraction. This review also looks at the methods employed for the determination of some of these fractions used in modelling and understanding of wastewater treatment processes. In particular, attention has been paid to the readily biodegradable and slowly biodegradable COD fractions, and the nitrate-N utilization rate method.

### ***3.1 FACTORS AFFECTING WASTEWATER CHARACTERISTICS***

Wastewaters are transformed during transport in the sewers. The nature and extent of these transformations will depend on several conditions such as residence time, temperature and state of aeration within the sewer system. For example, sewers with high residence times promote biological activity in the sewer resulting in the wastewater which entered the sewer being significantly different from the wastewater which enters the treatment plant. High temperatures will increase the biological activity in the sewers while low temperatures will reduce it. In addition it is found that sulphate reduction and acid fermentation are prevalent in anaerobic sewers with long solids retention time (SRT's). Aerobic sewers, on the other hand, foster COD reduction and biomass growth. Another factor which can influence wastewater characteristics is the use of combined or separate sewers. Combined sewers result in lower strength wastes due to dilutions and much higher flows with increased variability due to storm flows. In South Africa separate sewers are mandatory while in Europe a mixture of combined and separate sewers are used (Mbewe *et al.*, 1995).

One of the key factors that influence wastewater characteristics is the community that is served. If there is a significant input of industrial wastes into the sewer then the wastewater characteristics can be further

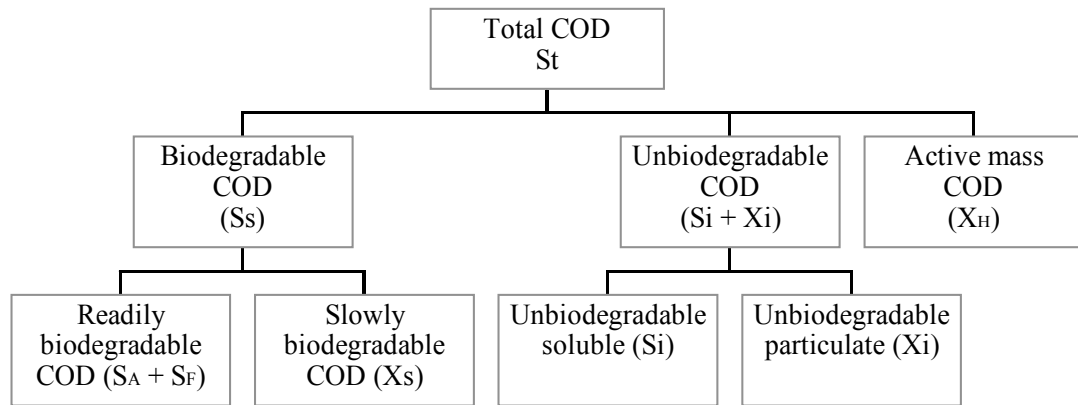


changed. The type of industry that is discharging to the sewer can also have a major impact on the characteristics e.g. dairy industries may discharge compounds which are largely biodegradable while chemical industries may discharge a larger proportion of slowly biodegradable or unbiodegradable compounds. Sewers receiving 100 % municipal wastes are also influenced by several factors. Water availability can determine whether the plant receives high or low strength wastes. The socio-economic status of the community is influential e.g. high income communities use more water per capita and the dietary habits are also different. The use of garbage grinders, detergents and wastewater treatment processes are important factors which can influence wastewater characteristics. For example the presence of a primary settling tank can reduce the COD load by as much as 40 %. Thus, settled wastewaters have higher total nitrogen to COD (TKN/COD) and total phosphorus to COD (TP/COD) ratios than raw wastewater. Other pre-treatment processes which affect wastewater characteristics include grit removal, degreasers (fats and oil removal) and dissolved air flotation. However, primary clarification (sedimentation) and the presence of equalization (balancing) tanks have a dominant effect (Mbewe *et al.*, 1995 ;and Henze *et al.*, 1997).

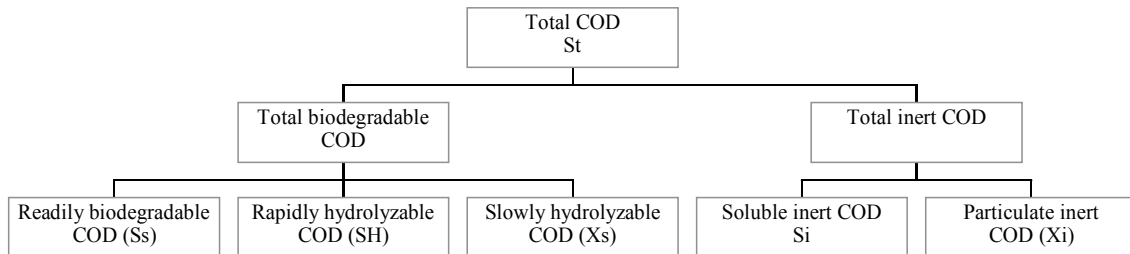
### **3.2 INFLUENT WASTEWATER COD FRACTIONATION**

The total organic matter content in wastewater can be measured as COD. In the UCT Model this is referred to as  $S_t$  (total influent substrate) but it may also be referred to as  $S_t$ ,  $C_T$ ,  $C_{Ti}$  or  $C_{TCOD}$ . The total COD of the influent wastewater can be divided into the biodegradable, unbiodegradable and active biomass fractions. These can be further divided into the readily and slowly biodegradable, and unbiodegradable fractions. According to Wentzel *et al.* (1995) the influent wastewater can be divided into five fractions : the readily biodegradable ( $S_s$ ), the slowly biodegradable ( $X_s$ ), the particulate inert ( $X_i$ ), the soluble inert ( $S_i$ ) and the active mass fraction ( $X_H$ ) (Figure 3-1 ; equation 3-1). The  $S_s$  fraction has since been divided into the  $S_A$  (acetate) and  $S_F$  (fermentable) fractions. This division was made largely to improve the models for enhanced biological phosphorus removal (EBPR) systems. The slowly biodegradable ( $X_s$ ) fraction division has been taken a step further by Orhon and  $\text{\textcircled{okg}}\text{\textcircled{Tr}}$  (1997) to include the rapidly hydrolyzable COD and slowly hydrolyzable COD fractions (Figure 3-2). Thus it is possible to combine these two figures to provide a more detailed profile of wastewater COD which includes the  $S_A$ ,  $S_F$  and  $X_H$  fractions (Figure 3-3). Based on this synopsis it is now possible to discuss these fractions more comprehensively.

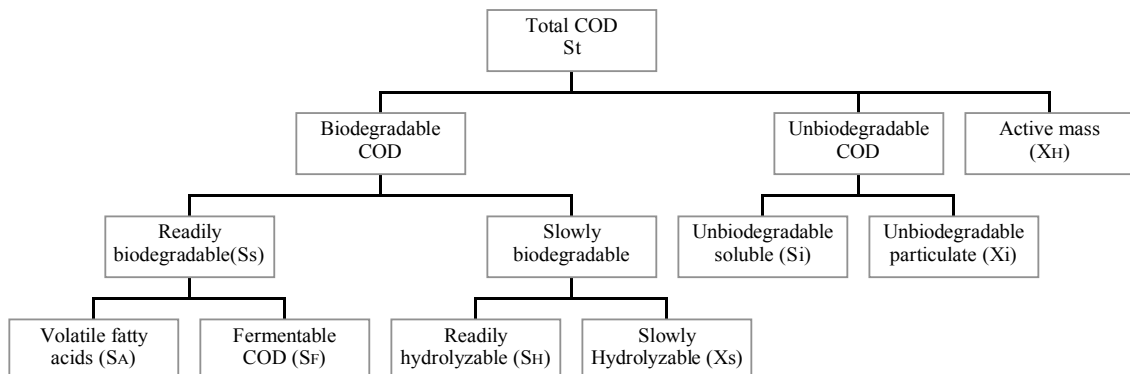
$$S_t = (S_A + S_F) + S_i + X_i + X_s + X_H \quad (3-1)$$



**Figure 3-1: Division of influent COD into its component fractions (from Wentzel et al., 1995)**



**Figure 3-2: Division of influent COD into its component fractions (from Orhon and Çokgör, 1997).**



**Figure 3-3: Division of influent COD into its component fractions (modified from Wentzel et al., 1995 and Orhon and Çokgör, 1997).**

### 3.2.1 Biodegradable COD

The biodegradable fraction is divided into a readily biodegradable (soluble) COD ( $S_s$ ) and slowly biodegradable (particulate) COD ( $X_s$ ). This division is a biokinetic one. Investigations by Stern and

Marais in 1974 showed that in the primary anoxic reactor, the rate of denitrification occurred in two linear phases (in Van Haandel, 1981). In the secondary anoxic reactor there is a single linear phase due to endogenous/adsorbed organic carbon utilization. In terms of the rate of utilization of nitrate-N they found that the single rate in the secondary anoxic reactor is about two-thirds that of the slow second rate in the primary anoxic reactor. It was therefore, hypothesized that the two linear phases were linked to the biodegradability of the organic carbon substrate, a readily biodegradable COD fraction and a slowly biodegradable one. In the secondary anoxic reactors of plugflow systems the single linear phase is due to the utilization of adsorbed SBCOD generated from organism death *i.e.* endogenous respiration. Further investigations verified that under dynamic loading conditions *eg.* plugflow, short SRT cyclic loading and batch tests, two distinct rates of utilization were observed for either oxygen (Ekama *et al.*, 1986) or nitrate (Van Haandel *et al.*, 1981 ; Ekama *et al.*, 1986) as an electron acceptor. Subdivision of this fraction is required if denitrification or phosphorus removal are included in the design or the system response is simulated with a dynamic model.

### **3.2.1.1 Readily biodegradable COD (RBCOD)**

The RBCOD ( or  $S_s$  fraction) consists of small simple molecules that pass directly through the cell wall (via passive or active uptake) for synthesis (growth) and catabolism (energy). The growth from RBCOD utilization is expressed according to the Monod equation (see equation 2-5) linking the specific growth rate of the active mass to the RBCOD concentration. The reaction rate associated with RBCOD catabolism is rapid. This component of wastewater may be represented as a fraction ( $f_s$ ) of the total COD:

$$S_s = f_s S_t \quad (3-2)$$

Recently the readily biodegradable COD was further subdivided into the fermentation products ( $S_A$ ) and fermentable biodegradable COD ( $S_F$ ) (Mbewe *et al.*, 1995 ; Henze *et al.*, 1997 ;and Orhon and Østergaard, 1997). As discussed earlier, this division is largely required for accurate design of EBPR systems. The RBCOD ( $S_s$ ) can be determined by biological methods, aerobic or anoxic, continuous or batch (Ekama *et al.*, 1986). The  $S_A$  fraction can be determined by chemical methods or gas chromatography. Thus, the  $S_F$  fraction can be determined by difference.

$$S_s = S_A + S_F \quad (3-3)$$

#### ***Volatile fatty acids ( $S_A$ )***

This fraction consists of fermentation products considered to be acetate. The acetate fraction is classed as  $S_A$  and comprises 2 to 10 % of the total COD (Table 3-1). In reality this fraction comprises a range of fermentation products (VFA's). The volatile fatty acids are present in the influent wastewater but can also be generated in the anaerobic reactor by acid fermentation. The rate of VFA uptake is so rapid that it can be assumed that all VFA's in the influent will be sequestered in the anaerobic reactor by polyphosphate accumulating organisms (if present).

#### ***Readily (fermentable) biodegradable fraction ( $S_F$ )***

This fraction consists of fermentable, readily biodegradable (F-RBCOD) organic substrates. This fraction of the soluble COD comprises 10 to 20 % of the total COD and is considered to be directly available for biodegradation by heterotrophic organisms (Table 3-1). It is assumed that  $S_F$  (or F-RBCOD) may serve as a substrate for fermentation and therefore, does not include the fermentation products. The  $S_A$  are generated by acid fermentation of  $S_F$  by the heterotrophs in the anaerobic reactor. The volatile fatty acids generated can then be sequestered by polyphosphate accumulating organisms. The rate of the fermentation reaction is slower than the sequestration rate and the amount of F-RBCOD fermented to VFA's depends on the influent F-RBCOD concentration and wastewater treatment system design.

### **3.2.1.2 Slowly biodegradable COD (SBCOD)**

The slowly biodegradable COD (SBCOD) is taken up more slowly and metabolized at rates that are about 10 % of the rate of RBCOD metabolism. This COD fraction is thought to be consist of complex organic molecules which cannot pass directly through the cell wall. The utilization of this organic carbon material involves enmeshment and adsorption to activated sludge flocs. This is followed by the extracellular enzymatic breakdown of the complex compounds to simpler molecules which are able to pass through the cell wall. The molecules are then metabolized by the microorganism for growth and metabolism. The overall reaction rate is limited by the hydrolysis rate of the adsorbed organic carbon rather than the rate of metabolism (Ekama *et al.*, 1986 ; Wentzel *et al.*, 1992).

This latter suggestion is supported by Henze *et al.* (1994) who stated that the dominating rate limiting factor in nutrient removal processes is the organic carbon source. The rate of hydrolysis of higher molecular weight compounds to readily biodegradable COD will limit the denitrification rate. The addition of readily biodegradable carbon to carbon limited sludge will speed up the denitrification rate as seen in Figure 2-7. However, once the readily biodegradable fraction has been utilized the denitrification rate falls back to the rate limited by the rate of hydrolysis of the slowly biodegradable COD.

The hydrolysis of these slowly biodegradable substrates is assumed to be catalyzed by extracellular enzymes. There are two hypothesis with regard to the locality of these extracellular enzymes :

- Some suggest that these large molecules are adsorbed to the surface of the biomass where hydrolysis is mediated by the cell bound extracellular enzymes. This was accepted and adopted in the UCT Model *i.e.* these hydrolysis products pass directly to the microorganism.
- However, according to the IAWPRC Model the organics are hydrolyzed by extracellular enzymes and are released in the bulk liquid (Dold *et al.*, 1991).

Rohold and Harremoes (1993) and Larsen and Harremoes (1994) investigated this phenomenon in biofilm reactors with molasses and starch, respectively, as slowly biodegradable substrates. They reported that the extracellular enzymatic breakdown of non-diffusible organics occurs in the bulk liquid and that the enzymes are washed out of the system when the residence time is decreased. However, San Pedro *et al.*

(1994) found that starch disappeared from the bulk liquid solution within a two 2 h period in suspended growth systems. This indicated a rapid adsorption to the biomass which suggests that the SBCOD becomes adsorbed to the biomass before hydrolysis.

In addition, San Pedro *et al.* (1994) found that the second phase was characterized by a gradual drop in OUR profile and was attributed to the metabolism of intracellular glycogen. They suggested that after the exhaustion of hydrolyzable starch the intracellular glycogen was metabolized. Phase three in the OUR profile was attributed to an endogenous respiration phase. San Pedro *et al.* (1994) suggested that the difference in rates for starch and intracellular glycogen was due to differences in the hydrolysis rates. It is observations such as these that has resulted in some researchers suggesting that the slowly biodegradable COD fraction can be further sub-divided into smaller fractions according to their rate of hydrolysis (Henze, 1992). Although originally this fraction was defined as particulate (Dold and Marais, 1986), this fraction is now said to cover a wide range of particle sizes from soluble to colloidal and larger organic particles. This provides the basis of the recent approach to sub-divide this group into the rapidly hydrolyzable COD ( $S_H$ ) and slowly hydrolyzable COD ( $X_S$ ) (Orhon and Çokgör, 1997). The rapidly hydrolyzable COD is generally assumed to be soluble, so that it may be defined for municipal wastewaters by means of a mass balance equation (3-4).

$$S_H = S_t - S_i - S_s - (X_H + X_i + X_s) \quad (3-4)$$

Endogenous respiration also provides a source of slowly biodegradable COD which occurs when the organic carbon substrate concentration is low and absent. Consequently, the bacterial cells die and release cell material, which are unbiodegradable and biodegradable. The biodegradable fraction becomes part of the SBCOD in the liquid and thus, the same cycle of adsorption, hydrolysis and utilization occurs (Randall *et al.*, 1992 ; Wentzel *et al.*, 1992). The endogenous denitrification rate is dependent on the respiration rate of the bacteria using the stored food reserves or substrate released from endogenous decay and not on the rate of hydrolysis (Randall *et al.*, 1992).

For denitrification, the rate of denitrification depends on whether RBCOD or SBCOD serves as electron donor (substrate) and the relative proportion of these two materials will influence the amount of nitrogen removed. Phosphorus removal, however, is dependent on the available VFA ( $S_A$ ) fraction.

### **3.2.2 Unbiodegradable COD**

The unbiodegradable (inert) COD can be divided into unbiodegradable soluble COD ( $S_i$ ) and unbiodegradable particulate COD ( $X_i$ ). These organic compounds cannot be further degraded in the wastewater treatment plants under normal operating conditions.

#### **3.2.2.1 Unbiodegradable soluble**

Raw wastewater contains a certain proportion of inert soluble organic compounds. During the nutrient removal process more soluble organics are produced and thus the final inert soluble concentration should

be higher than that in the influent (Henze, 1992). The total effluent soluble COD includes the unbiodegradable organic compounds which originate from the wastewater and soluble residual COD generated as soluble metabolic products ( $S_p$ ). Therefore the effluent unbiodegradable ( $S_R$ ) generally contains more soluble unbiodegradable COD than the wastewater. The generation of soluble metabolic products is modelled by means of growth-associated or decay-associated processes (Orhon and Doglar, 1997).

This is not considered in the UCT Model which hypothesizes that for unbiodegradable soluble material at steady state for systems with a sludge age of 10 to 20 d the mass of unbiodegradable material that enters the system is equal to the mass of unbiodegradable that leaves the system. The soluble unbiodegradable materials ( $S_i$ ) pass out in the secondary effluent as the COD effluent. This is done by accepting that the effluent soluble COD concentration ( $< 0.45 \mu\text{m}$  filtered COD) ( $S_{use}$ ) is equal to the influent unbiodegradable soluble COD ( $S_i$ ) (Dold *et al.*, 1991). It is therefore, assumed that no soluble unbiodegradable organics are generated during biological treatment in the biological reactor. This has been accepted as a reasonable assumption based on years of study. Henze *et al.* (1995) suggested a different method for the determination of the soluble inert fraction. It consisted of removing an aliquot from the mixed liquor from a continuously fed completely mixed reactor operating at a SRT in excess of 10 d and aerating it in a batch reactor (Orhon and Doglar, 1997). Hence, the major set-back of both these methods is the inability of these methods to differentiate between the soluble inert COD of the effluent and the soluble residual fraction of microbial products which may or may not be biodegradable.

$$S_i = S_R - S_p \quad (3-5)$$

### 3.2.2.2 Unbiodegradable particulate

The unbiodegradable particulate material becomes enmeshed in the sludge and settles out in the secondary clarifier and is retained in the system to accumulate as unbiodegradable organic settleable solids (VSS). At steady state the mass of unbiodegradable particulates entering the system is balanced by the mass of particulate inert compounds leaving via sludge wastage. Thus, the mass of inert particulates in the system is equal to the mass of unbiodegradable particulate fed per day multiplied by system sludge age. The unbiodegradable particulate organic material is generated by the bacteria during the treatment process. This material is referred to as 'endogenous residue'. The generated particulate unbiodegradable organic material occurs as a result of microbial metabolic activity during the endogenous decay or death-regeneration phase (Ekama *et al.*, 1986 ; Henze *et al.*, 1995).

Unlike the soluble RBCOD fraction which is exposed to biological treatment for as long as the liquid remains in the system *i.e.* the hydraulic residence time (HRT), the SBCOD fraction is exposed to biological treatment for as long as the solids are retained in the system *i.e.* solids retention time (SRT). Therefore, even though the utilization of SBCOD is about 10 % that of RBCOD because the SRT in most systems is usually more than 10 times longer than the HRT, the SBCOD is completely utilized. Modelling

has shown that all the SBCOD is completely utilized for SRT's >2 to 3 d and at temperatures of about 20 °C. At lower temperatures, longer SRT's are required (Mbewe *et al.*, 1995).

**Table 3-1: Typical ranges for the wastewater fractions (from Henze *et al.*, 1995).**

Symbol	Fraction	% of total COD
S <sub>F</sub>	readily biodegradable fermentable fraction	10 to 20
S <sub>A</sub>	Volatile acids (acetate)	2 to 10
S <sub>i</sub>	Inert, non-biodegradable soluble	5 to 10
X <sub>i</sub>	Inert, non-biodegradable particulate	10 to 15
X <sub>S</sub>	Slowly biodegradable fraction	30 to 60
X <sub>H</sub>	Heterotrophic biomass	5 to 15

### 3.2.3 Active mass fraction (X<sub>H</sub>)

Some of these organisms can grow aerobically and anoxically (denitrification) and others may be active anaerobically. They are responsible for the hydrolysis of particulate substrates X<sub>S</sub> and the removal of the soluble organic carbon (Henze *et al.*, 1995). In South Africa, the sewers are generally short (retention time < 6 h) and anaerobic and it is therefore, considered unlikely to support active biomass generation. However, European wastewaters can contain a significant heterotrophic active mass fraction *i.e.* up to 20 % of the total COD (Henze, 1989 and Kappelar and Gujer, 1992). Seeding of this fraction into the activated sludge system can have a significant impact on modelling and design. Therefore, the active mass is included as an influent COD wastewater fraction.

## 3.3 CHARACTERIZATION METHODS

As discussed earlier the accuracy of the input data determines the reliability of models simulating wastewater treatment processes. The accuracy of the input data, however, is largely dependent on methods used to determine the wastewater fractions such as RBCOD. To date it is largely the biological methods (oxygen and nitrate-N utilization rate) which are considered reliable for depicting the biological state of the influent substrate. Since the RBCOD is modelled as simple, soluble compounds, physical and chemical methods have been tested in order to find a method which is as comparable and reliable results as the biological respirometric tests.

### 3.3.1 Physical and chemical methods

It has been suggested that the difference in biokinetic response to the RBCOD and SBCOD is due to differences in molecular size. RBCOD consists of small molecules which can easily pass into the microbial cells. SBCOD, however, comprises complex molecules which require extracellular breakdown

before cell utilization. This has led to a need to separate and to define wastewater fractions for the purposes of studying, understanding and optimizing organic carbon utilization.

Organic matter in municipal wastewater has a very complex composition which contains organic compounds which occur in concentrations that are small, except acetate which comprises 2 to 10 % of the total COD (Table 3-1). As a totality however, these compounds are important for reaction rates and removal capacities. Methods used for separating wastewater fractions include: sedimentation, centrifugation, filtration and precipitation. Filtration methods with several pore sizes have been investigated. It has been found that membranes with a molecular weight limit of less than 10 000 daltons gave RBCOD concentrations similar to that determined in biological respirometric tests. However, it has also been reported that with textile wastewater, these membranes gave RBCOD values lower (13 % of total COD) than that derived in batch bioassays (20 % of total COD) (Bortone *et al.*, 1994 ; Wentzel *et al.*, 1995).

Dold *et al.* (1980) assessed 0.45  $\mu\text{m}$  filters and found that a small fraction of the SBCOD of domestic wastewater passed through the filter. This resulted in an overestimation of RBCOD fraction. Torrijos *et al.* (1993) found that wastewater passed through a 0.1  $\mu\text{m}$  filter gave a true indication of the RBCOD fraction.

Several other researchers have attempted to classify the soluble fraction. Their results and methods vary. For example, Pouet and Grasmick (1994) have divided wastewater into four fractions based on different fractionation techniques (see Table 3-2). The cut-off utilized for the characterization of the soluble fraction varies from  $< 0.001 \mu\text{m}$  (Pouet and Grasmick, 1994) ;  $<0.01$  or  $<0.03$  (Henze and Harremoes, 1990) and 0.45  $\mu\text{m}$  (Henze *et al.*, 1995). This fraction comprises approximately 24 to 30 % of the wastewater (Pouet and Grasmick, 1994 ; Henze and Harremoes, 1990) (Table 3-2). Henze and Harremoes (1990) cited colloidal particles sizes between 0.01 and 10  $\mu\text{m}$  and 0.03 and 1.5  $\mu\text{m}$ , while Pouet and Grasmick (1994) classified this fraction as 0.001-1  $\mu\text{m}$ . In addition, another fraction called the supracolloids was classified as 1-100  $\mu\text{m}$  in size. It is also these differences in sizes that have led to variations in the percentage of these fractions found in wastewater (Table 3-2). The difference is partly due to the difference in wastewater composition. However, there does appear to be a lack of standardization with regard to classification of wastewater fractions according to size.

**Table 3-2:** List of the different components of raw wastewater and the percentage of each fraction.

Fraction	Pouet and Grasmick (1994)		Henze and Harremoes (1990)	
	size ( $\mu\text{m}$ )	wastewater (%)	size ( $\mu\text{m}$ )	wastewater (%)
soluble	$<0.001$	30	$< 0.01$	24
colloidal	0.001 to 1	35	0.01 to 10	19
supracolloidal	1 to 100	(included in colloidal fraction)	$>10$	-



settleable	>100	35	-	57
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The major shortfall of these physical separation methods is the inability to differentiate between biodegradable and unbiodegradable compounds. It therefore, assumes that all of the soluble fraction (depending on the method) comprises RBCOD. The soluble component of wastewater may in fact contain other compounds which are inert or readily hydrolyzable.

Mamais *et al.* (1993) flocculated the colloidal material (SBCOD) of wastewater and then passed the soluble fraction through a 0.45 µm membrane. This method makes use of an equation proposed by Ekama *et al.* (1984) and the IAWPRC Task Group which equates the influent  $S_s$  to the truly soluble influent COD (equation 3-7). This method is based on the rationale that membrane filtration of a sample that has been coagulated with  $ZnSO_4$  at pH 10.5, will produce a filtrate containing only ‘truly’ soluble ( $COD_{sol}$ ) organic matter. The filtrate contains both biodegradable and unbiodegradable COD. Thus, the unbiodegradable fraction ( $S_i$ ) has to be quantified independently which requires effluent from a continuous system or the measurement of filtered COD in a 10 day batch test (Wentzel *et al.*, 1995).

$$S_s \text{ (RBCOD)} = COD_{sol} - S_i \quad (3-7)$$

$S_s$  = influent readily biodegradable soluble COD

$COD_{sol}$  = influent truly soluble COD *i.e.* after coagulation

$S_i$  = influent inert COD

The  $S_i$  component is considered equal to the ‘truly’ soluble ( $COD_{sol}$ ) effluent COD of an activated sludge system treating the influent at a sludge residence time greater than three days. Therefore,  $S_i$  can be determined by performing a  $COD_{sol}$  measurement on the effluent after coagulation and  $COD_{sol}$  by performing the same test on the influent. The difference between the two provides the  $S_s$  value (Table 3-3). Results of  $S_s$  which were obtained from the flocculation and the biological method were highly comparable (Mamais *et al.*, 1993).

**Table 3-3: Comparison of readily biodegradable COD ( $S_s$ ) values from the physico-chemical (floc) and biological method for different wastewater sources (Mamais *et al.*, 1993).**

Wastewater source	floc $COD_{sol}$	floc $S_i$	$S_s$ (floc)	$S_s$ (biological)
	mgO <sub>2</sub> /l			
primary effluent 1	99	37	62	65
primary effluent 2	84	52	32	32
raw wastewater 1	63	41	23	22
primary effluent and acid digester centrate	163	53	110	119

A disadvantage of this method is the necessity to quantify the inert fraction independently which is time-consuming procedure (Wentzel *et al.*, 1995). In addition, this  $S_i$  unbiodegradable COD value may be a false since this fraction may also contain soluble microbial products produced by the biomass which are biodegradable. Another point of contention may be the definition of the soluble fraction. While Mamais *et al.* (1993) have hypothesized that the soluble fraction of wastewater contains only RBCOD and inert soluble, Orhon and Doglar (1997) contend that the soluble fraction consists of RBCOD, inert soluble and readily hydrolyzable COD. In this case the RBCOD calculated by the method presented above would result in an overestimation of the RBCOD fraction.

Henze *et al.* (1994) provided a more detailed profile of wastewater by dividing it into its physical, chemical and biological components (Figure 3-4). The readily biodegradable fraction, as described by Ekama *et al.* (1986), is divided into the directly biodegradable and easily biodegradable fraction. The directly biodegradable fraction, *i.e.* fermentation products, comprises of acetic acid and forms the soluble fraction which is non-precipitable. The easily biodegradable fraction comprises VFA's, alcohols, amino acids and simple carbohydrates *i.e.* fermentable substrates. The slowly biodegradable fraction is present in the biomass and the wastewater.

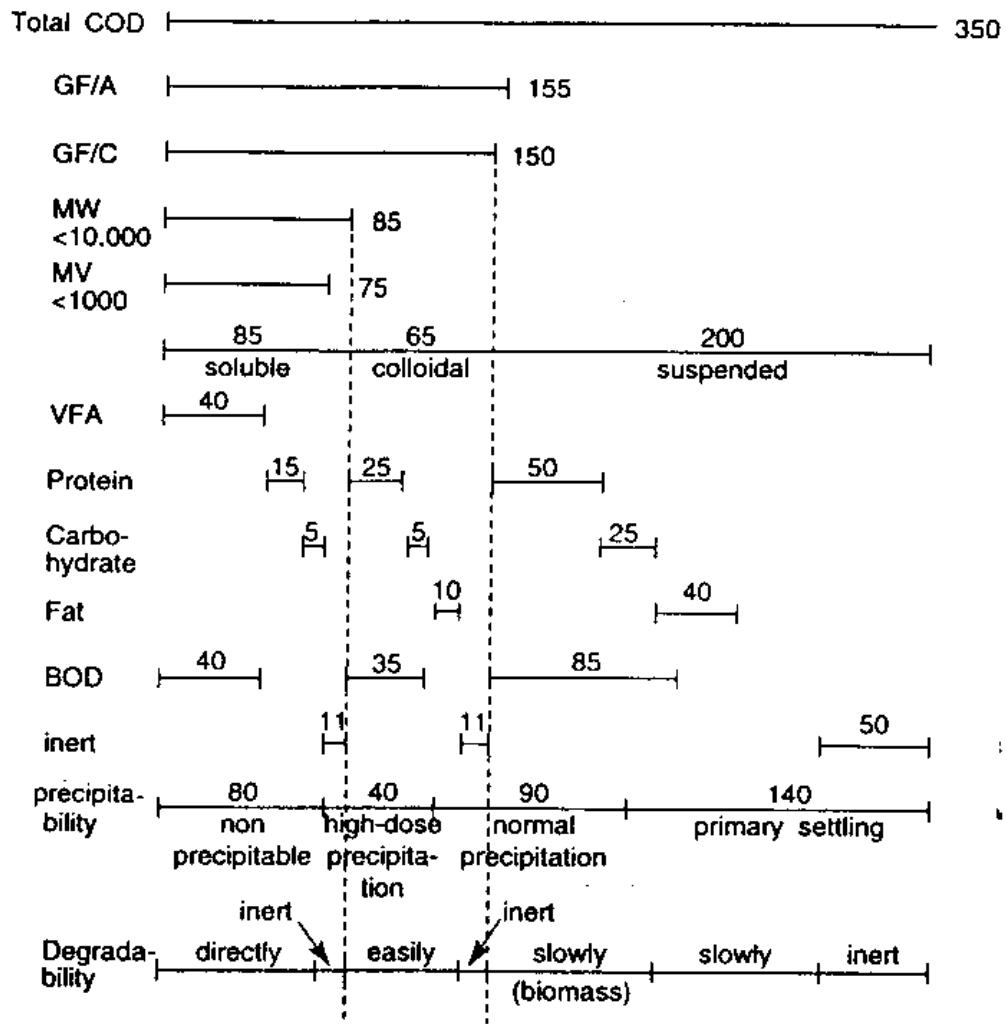


Figure 3-4: Fractionation of organic matter in municipal wastewater in gCOD/m<sup>3</sup> (Henze *et al.*, 1994).

### 3.3.2 Biological methods for wastewater characterization

Several biological methods have been discussed in the literature for the study of biological processes and the use of these methods for the determination of wastewater components (Ekama *et al.*, 1986). Since this study is aimed primarily at the determination of the RBCOD fraction by using the NUR method, this method will be discussed more comprehensively.

#### 3.3.2.1 The OUR method

The aerobic batch test monitors the oxygen uptake rate (OUR) which indicates the amount of oxygen consumption per unit time, per unit reactor volume resulting from microbial activity. The initial OUR, which may stay constant for 1 to 3 h if a suitable substrate to biomass (S/X) ratio is applied, is associated with the utilization of readily biodegradable organic compounds. Once the readily biodegradable compounds are consumed, the OUR drops to a lower level. The lower OUR is associated with the utilization of slowly biodegradable substrate and endogenous respiration products (Ekama *et al.*, 1986; Orhon and Dog˘u, 1997). An example of the observed OUR profile is presented in Figure 3-5.

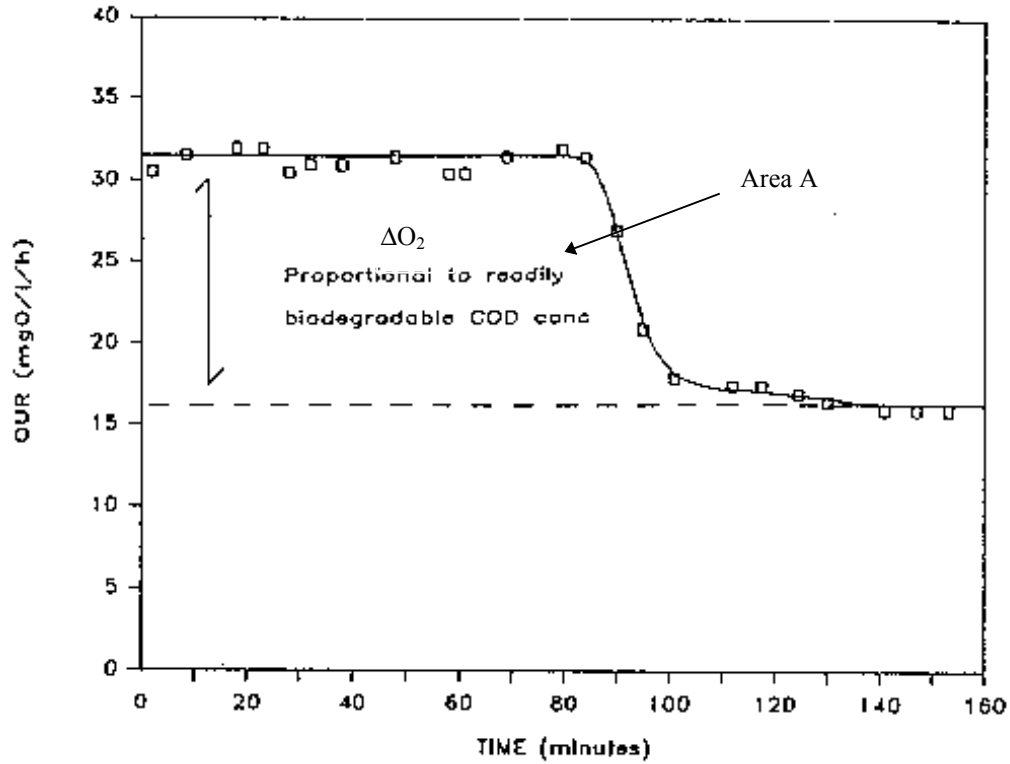


Figure 3-5: An example of an OUR curve in an aerobic batch test used to calculate the readily biodegradable COD fraction (Ekama *et al.*, 1986).

The readily biodegradable COD may be calculated from the following relationship :

$$S_s = [1 / (1 - Y_H)] \times \Delta O_2 \quad (3-6)$$

where  $\Delta O_2$  is the area under the OUR curve (Area A) and  $Y_H$  is the heterotrophic yield coefficient. For municipal wastewaters the stoichiometrically derived value is  $0.64 \text{ mgO}_2/\text{mgO}_2$ , but values of  $0.63$  and  $0.66 \text{ mgO}_2/\text{mgO}_2$  are also used (Ekama *et al.*, 1986; Henze *et al.*, 1995; Orhon and Dog˘og˘ru, 1997).

### 3.3.2.2 The NUR Test

Denitrification kinetics can be studied in continuous or batch systems. The latter system is frequently used to study kinetics as it is simple and easy to operate. The anoxic batch test described by Ekama *et al.* (1986) was referred to as the nitrate utilization rate method (NUR). This test is similar to that of the aerobic batch test (oxygen utilization rate-OUR) method which was first developed for the study of nitrification.

At the start of the NUR test nitrate is added and is monitored over a period of approximately 4 to 5 h. In the absence of oxygen, nitrate serves the same function as oxygen *i.e.* as electron acceptor. In these tests nitrite ( $\text{NO}_2^-$ ) was not considered as little or no nitrite accumulation was found in the samples taken.

Therefore  $\text{NO}_3\text{-N}$  vs time curves were plotted and the equation considered only the nitrate ( $\text{NO}_3^-$ ) concentration.

### ***Theory***

In the anoxic batch test, the nitrate concentration will initially decrease at a constant rapid nitrate utilization rate reflecting the utilization of the readily biodegradable fraction (RBCOD) from the wastewater. This initial rapid rate is analogous to the initial high OUR in aerobic batch systems. The RBCOD consists of simple soluble molecules that can be taken up rapidly by the organisms and metabolized for energy and cell synthesis. The decrease in nitrate concentration is linear. Once the RBCOD from the influent has been depleted, the denitrification rate is reduced to the rate of utilization of slowly biodegradable compounds (SBCOD) which has to undergo hydrolysis of the complex molecules and particulate material before being used. This second rate is analogous to the second OUR slope in the aerobic batch test (see Figure 3-5).

The results from an anoxic batch test can be used to calculate the readily biodegradable fraction (RBCOD) which is related to the decrease in the nitrate (electron acceptor) concentration. This is given by the intercepts with the vertical axis of straight lines drawn through the initial rapid and second slower rates of denitrification *i.e.*  $\Delta\text{NO}_3^-$  (Figure 3-6).

The readily biodegradable COD (RBCOD) can be calculated by using the values derived from a nitrate-nitrogen-time plot and equation 3-7. Equation 3-7 relates the electron acceptor disappearance ( $\Delta\text{NO}_3^-$ ) in the batch reactor to the COD consumed by the heterotrophic organisms.

$$\text{COD} = [2.86/(1-Y_H)] \times \Delta\text{NO}_3 \times [(V_{\text{ww}} + V_{\text{ml}})/V_{\text{ww}}] \quad (3-7)$$

$S_{\text{si}}$  = readily biodegradable COD concentration (mg COD/l)

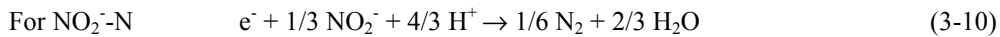
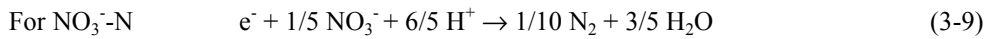
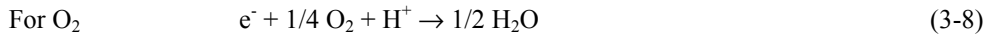
$V_{\text{ww}}$  = the volume of the wastewater (l)

$V_{\text{ml}}$  = the volume of the mixed liquor / sludge (l)

$Y_H$  = yield coefficient (mgCOD/mgCOD)

The yield,  $Y_H$ , is the proportion of substrate (as COD) directly incorporated in the biomass. The term  $1-Y_H$  is related to the electron flow from the organic carbon source to the terminal electron acceptor,  $\text{NO}_3^-$  in this case. It is hypothesized that for every one mg of COD used for growth,  $(1-Y_H)$  mg of COD is used for catabolism. The aerobic yield coefficients of 0.66  $\text{mgO}_2/\text{mgO}_2$  and 0.63  $\text{mgO}_2/\text{mgO}_2$  are also used for anoxic processes. The former value is used by Ekama *et al.* (1986) while 0.63  $\text{mgO}_2/\text{mgO}_2$  is suggested in Henze *et al.* (1995). However, it should be noted that results published by Sperandio *et al.* (1997) and Sozen *et al.* (1998) have suggested that the  $Y_H$  value is lower for anoxic processes (about 14 % lower than the aerobic values).

The value 2.86 in equation 3-7 relates the electron acceptor capacity of nitrate to oxygen. The removal of nitrogen is as a result of biological redox reactions where the biodegradable organic material serves as an electron donor and nitrate (and nitrite if observable) serves the same function as oxygen i.e electron acceptor. The equivalence between oxygen and nitrate is evident from the following half reactions (Van Haandel *et al.*, 1981).



In transferring the electrons from the donor to the acceptor ( $\text{O}_2$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ) there are approximately equal changes of free energy per electron transferred. This is irrespective of the donor or acceptor (McCathy, 1964). From equations 3-8 and 3-9 the transfer of one electron equivalent involves the reduction of 1/4 mol of  $\text{O}_2$ , or 1/5 mol of  $\text{NO}_3^- \text{-N}$ . Thus,

$$32/4 \text{ g O}_2 \equiv 14/5 \text{ g NO}_3^- \text{-N}$$

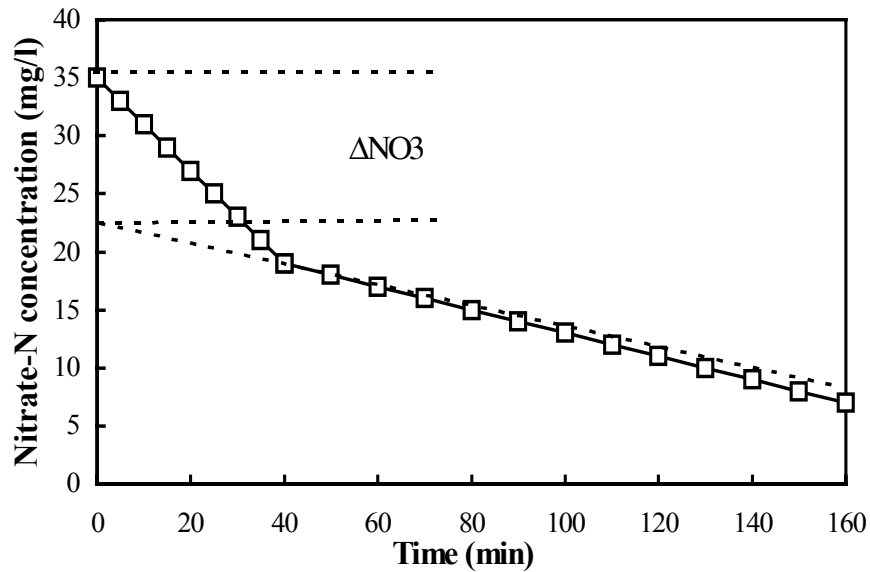
In other words, 1 mg of  $\text{NO}_3^- \text{-N} \equiv 2.86 \text{ mg O}_2$  (or COD). Similarly for nitrites, 1 mg  $\text{NO}_2^- \text{-N} \equiv 1.71 \text{ mg O}_2$ . Thus, stoichiometrically the electron acceptor capacity of nitrate (as N) is 2.86 times that of oxygen.

The term  $2.86 / (1 - Y_H)$  relates to the mass of nitrate utilized to the mass of COD consumed by the heterotrophic microorganisms under anoxic conditions. Accepting a yield coefficient of  $0.63 \text{ mgO}_2/\text{mgO}_2$ , the equation can be simplified:

$$\text{COD (mgO}_2/\text{l)} = 7.7 \times \Delta\text{NO}_3 \times [(V_{\text{ww}} + V_{\text{ml}})/V_{\text{ww}}] \quad (3-11)$$

The readily biodegradable COD fraction ( $f_s$ ) with respect to the total COD (St) is calculated as follows:

$$f_s = \text{COD}_{\text{calculated}} / \text{St} \quad (3-12)$$



**Figure 3-6: Nitrate-nitrogen-time response in an anoxic batch test for determining the RBCOD fraction. The S/X ratio of the test is  $0.37 \text{ gO}_2/\text{gVSS}$  or  $0.25 \text{ gO}_2/\text{gO}_2$  (from Ekama *et al.*, 1986).**

#### ***Evaluation of the NUR method***

The reliability of the RBCOD concentration in wastewaters is of great theoretical and practical importance. This parameter is the only substrate component directly utilized for microbial growth in the current activated sludge models. In addition, it allows for the accurate calculation of the SBCOD which represents the bulk of the influent COD content. This fraction is often the critical model component for the modelling and design of activated sludge systems. However, recently work by several authors have discussed several points of contention with regard to the NUR test and RBCOD determination (Orhon and  $\text{\textcircled{O}}\text{kg}\text{\textcircled{I}}\text{r}$ , 1997 ; Sozen *et al.* 1998 ;  $\text{\textcircled{O}}\text{kg}\text{\textcircled{I}}\text{r}$  *et al.*, 1998 ; Nogueira *et al.*, 1998 and Sperandio *et al.*, 1997).

- ***Yield coefficient,***

One of the major contentions of the NUR method is the assumption that the  $Y_H$  remains the same under aerobic ( $Y_H$ ) and anoxic ( $Y_{HD}$ ) conditions. Theoretical considerations using the energetics of aerobic and anoxic respiration yielded lower yield coefficients ( $Y_{HD} < Y_H$ ) under anoxic conditions.  $Y_{HD}$  values of 0.50 to 0.61 g cell COD /g COD were derived on an energetic consideration basis (Sozen *et al.*, 1998). This was confirmed by comparative tests with NUR and OUR which showed that the NUR derived RBCOD values for municipal wastewaters were consistently higher than the OUR derived values by an average value of 1.14. This 14 % overestimation correlates well with the results from Sperandio *et al.* (1997) using  $\text{CO}_2$  evolution rates for heterotrophic yield determination which showed that the anoxic yield is approximately 15 % (*i.e.*  $0.85 Y_{\text{Haerobic}}$ ) lower than the aerobic one. Tests with acetic acid gave anoxic yields of ca. 0.54 and aerobic yields of 0.66. However, it is equally important to note that Ekama *et al.* (1986) found the NUR and OUR methods to be comparable and that the yield coefficient may vary.

Substrate profiles vs time have been used under the assumption that autocatalytic growth will cause substrate uptake at an increasing rate whereas substrate uptake at a constant rate has been assumed as an indirect evidence of storage. A high yield coefficient suggests the occurrence of storage, accumulation or biosorption. These yield coefficients are likely to change during transient periods in an activated sludge process since competition for substrate is high. High yields ( $0.71 \text{ mgO}_2/\text{mgO}_2$ ) have been calculated for acetate. Normally the yield is  $0.5 \text{ mgO}_2/\text{mgO}_2$  for acetate and for bacteria growing without storage. Thus, the increase in yield was hypothesized to be due to storage (Majone *et al.*, 1999).

- ***Nitrite accumulation and correction***

An equally significant factor is the determination of the amount of electron acceptor utilized. When  $\text{NO}_2^-$  accumulation is appreciable then consideration of only  $\text{NO}_3^-$  is unacceptable. Orhon *et al.* (1997) showed that  $\text{NO}_2^-$  accumulation can occur and this will influence the change in  $\text{NO}_x$  (Figure 3-7). In these cases, the electron equivalence of the RBCOD consumption is best represented by the following expression (Cokgor *et al.*, 1998) :

$$N = \text{NO}_3\text{-N} + 0.6 \text{NO}_2\text{-N} \quad (3-13)$$

The 0.6 conversion factor can best be explained by the oxidation half reactions (3-9) and (3-10) which show that for nitrates 5 electrons are required for complete oxidation to  $\text{N}_2$  while for nitrites only 3 electrons are required. Thus,  $3/5$  is equal to 0.6. Cokgor *et al.*, 1998 showed that for NUR tests the erratic nature of the data could be smoothed to linear trends after  $\text{NO}_2^-$  correction.

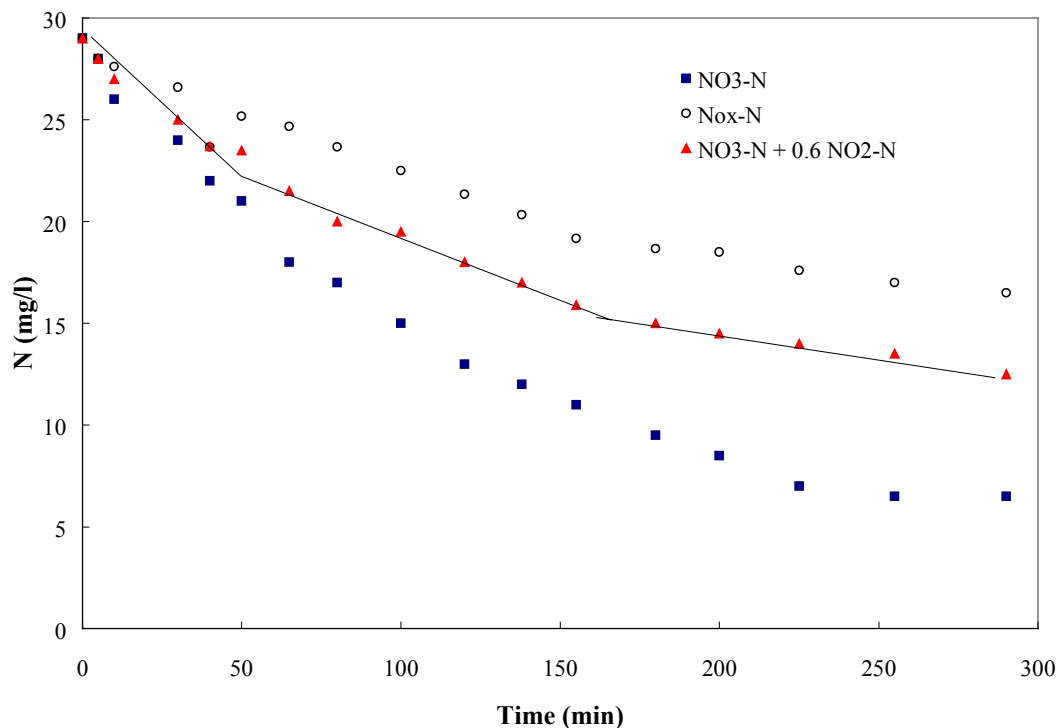


Figure 3-7: Calculation of  $\text{NO}_x$  when  $\text{NO}_2^-$  accumulation occurs (Cokgor *et al.*, 1998).



- ***S/X (F/M) ratios and NUR profiles***

The choice of the initial substrate to biomass ( $S/X_T$ ) ratio for anoxic batch test should provide a defined nitrate-N vs time profile with easily distinguishable breaks (Ekama *et al.*, 1986). This needs to be determined by trial and error. For example, initial S/X (mgCOD / mgVSS) of 0.45 to 0.60 with synthetic substrates were found to be too high for the completion of the NUR tests. Therefore, the initial COD was only partially consumed at the end of the experiment. S/X (COD/VSS) ratios of 0.13 to 0.22 were found to be adequate for appropriate NUR profiles (Jokir *et al.*, 1998).

Tests by Jokir *et al.* (1998) also showed that mixed synthetic substrates were not reduced at a single overall rate but at appreciably different rates. They suggested that the storage of some of the RBCOD may also exert some influence on the differing rates. They also found for a 2 to 3 h test the second change in rate was not necessarily the endogenous respiration rate as was initially expected. Instead the change in rate was linked to the influent COD fraction with a lower biodegradation rate. However, it is important to note that Majone *et al.* (1999) reported that OUR profiles showed a tailing phenomenon after the RBCOD utilization which was considered to be linked to the reuse of storage compounds.

- ***Biological phosphorus (bio-P) removing sludge***

It is known that nitrate has a negative effect on the biological phosphorus removal system since denitrification removes some of the readily biodegradable organic material which is supposed to be taken up and stored in the polyphosphate accumulating organisms (PAO's). Thus, some of the RBCOD is removed (Henze *et al.*, 1997). However, when considering factors which influence the NUR test, the same argument may be made against PAO's *i.e.* the presence of PAO's reduces the amount of RBCOD available to the denitrifiers. Therefore, calculation of the RBCOD based on amount of electron acceptor consumed would result in the underestimation of the RBCOD when a significant fraction of PAO's are present in the activated sludge. Substrate removal mechanisms such as accumulation and storage may also affect the RBCOD determination. Substrate can be taken up by microorganisms and maintained in an unchanged form or transformed to low molecular weight metabolic intermediates. This is referred to as accumulation. In addition, under dynamic conditions storage becomes an alternative mechanism for substrate removal even in the absence of any external limitation for the growth (Majone *et al.*, 1996 ; Majone *et al.*, 1999).

# Chapter Four

## ***EXPERIMENTAL APPROACH AND DEVELOPMENT***

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This chapter defines and justifies the experimental approach adopted for the realization and assessment of the nitrate-N utilization rate batch tests. Chapter 4 is divided into two sections. The first section is essentially a materials and methods section which describes and discusses all the sampling, separation, analytical and experimental techniques employed during this study. The second section deals with the assessment and interpretation of the NUR tests, and describes the experimental conditions of the individual investigations.

### ***4.1 MATERIALS AND METHODS***

#### ***4.1.1 Samples***

- *Sample source* : The raw wastewater from a total of 23 plants were tested. Eighteen of these plants are situated in Europe with 15 of them located in France. Samples from four South African plants, located in the KwaZulu-Natal, Durban region, were also tested. Table I-1 (Appendix I) lists some of the main characteristics of these plants. Since these plants were chosen randomly, the plant capacities and characteristics vary. The plant schematics of 3 plants of small, medium and large capacity are provided in **Appendix I (Figures I-1, I-2, and I-3)**.
- *Sampling procedure* : Samples were collected in 10 l and 2 l plastic containers with little or no headspace volume to minimize aerobic biodegradation of organic substrates. Grab samples of activated sludge were removed from a sampling point near the exit of the biological reactors. Raw wastewater was sampled just after the screening stage but prior to the primary settling tank (when present- see Appendix I ; Table I-1). The samples were collected prior to the internal loading stage. In some cases, samples were collected after the primary settling tank and are discussed in the results as primary settler effluent samples. These samples were grab or composite samples (see Table 4-1). The

raw wastewater samples were placed in a cooler box to lower the temperature and thus, reduce biological activity and sample deterioration during transport.

- *Sample storage* : Once at the laboratory (CIRSEE-Suez-Lyonnaise-des-Eaux, Paris or the University of Natal, Durban), samples were removed so that specific fractions could be characterized by administering different separation techniques such as filtration, centrifugation, and coagulation. Activated sludge and raw wastewater samples, which were used for the NUR batch tests, were stored in smaller 2 l and 1 l containers, respectively with no headspace volume at 4 °C. The duration of the storage period varied between 0 to 1 d but occasionally samples were stored for longer periods of time (Table 4-1).

### 4.1.2 Analysis

- *COD analysis* : Chemical oxygen demand (COD) analysis was done on 2.5 ml samples according to the closed reflux colorimetric method in Standard methods (APHA, 1992). COD samples were acidified with concentrated sulphuric acid and stored at 4°C until analysis. Raw wastewater and sludge was determined within the range 0 to 500 mgO<sub>2</sub>/l. Thus, concentrated raw wastewater samples were diluted 1 in 2 or 1 in 3 while sludge samples were diluted 1 in 10 for all tests (see Appendix II- Section II-1.2.).
- *COD analysis of sodium acetate* : Tri-hydrated sodium acetate was used as a synthetic substrate in NUR batch tests. Since all the organic substrates were represented in electron equivalents *i.e.* COD, it was necessary to do the same for sodium acetate. The theoretical oxygen demand (TOD) was found to be 0.47 x sodium acetate concentration (mg/l). Experimentally, the conversion factor for sodium acetate was found to be 0.43 (see Appendix II - Section II-1.1.2.). For these studies it was decided to use the theoretical value of 0.47 for all conversions of sodium acetate as COD since the COD test is considered to be 90 to 100 % accurate (APHA, 1992).
- *Nitrate, nitrite and ortho-phosphate analysis* : Nitrate (mg NO<sub>3</sub><sup>-</sup>-N/l) and nitrite (NO<sub>2</sub><sup>-</sup>-N/l) were analysed by the cadmium reduction method in an automatic continuous flow system (Skalar). Ortho-phosphate (mgP/l) was also done using the continuous flow system.
- *Total suspended solids (TSS) and volatile suspended solids (VSS)* : These were determined on 100 ml samples which were first centrifuged (14 000 g, 10 min at 4°C). The pellet was dried at 105°C in a glass crucible for 24 h and at 550°C for 2 h (APHA, 1992).
- *Volatile fatty acids analysis* : The volatile fatty acids were analyzed by gas chromatography with the aid of the technical staff at the CIRSEE-Suez-Lyonnaise-des-Eaux laboratory.

**Table 4-1 : List of the plants tested, the type of sampling method adopted and the period of storage of the sample in the laboratory.**

<b>Plant</b>	<b>Sample Type</b>	<b>Storage Time (d)</b>
Asnières-sur-oise	Composite	1
Berwick	Grab	2 to 3
Boran-sur-oise	Grab	0 to 3 *
Boves	Composite	1
Brno	Grab	2
Compiègne	Composite	0
Creil	Composite	1
Crespières	Composite and grab	0
Darvil	Grab	1
Evry	Grab	1
Gouvieux	Composite	1
Kwa-Mashu	Grab	1
Laon	Composite	1
Morainvilliers	Grab	0
Northerns - Durban	Grab	1
Orense	Grab	2
Plaisir	Grab	0
Rostock	Grab	3
Samaritaine	Composite	0
Southerns - Durban	Grab	1
Thiverval-Grignon	Composite	0
Artemps-Seraucourt	Composite	1
Villiers sous St. Leu	Composite	1

composite samples are 24 x 1 h samples ; \*-Several samples were taken at different times in 1996 and 1997 from Boran WTP , thus different storage periods

### **4.1.3 Chemicals and Instrumentation**

The instruments used for the tests and for analysis are listed in Table 4-2.

**Table 4-2: Materials used for batch tests.**

<b>Equipment</b>	<b>References</b>
reactors (2.0 litre)	Biolafitte
temperature control apparatus	Haake K20
redox electrodes	Ingold - type Pt 4805
pH electrodes	Ingold - type 405
mixing apparatus	LSL Biolafitte SA
computer	Compaq 386s/20N (Notebook)
gas used for sparging	Nitrogen - type HP45
spectrophotometer	Beckman DU 64
centrifuge	Sorvall RC-5B

#### **4.1.4 Preparation and determination of COD fractions**

Raw wastewater can be divided into different components depending on the method of separation chosen. In this study, the organic carbon components of wastewater were separated by various physico-chemical methods such as settling, centrifugation, filtration and coagulation. Certain components such as the particulates and truly soluble constituent of wastewater were also calculated based on a combination of theoretical considerations and physico-chemical determinations. These were represented in terms of COD (mgO<sub>2</sub>/l) and are given the abbreviation S- for wastewater and X- for sludge.

- *Non-settleable fraction (S-ns.)* : Raw wastewater was added to an Imhoff cone and allowed to stand for 2 h (Figure 4-1). The COD of the supernatant was then measured. This non-settleable fraction should not be confused with samples taken from the primary settling tanks for NUR tests. The sample was taken directly from the primary settling tanks of the treatment plant and not from the settling tests conducted in the laboratory and is accordingly referred to as primary settler effluent.
- *Centrifuged fraction (S-ce)* : Raw wastewater was centrifuged at 14 000 g for 10 mins at 4°C using 500 ml tubes and the supernatant was then used in the batch tests. Samples were also removed for COD determinations.
- *Filtered fraction (S-f<sub>0.45</sub>)* : Raw wastewater samples were filtered through 0.45µm membrane filters (Sartorius) with a 25 ml syringe for COD determination (S-f<sub>0.45</sub>). Gelman SuporCap 100 (0.45µm) filters were used with the aid of a pump to filter larger volumes which were used as substrates in NUR batch tests.

- *Non-coagulated fraction (S-co)* : Coagulation is regarded as a highly efficient chemical separation technique. The supernatant after coagulation is referred to as the truly soluble fraction. Initial experiments (from February to July, 1997) were conducted by the Jar test method with ferric chloride (300 mg/l). This method was done using the Jar test apparatus. It consists of a 2 min rapid mixing stage (150 rpm), followed by a 10 min slow mixing (40 rpm) stage and a 30 min settling step. However, the 30 minute settling period was found to be insufficient for the complete settling of all flocs. This method was thus modified to include a centrifugation step in order to facilitate floc and soluble fraction separation more rapidly and efficiently.

This method was further modified to make the test more rapid. This was referred to as a rapid coagulation (RC) test. After the addition of ferric chloride the sample bottles were vigorously shaken for 1 min. This was followed by a 5 min centrifugation step (14 000 g at 4 °C). A comparative study was conducted using the two methods outlined below and both were found to be fairly comparable (See Appendix II - Section II.1.3). Thus, the rapid coagulation method was used for all remaining tests from August 1997 to August 1998.

- *Soluble unbiodegradable fraction (S<sub>i</sub>)* : The derivation of this fraction is based on the hypothesis provided by Ekama *et al.* (1986) for the determination of the soluble inert (unbiodegradable) fraction. It is hypothesized that soluble effluent COD is equal to the influent unbiodegradable COD for systems operating at SRT's > 10 d. According to Henze *et al.* (1995) the soluble fraction may be determined by 0.45 µm filtration. Therefore, activated sludge samples taken from systems operating at SRT's > 10 d were filtered through 0.45 µm filters and the the soluble component was classed as the soluble unbiodegradable fraction. This fraction may also be referred to as the filtered soluble sludge fraction (X-f)
- *Particulate fraction (S-p and X-p)* : Particulate COD values were determined by difference as shown in equation (4-1). In the case of wastewater it is the difference between the total raw wastewater concentration (as mgO<sub>2</sub>/l) and the 0.45 µm filtered raw wastewater fraction, while for activated sludge samples it is the difference between the total sludge concentration (X<sub>T</sub>) (mgO<sub>2</sub>/l) and the filtered sludge fraction (X-f). The calculation of these values were necessary to determine the substrate to biomass (S/X) and COD/VSS ratios of sludge.

$$S-p = S_t - S-f_{0.45} \quad (4-1a)$$

$$X-p = X_T - X-f \quad (4-1b)$$

where S<sub>t</sub> represents the total raw wastewater COD concentration.

- *Readily biodegradable fraction (S<sub>s</sub>)* : According to Mamais *et al.* (1993) this fraction may be determined by the difference between the truly soluble fraction (S-co) and the soluble unbiodegradable fraction (S<sub>i</sub>).



*Figure 4-1 : Photo of settling test using Imhoff cone.*

## **4.2 ASSESSMENT AND DEVELOPMENT OF NUR TEST PROTOCOL**

The basic set-up of this test is taken from the procedure provided by Ekama *et al.* (1986). However, some changes have been made to this procedure based on recent work by Sozen and Orhon (1996), and Sozen *et al.* (1998) (see **Chapter 3**). All experimental conditions and results are presented in **Appendices III, IV and V**.

### **4.2.1 Batch test set-up**

Denitrification kinetics were conducted in batch reactors which were continuously stirred and temperature controlled at 20°C (Figure 4-2 and 4-3). The total reactor volume was 2 l with a working volume of 1.4 to 1.6 l. Nitrogen (N<sub>2</sub>) gas was used to maintain an oxygen-free environment. At the start of the experiment, N<sub>2</sub> was bubbled through the liquid to remove trace amounts of oxygen (O<sub>2</sub>) (Figure 4-2 ; No.1). During sampling, nitrogen gas was passed over the liquid to minimise foaming, pH increase and to prevent oxygen introduction (Figure 4-2 ; No.2). Each reactor contained a gas outlet port which passed through a

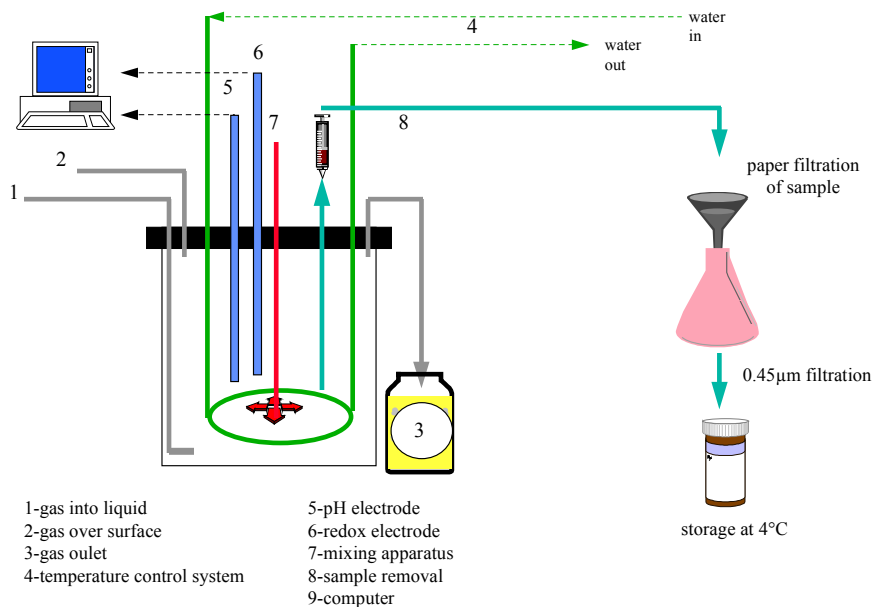
water trap to avoid pressure increase due to nitrogen and carbon dioxide (CO<sub>2</sub>) production. The contents of the batch reactor were mixed throughout the duration of the test in order to ensure homogeneity (Figure 4-2 ; No.7). The duration of the tests was between 4 to 6 h but initial tests were run for longer periods (8 h). The materials used for the batch kinetics are listed in Table 4-2. A step by step procedure of the NUR test is presented in the Appendix II, II.3.5.

#### 4.2.1.1 pH

During denitrification the pH increases (Figure 4-4 ; (B)). This results in nitrite accumulation. Thus, controlling the pH at 7.5 is important for optimizing the NUR procedure (Figure 4-2 ; No.5) (Figure 4-3). The pH was regulated at  $7.5 \pm 0.1$  with 1M hydrochloric acid and 0.75 M sodium hydroxide (Figure 4-4 ; (A)). The pH was monitored with Ingold electrodes (Figure 4-2 ; No.5) connected to a computer (Figure 4-2).

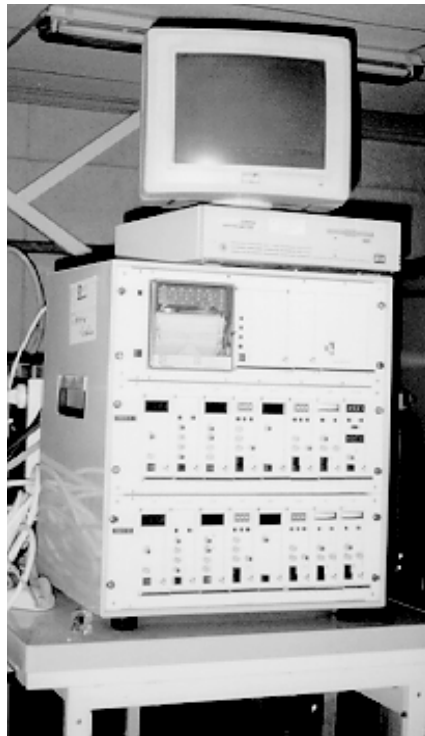
#### 4.2.1.2 Redox

Redox was tested as a monitoring and analytical tool (see Appendix II, II.3.1). It was found to be more useful as a monitoring tool to determine oxygen ingress or nitrate depletion ((A) in Figure 4-5). A typical redox curve consisted of an initial rapid drop in redox, followed by a stable redox profile. A further rapid drop in redox represents the complete utilization of nitrate in the reactor and the onset of anaerobiosis ((B) in Figure 4-5).



**Figure 4-2: Illustration of batch experimental apparatus used for nitrate-N utilization rate tests.**





*Figure 4-3: Photographs of batch reactors and data capture set-up for denitrification tests.*

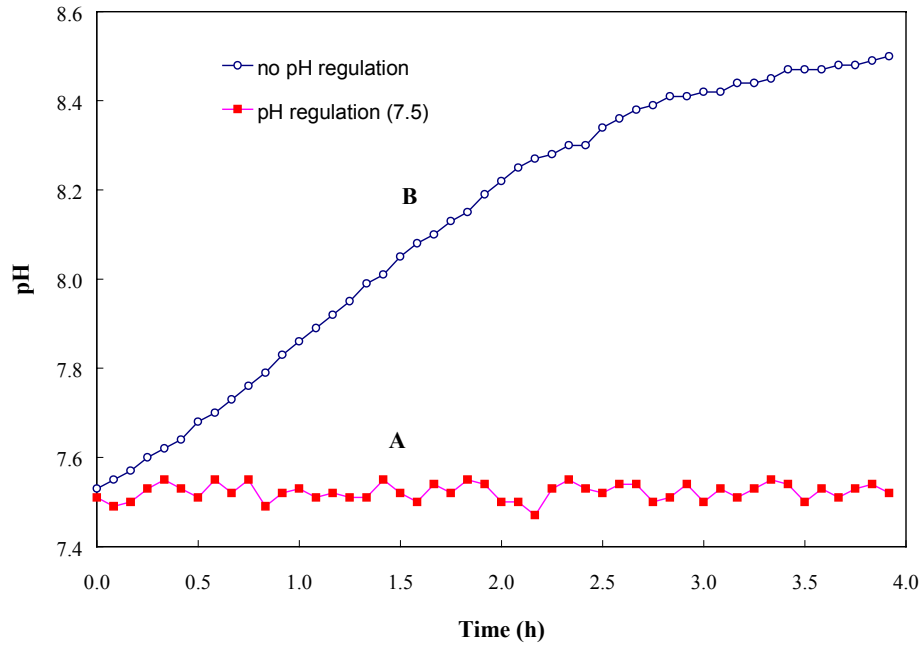


Figure 4-4: Examples of pH curves regulated at pH  $7.5 \pm 0.1$  (A) and unregulated (B).

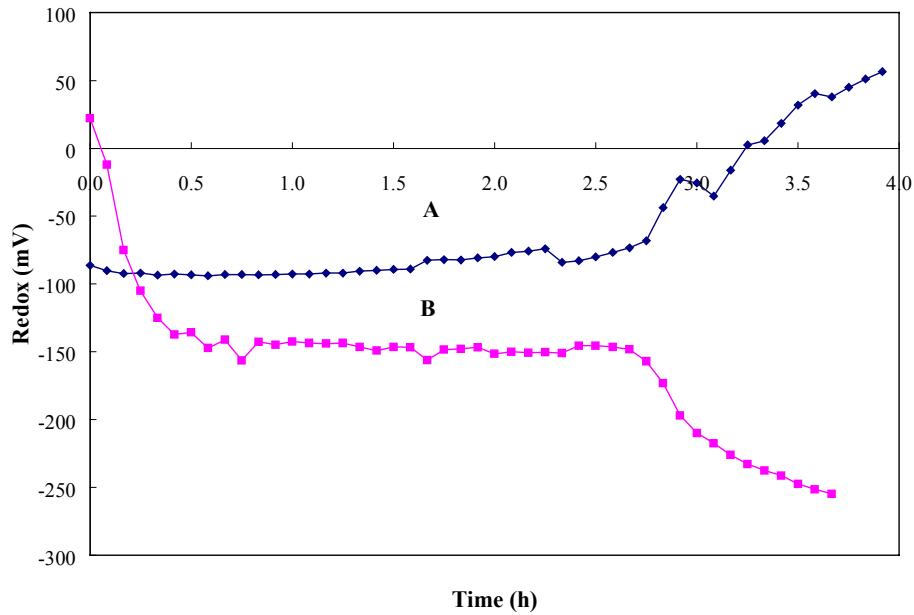
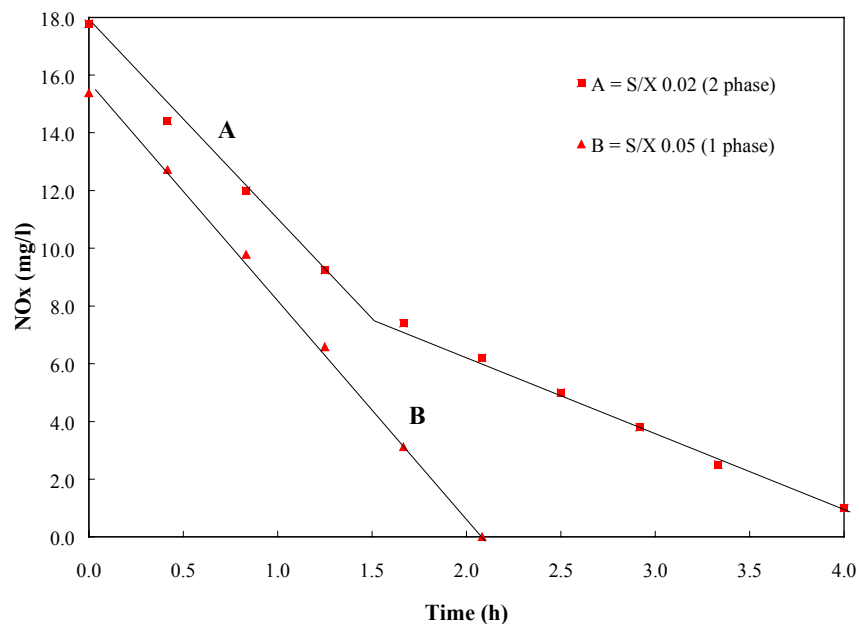


Figure 4-5 : Redox curves : (A) showing non-ideal anoxic conditions due to  $O_2$  ingress and (B) showing a typical redox profile with complete nitrate utilization.

### 4.2.1.3 Choice of S/X ratio

The choice of substrate to biomass ratio (S/X) forms an important part of the NUR test as it is one of the factors which defines the nature of the NUR profile. High S/X ratios do not realistically represent conditions at treatment plants which generally operate at low S/X ratios. However, S/X ratios which are too low may result in substrate limitation.

- **The S/X ratio for acetate** : Four S/X ratios, 0.02 ; 0.05 ; 0.1 and 0.2 were tested for acetate. A S/X ratio of 0.02 was found to reveal two phases for the 4 h batch test while S/X ratios, 0.05 to 0.2 revealed a single phase. The denitrification profiles for tests done at S/X ratios, 0.05 and 0.2 are plotted in Figure 4-6. The S/X ratio, 0.02 was chosen for acetate since the 2 phase profile provides a second slower rate which allows for the calculation of the amount of acetate (as COD) consumed during denitrification *i.e.* the acetate mass balance ((A) in Figure 4-6). The method of calculation is presented in section 4.2.6.



**Figure 4-6 : Different S/X ratios (0.02 and 0.05) for acetate showing 1 (B) and 2 (A) phase profiles during the NUR test.**

- **The S/X ratio for raw wastewater** : Initially the S/X ratios for raw wastewater were based on the total COD concentration (St). This proved to be unfavourable as highly concentrated wastewaters with low S-f<sub>0.45</sub> COD concentrations gave unsuitable curves *i.e.* flat curves with indistinguishable breaks. Therefore, it was decided to base the substrate to biomass ratios on the S-f<sub>0.45</sub> COD values. S-f<sub>0.45</sub>/X ratios > 0.02 (*i.e.* with a S-f<sub>0.45</sub> COD concentration > 50 mgO<sub>2</sub>/l) gave more suitable curves.

Occasionally, however, a situation may arise where even though the S/X ratio is correct, the NUR profile will be unsuitable due to the biodegradability of the soluble compounds.

Thus, by knowing the concentration required in the batch reactor, it is possible to calculate the volume of raw wastewater required by using equation 4-2, below.

$$V_{ww} = \frac{C_R \times V_T}{C_M} \quad (4-2)$$

$V_{ww}$  = volume of wastewater that is required to avoid RBCOD limitation (l)

$C_R$  = refers to the concentration of soluble COD required (*i.e.* > 50 mgO<sub>2</sub>/l)

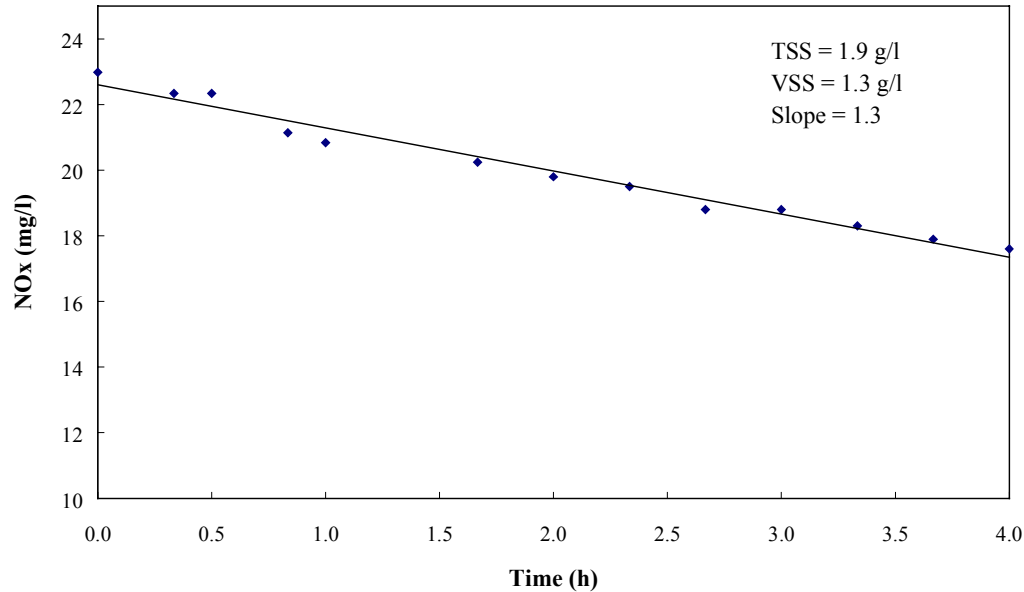
$V_T$  = total working volume of the reactor (l)

$C_M$  = measured S-f<sub>0.45</sub> COD concentration (mgO<sub>2</sub>/l)

### 4.2.2 Examples of NOx profiles

This section shows the typical NOx profiles obtained for NUR tests carried out with different substrates. Some atypical observations are also discussed.

- **Endogenous denitrification profiles** : A single linear phase was observed from batch tests with only sludge *i.e.* no exogenous substrate was added (Figure 4-7). In this case the bacteria use the substrates provided by endogenous respiration and could also use the slowly biodegradable COD attached to the sludge.



*Figure 4-7 : An example of a typical endogenous denitrification profile.*

- **Raw wastewater** : Two types of profiles were observed for raw wastewater during the 6 h batch test (Figure 4-8). Some tests with raw wastewater revealed 2 phases while others produced 3 phases. The first phase in both curves (A) and (B) is due to the utilization of the RBCOD fraction of wastewater. For profile (A) the second phase is due to the utilization of SBCOD from the influent as well as endogenous respiration products. However, sludge samples were taken from plants which were said to be operating at SRT's > 10 d. Therefore, the contribution of adsorbed SBCOD should be small. Phase 2 of (B) is thought to reflect the utilization of readily hydrolyzable COD of the influent. Phase 3 of (B) is considered to be due to the utilization of SBCOD of the influent wastewater as well as endogenous respiration products.

Sometimes, however, atypical NOx vs time profiles were observed revealing 4 phases (Figure 4-9). Since the first phase was extremely rapid and of short duration (10 to 30 min) it was decided to combine the first two phases of these curves as that occurring from the utilization of readily biodegradable COD. In this case, phase 3 and 4 are associated with readily hydrolyzable COD and SBCOD (biomass and influent) utilization, respectively.

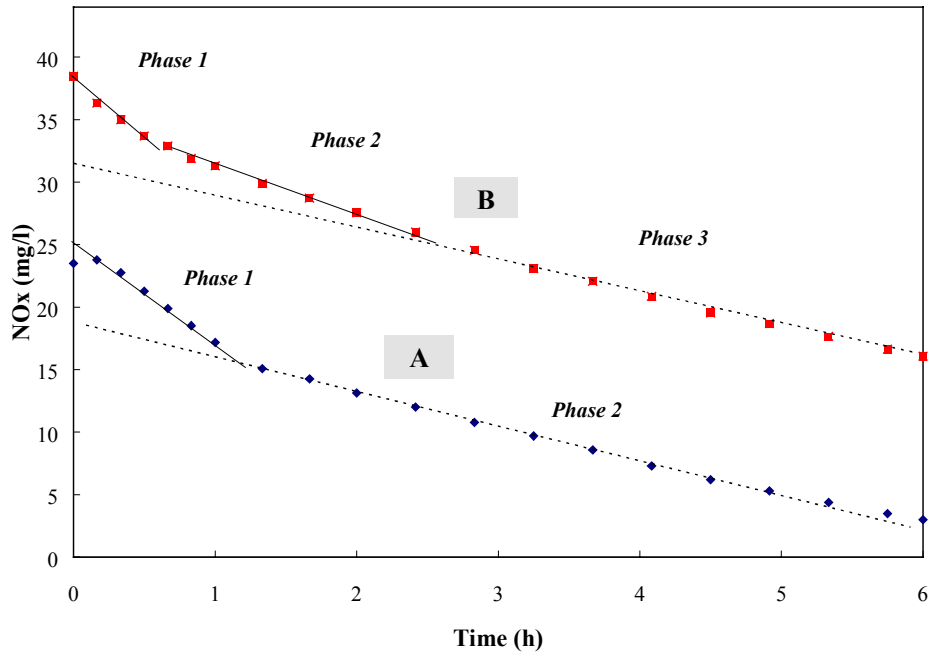


Figure 4-8: Examples of typical NUR tests with raw wastewater as substrate (A and B : wastewater and sludge from Crespi@res and Gouvieux WTP, respectively).

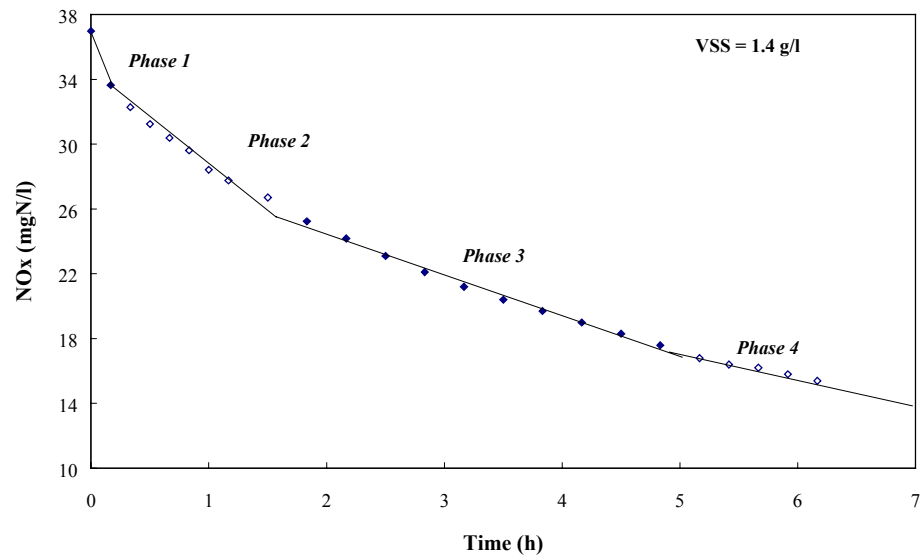
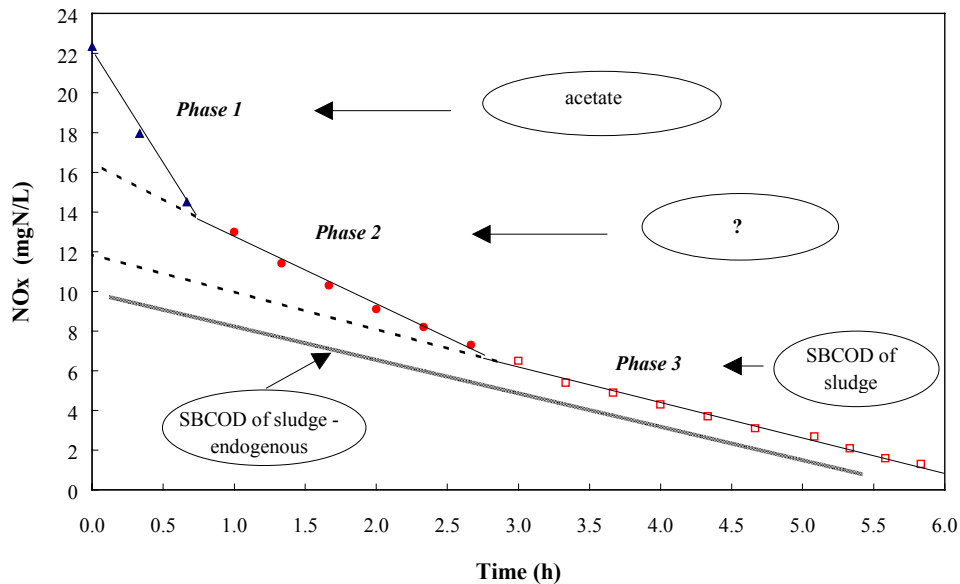


Figure 4-9 : An example of an atypical denitrification profile with wastewater (centrifuged) and sludge samples from Rostock WTP (17/03/97).

- Acetate** : Based on the S/X ratio adopted, 2 phases were expected for acetate-fed reactors. However, as was the case with raw wastewater, both 2- and 3-phase profiles were observed. For 2-phase profiles, the first phase is due to acetate utilization while phase 2 is due to the utilization of endogenous substrates provided for by bacterial death and lysis as well as SBCOD that may be attached to the biomass or released internally by the bacteria e.g. storage compounds. Three-phase profiles, however, presents a more complicated scenario. Phases 1 and 3 may be explained in terms of the utilization of acetate, and endogenous substrate and SBCOD, respectively (Figure 4-10). Phase 2 however, may be hypothesized to be due to one of 2 factors : i) the utilization of pre-existing storage compounds during denitrification, or, ii) the utilization of stored compounds that had been formed from the acetate added to the reactor. in this case, bacteria like denitrifying polyphosphate accumulating organisms converted some of the acetate to storage compounds which were subsequently re-utilized during denitrification for energy and growth. The second hypothesis was chosen since endogenous denitrification profiles for Rostock (17/03/97) revealed a single phase which suggested that the second phase may be acetate-linked (Figure 4-10). This reaction is therefore thought to be triggered by the presence of acetate and possibly readily biodegradable COD. This aspect will be discussed more comprehensively in Chapter 6.



**Figure 4-10** : NUR profiles for acetate-fed reactors revealing 3 phases(taken from tests with Rostock samples, 17/03/97).

- Particulate profiles** : A single phase was also observed for reactors fed with only the particulate fraction of the wastewater. This single phase observation appears to be linked to the S/X ratio (see **Appendix II - Section II.3.4.2.**). These experiments also showed that it was correct to label the second phase as readily hydrolyzable COD (RHCOD) since reactors fed with only the particulate

fraction of raw wastewater produced rates closer to the final rates observed (phase 3) in the 6 h batch test for reactors fed with raw wastewater *i.e.*  $\cong 1.5$  to  $1.2 \text{ mgN/gVSS.h}$ .

### 4.2.3 Calculation of NO<sub>x</sub> and N

When substrate concentrations (COD and NO<sub>3</sub><sup>-</sup>) are not limiting denitrification follows zero order reaction kinetics. Since nitrites are sometimes detected it is necessary to take these concentrations into consideration. For these studies the denitrification profiles gave two important pieces of information. By following the NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> concentration it is possible to determine the change in N concentration (rate) as well as the change in NO<sub>x</sub> concentration (for biodegradable COD calculation). These may be calculated in two ways:

1. For denitrification rates : 
$$N = \text{NO}_3\text{-N} + \text{NO}_2\text{-N} \quad (4-3)$$

2. For biodegradable COD : 
$$\text{NO}_x = \text{NO}_3\text{-N} + 0.6 \times \text{NO}_2\text{-N} \quad (4-4)$$

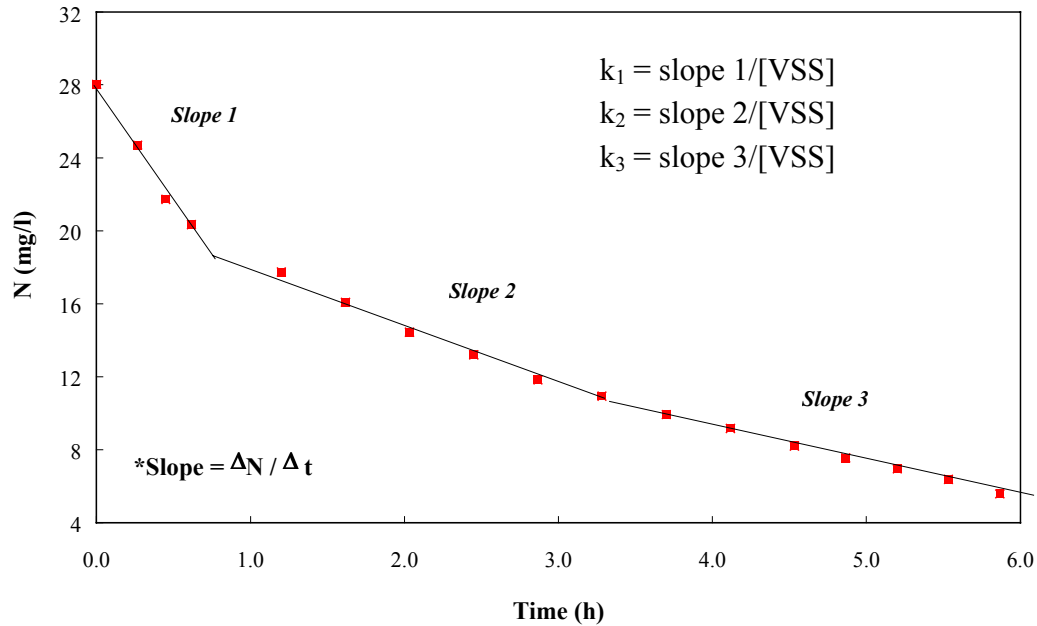
Equation 4-3 is based on the nitrogen balance and is used to calculate denitrification rates. For the calculation of COD, however, it is necessary to express NO<sub>x</sub> in terms of an electron balance. This aspect was discussed in **Chapter 3**.

### 4.2.4 Calculation of maximum specific denitrification rates

The N concentration (*i.e.* NO<sub>3</sub>-N + NO<sub>2</sub>-N) is used for calculations based on the assumption that no NO or N<sub>2</sub>O intermediates are accumulated. The specific denitrification rates can be calculated from the slope of the linear parts of the N utilization curve (Figure 4-11 ; equation 4-5), using the VSS concentration (g/l) as the reference for the biomass concentration *i.e.* the specific denitrification rate is given by the slope of the linear segment divided by the X<sub>VSS</sub> concentration (equation 4-5). Since more than a single linear phase is observed the rates, k', are given the subscripts k<sub>1</sub> , k<sub>2</sub> and k<sub>3</sub> (Figure 4-11).

$$k' = \text{slope}' / [X_{VSS}] \quad (4-5)$$





**Figure 4-11 : Calculation of specific denitrification rates.**

#### 4.2.5 Calculation of RBCOD and RHCOD

With reference to the readily biodegradable fraction (RBCOD), this is calculated by determining the  $\Delta\text{NO}_x$  1 value. This is given by the difference between the initial  $\text{NO}_x$ -N concentration (A) and the extrapolated value (B) drawn from the second phase *i.e.*  $\Delta\text{NO}_x$  1 = A-B (Figure 4-12)

A second biodegradable fraction, the readily hydrolyzable fraction can also be determined for kinetics revealing three phases. The second  $\Delta\text{NO}_x$  (*i.e.*  $\text{NO}_x$  2) can be determined by the difference between values determined by the extrapolation of phases 2 (B) and 3 (C) *i.e.*  $\Delta\text{NO}_x$  2 = B-C (Figure 4-12). In this case, it is assumed that the second phase is due to the utilization of RHCOD of wastewater since the phase is of short duration (2-3 h) and the fraction of COD calculated is significantly smaller than that cited in the literature for SBCOD (*i.e.* 30 to 60 % of the total COD concentration).

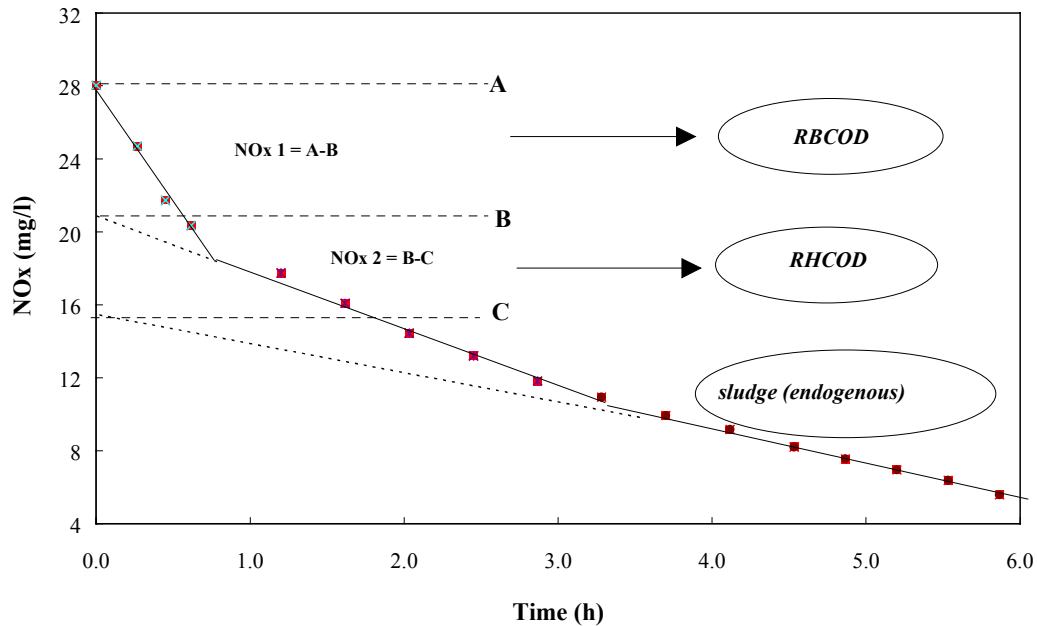
These  $\Delta\text{NO}_x$  values,  $\Delta\text{NO}_x$  1 and  $\Delta\text{NO}_x$  2, can then be substituted in equation 3-8 to calculate the RBCOD and RHCOD, respectively. In this study for raw wastewater, the aerobic yield coefficient, 0.63 ( $\text{mgO}_2/\text{mgO}_2$ ) was used.

$$\text{COD (mgO}_2\text{/l)} = [2.86/(1-Y_H)] \times \Delta\text{NO}_x \times (V_t/V_{ww}) \quad (\text{see eqn 3-8})$$

$V_{ww}$  volume of wastewater that is required to avoid RBCOD limitation (l)

$V_t$  total working volume of the reactor (l)

$Y_H$  is the yield coefficient ( $\text{mgO}_2/\text{mgO}_2$ )



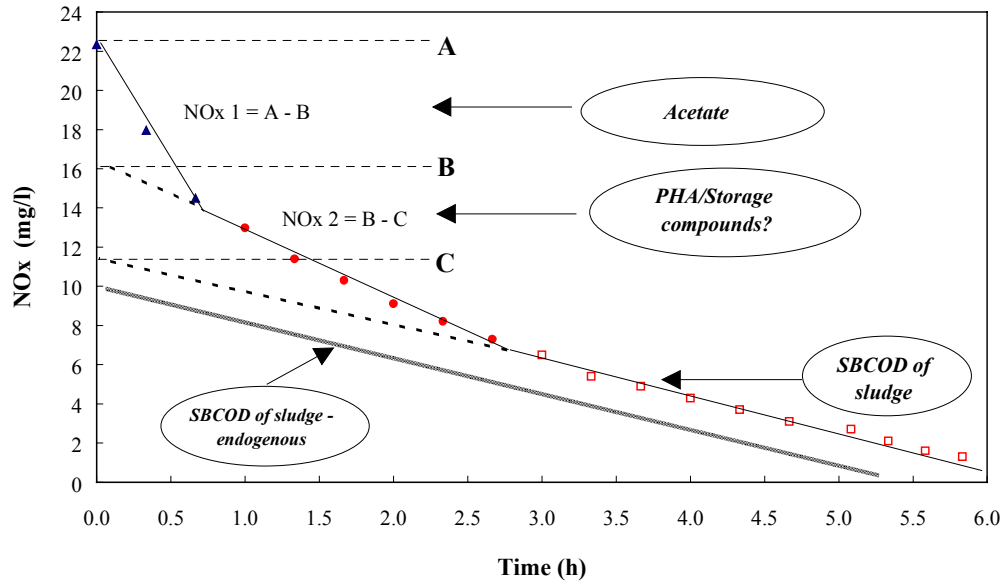
**Figure 4-12 : Interpretation of 3-phase NUR profiles with raw wastewater as substrate.**

#### 4.2.6 Calculation acetate consumption

As discussed previously, acetate-fed reactors also revealed 2 or 3 phases. Since a known concentration of acetate was added, it was possible to calculate the amount of acetate (as COD) consumed to determine if all the acetate could be accounted for. Thus,  $\Delta\text{NO}_x$  1 and  $\Delta\text{NO}_x$  2 were calculated in the same manner as described for raw wastewater and the acetate consumed was determined by using equation 4-6. This is the same basic equation used for the calculation of RBCOD and RHCOD, except that the dilution factor was removed since the concentration of acetate (as COD) added to the reactor was known. In these studies, yield coefficients ( $Y_H$ ), 0.5 and 0.63 ( $\text{mgO}_2/\text{mgO}_2$ ), were used to calculate the acetate consumed. The acetate recovery or mass balance (%) can then be calculated by equation 4-7. For 3-phase profiles, acetate recovery 1, and acetate recovery 2 may be calculated based on  $\Delta\text{NO}_x$  1 and  $\Delta\text{NO}_x$  2, respectively (Figure 4-13).

$$\text{Acetate (mgO}_2/\text{l)} = [2.86/(1-Y_H)] \times \Delta\text{NO}_x \quad (4-6)$$

$$\text{Acetate Recovery (\%)} = [\text{Acetate}_{\text{calc}}] / [\text{Acetate}_{\text{added}}] \times 100 \quad (4-7)$$



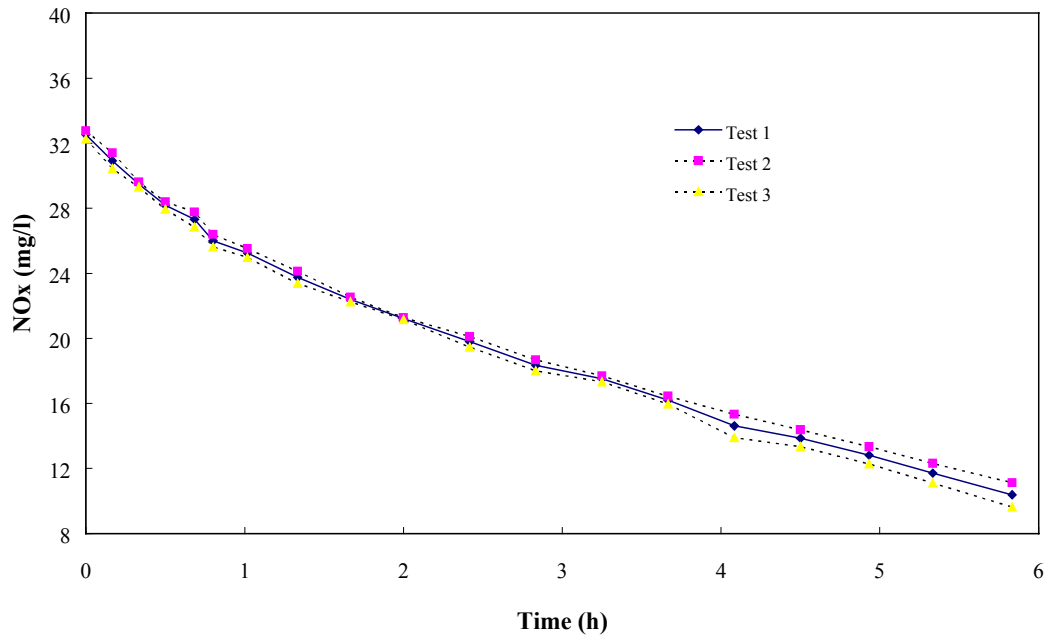
**Figure 4-13 : A NO<sub>x</sub>-N-time profile with acetate revealing 3 phases of biodegradability and an endogenous curve (results from Rostock 17/03/97)**

#### 4.2.7 Reproducibility of data obtained from NUR tests

The reproducibility experiment was carried out to determine the experimental precision of the NUR batch test procedure for the determination of the :

1. biodegradable COD fractions, and
2. denitrification rates.

Three replicate batch tests were carried out under identical conditions with sludge and wastewater from Boran-sur-oise Wastewater Treatment Plant. NO<sub>x</sub> vs time profiles obtained in the 3 separate experiments conducted are presented in Figure 4-14. These curves showed that repeatability of the curves was good. Table 4-3 shows that the RBCOD and RHCOD fractions calculated from these tests were reproducible at  $25 \pm 1\%$  and  $11 \pm 1\%$ , respectively. The coefficient of variation (SD / mean) on the RBCOD and RHCOD in the reactors were found to be 5 % and 8 %, respectively. The denitrification rates,  $k_1$ ,  $k_2$ , and  $k_3$ , were also found to be fairly repeatable with the coefficients of variation < 10% (Table 4-4). These results show that the RBCOD, RHCOD and denitrification rates can be ascertained from single batch tests with reasonable confidence in the method.



*Figure 4-14 : Precision of 3 replicate batch NUR tests.*

*Table 4-3 : Repeatability of RBCOD and RHCOD calculations from 3 replicate NUR batch tests.*

		Test 1	Test 2	Test 3	mean	SD	CV (%)
RBCOD	mgCOD/l	257	253	231	247	11	5
	fraction of St (%)	26	25	23	25	1	5
RHCOD	mgCOD/l	100	119	101	107	9	8
	fraction of St (%)	10	12	10	11	1	8

The biodegradable fractions (RBCOD and RHCOD) are given as a % of the total raw wastewater concentration (St).  
(SD - standard deviation ; CV - coefficient of variation)

**Table 4-4: Repeatability of denitrification rates (mgN/gVSS.h) from 3 replicate NUR batch tests.**

Rates	Test 1	Test 2	Test 3	mean	SD	CV (%)
k1	6.1	7.1	7.4	6.9	0.6	8
k2	2.9	3.3	3.2	3.1	0.2	5
k3	2.4	2.6	2.6	2.5	0.1	4

(SD - standard deviation ; CV - coefficient of variation)

## 4.2.8 Experimental conditions for NUR tests

### 4.2.8.1 The influence of storage time on wastewater characteristics

Raw wastewater and activated sludge samples were collected from Evry Wastewater Treatment Plant to determine the influence of storage time on wastewater characteristics. The wastewater and sludge were separated into 3x 2 l containers with no headspace and stored at 4°C. Three sets of experiments were carried out. The first set was conducted on the day the samples were collected from Evry Wastewater Treatment Plant (0 h or Day 0), while the second and third sets were conducted with raw wastewater and sludge that had been stored for 24 h (Day 1) and 72 h (Day 3), respectively. The wastewater and sludge were characterized by physical, chemical and biological methods on day 0, 1 and 3.

The biological tests were conducted with raw wastewater (*i.e.* sampled before the primary settler), primary settler effluent samples and the ‘*endogenous*’ (*i.e.* sludge only) carbon as substrates. The working volume for the batch tests was 1.41 l consisting of 1.0 l sludge settled and 0.75 to 0.70 l and 0.65 to 0.7 l raw wastewater. The substrate / biomass ratios were similar for the three sets of tests.

### 4.2.8.2 The influence of the sludge acclimatization on wastewater characterization tests

It may sometimes be necessary to characterize a particular wastewater with an external sludge sample since not all plants are capable of denitrification and sludge from enhanced biological phosphorus removal (EBPR) plants may be unsuitable due to a higher proportion of polyphosphate accumulating bacteria. Table 4-5 provides a matrix of the three experiments done to investigate how sludge source may influence wastewater characterization. Raw wastewater samples from Boran and Gouvieux were tested against the acclimatized sludge (*i.e.* sludge taken from the same plant as the wastewater being tested) and the unacclimatized sludges (*i.e.* sludges taken from a different plant to the wastewater source). Three tests

were conducted with raw wastewater from Boran and one from Gouvieux. The total working volume of the batch reactors was 1.4 l, with 1.0 l of sludge and 0.25 to 0.3 l raw wastewater. (see Table 4-5).

**Table 4-5 : Matrix of the experiments conducted with acclimatized and unacclimatized sludges.**

Test	Rw source	Vol. added *	Activated sludge					
			Boran	Crespières	Artemps	Creil	Compiègne	Gouvieux
22/08/97	Boran	0.30	x	x	x	-	-	-
19/11/97	Boran	0.25	x	-	-	-	-	x
19/11/97	Gouvieux	0.30	x	-	-	-	-	x

\*- raw wastewater volume ; - no test conducted

#### 4.2.8.3 Acetate utilization

Activated sludge sampled from the different wastewater treatment plants were tested with acetate to determine the accuracy of the NUR test in determining the RBCOD concentration. Acetate was added at concentrations of 50 to 70 mg/l as COD at the start of the tests (the exact concentrations for each experiment are shown in **Appendix III**). Experiments with acetate were deliberately conducted at low COD/N and S/X ratios so that subsequent slower rates could be observed and the  $\Delta\text{NO}_x$  could be determined. A preliminary study with acetate showed no significant changes in maximum denitrification rates for S/X and COD/N ratios between 0.02 to 0.2 and 2.0 and 20, respectively (**Appendix II, II.3.4.1**).

#### 4.2.8.4 The influence of EBPR sludge on wastewater characterization tests

Two biological phosphorus removal plants, Compiègne and Thiverval, were selected to study this phenomenon of readily biodegradable COD (RBCOD) loss to denitrifying polyphosphate accumulating organisms and polyphosphate accumulating organisms during NUR tests. Compiègne is a large plant which has a capacity of 220 000 population equivalents (p.e.) whilst Thiverval has a capacity of 12 000 p.e (see **Appendix I -Table I-1**). Four tests were conducted with sludge and wastewater from Compiègne over a period of one week, and two tests were conducted with sludge and wastewater from Thiverval over a 2 week period. Sludge from Boran Wastewater Treatment Plant was used for both studies as a non biological phosphorus removing (non-EBPR) sludge. The sludge and wastewater samples were grab and composite samples, respectively. The initial soluble COD concentration within the reactors ranged between 65 to 80 and 30 to 40  $\text{mgO}_2/\text{l}$  for Compiègne and Thiverval, respectively.

#### 4.2.8.5 Wastewater characterization tests

Several different wastewaters were tested between July 1996 and July 1998. **Appendix IV** gives the volumetric additions for the different plants tested and the dilution factors ( $V_t / V_{ww}$ ). These are

important for the calculation of the RBCOD and RHCOD fractions using the NUR method. In addition, all the raw data from the batch tests carried out with samples from several different plants are listed in **Appendix IV**. The COD fractions of the different wastewaters and sludges were also characterized by physico-chemical methods *i.e.* centrifugation, filtration and coagulation. These results are presented in Chapter 7.

# ***Chapter Five***

## ***FACTORS INFLUENCING WASTEWATER CHARACTERISTICS***

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This chapter discusses experiments which were aimed to understand the factors which may contribute to inaccuracies or variations in wastewater characteristics determined by the NUR method. These factors include the influence of storage on wastewater samples prior to the NUR tests, and the impact of acclimatization of activated sludge on the NUR data derived or calculated. A third study looked at different separation techniques for raw wastewater and their influence on the readily biodegradable COD results. Weekly and annual variations in the wastewater characteristics are also presented. The data for these tests are given in **Appendix IV**.

### ***5.1 THE INFLUENCE OF STORAGE TIME ON WASTEWATER SAMPLES***

Ideally, batch tests for the purposes of wastewater characterization should be carried out as soon as possible after sampling. However, not all treatment plants are equipped with or situated near laboratories. In such cases, storage of wastewater and sludge for experimental purposes is necessary.

In this study, the samples were stored for 17 to 24 hours at 4°C until the tests could be performed at the CIRSEE laboratory. In addition, if samples were collected from wastewater treatment plants that were located far from the laboratory then the samples had to be stored for longer periods (*i.e.* 2 to 3 days). Therefore, three main factors were investigated : (1) change in COD measurements, (2) change in the biodegradable fractions, RBCOD and RHCOD, and (3) the impact of storage on denitrifying activity.

Raw wastewater, primary settler effluent and sludge (mixed liquor suspended solids) samples were collected from Evry WTP (24/11/97). Three sets of NUR experiments were done on day 0 (0 h) (Appendix IV-E (24/11/97)), day 1 ( after 24 h storage)( Appendix IV-E (25/11/97)), and day 4 (after 72 h storage) (Appendix IV-E (27/11/97)). Each set consisted of 3 reactors operating under identical conditions but with different substrate types. The substrates tested were raw wastewater. The third reactor monitored endogenous denitrification *i.e.* sludge without any substrate addition (Appendix V-E (24/11/97 to 27/11/97)).



### 5.1.1 Chemical analysis of sludge and wastewater samples

As discussed earlier, two types of raw wastewater samples were collected from Evry WTP for these tests. Accordingly Table 5-1 provides the results from COD analysis conducted on both raw and unsettled primary settler samples on day 1, day 2, and day 4. The COD analysis is divided into total COD (St), and COD after settling (2 h) (S-ns), centrifugation (S-ce), filtration (S-f<sub>0.45</sub>) and coagulation (S-co).

COD measurements showed that the raw wastewater and the primary settler effluent samples did not undergo any significant modifications during storage at 4 °C for 24 and 72 h. It would appear that storage under the conditions outlined in section 4.2.8.1 resulted in no significant change in the wastewater quality. This is probably due to the fact that COD measurements give a representation of the global change in the wastewater rather than the change in the biodegradability of the fractions. It is nevertheless a useful first step when assessing wastewater changes.

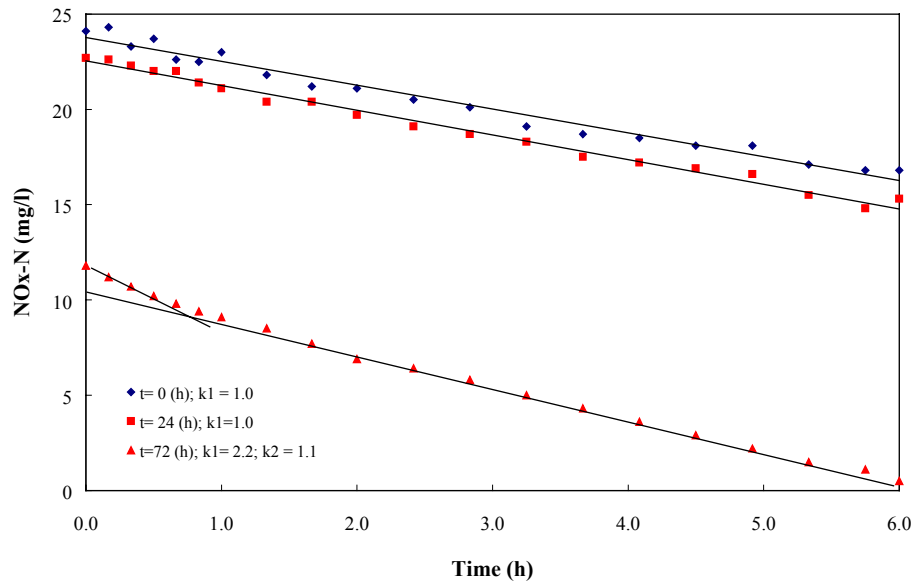
**Table 5-1: Wastewater characteristics after storage.**

Parameters	raw wastewater			primary settler effluent		
	t0 (h)	t24 (h)	t72 (h)	t0 (h)	t24 (h)	t72 (h)
Total COD (St)	660	684	684	329	333	320
Non-settleable COD (S-ns)	377	406	383	320	329	304
Centrifuged COD (S-ce)	208	211	195	201	189	182
Filtered COD (S-f <sub>0.45</sub> )	211	262	214	205	198	195
Non-coagulated COD (S-co)	137	144	153	122	109	118

### 5.1.2 Determination of COD contribution from sludge

Monitoring of endogenous denitrification profiles and rates were important as it allowed for the observation of any biological changes in sludge during storage (0 to 72 h) *i.e.* COD contribution from the sludge which may arise from the utilization of storage compounds. Figure 5-1 shows the denitrification profiles determined from tests done on day 0, 1, and 4. No nitrite accumulation was observed for any of these tests (Appendix V, V-E (24/11/97 to 27/11/97)). Tests conducted with sludge samples on day 0 and 1 produced similar results *i.e.* a single phase and the same rate (1.0 mgN/gVSS.h) which suggested that sludge stored up to 24 h did not change sludge activity or characteristics (Table 5-2 and Figure 5-1). The day 4 test, however, revealed two phases, a short first phase and a slower second phase with a rate ( $k_2$ ) that was half that of  $k_1$ . The second denitrification rate ( $k_2 = 1.1$  mgN/gVSS.h) for  $t = 72$  h samples was similar to the rates determined for samples stored for 0 h and 24 h ( $k_1 = 1.0$  mgN/gVSS.h).

Extrapolation of the second phase and determination of the  $\Delta\text{NO}_x$  value for the tests conducted with 72 h stored sludge samples, allowed for the calculation of the biodegradable COD concentration which was responsible for the first rate of 2.2 mgN/gVSS.h (Figure 5-1). A biodegradable COD concentration of 16 mgO<sub>2</sub>/l was calculated. Therefore, it is probable that the 72 h sludge contributed about 16 mg/l of organic carbon to the biodegradable COD fractions calculated from raw wastewater and primary settler effluent samples that were calculated on day 4.



**Figure 5-1: Comparison of endogenous denitrification rates after 0, 24 and 72 h storage of sludge samples at 4 °C.**

**Table 5-2: Endogenous denitrification rates for sludge stored for 0 h, 24 h and 72 h at 4 °C.**

	Denitrification rates after		
	t0 (h)	t24 (h)	t72 (h)
k <sub>1</sub> (mgN/gVSS.h)	-	-	2.2
k <sub>2</sub> (mgN/gVSS.h)	1.0	1.0	1.1

### 5.1.3 Readily biodegradable COD and readily hydrolyzable COD concentrations

Biological organic carbon fractions were determined in NUR tests conducted with samples that had been stored for 0 h, 24 h and 72 h (Table 5-3). Tests conducted with raw wastewater samples that had been

stored for 0 and 24 h revealed 2 phases while tests with samples stored for 72 h revealed 3 phases. However, three phases were revealed for all the tests with primary settler effluent samples.

Table 5-3 shows the RBCOD and RHCOD fractions calculated from tests with raw wastewater and primary settler effluent samples from Evry WTP. The fractions are represented as a percentage of the total COD concentration of raw wastewater on the day of the tests (see Table 5-1). The biodegradable COD concentrations calculated for  $t = 0\text{h}$  to  $t = 72\text{h}$  samples were comparable i.e. there was no change in the RBCOD component of raw wastewater during storage (Table 5-3). No readily hydrolyzable COD (RHCOD) fraction could only be calculated for tests with raw wastewater samples that had been stored for 0 h and 24 h. However, a RHCOD fraction of 14 % (95 mg/l) was calculated for those raw wastewater samples that had been stored for 72 h. The observation of this fraction after 72 h could be due to the hydrolysis of SBCOD of the sludge (attached and endogenous) and / or hydrolysis of the SBCOD in the wastewater sample. As discussed in section 5.12, day 4 denitrification profiles revealed 2 phases which allowed for the calculation of a biodegradable COD fraction. The sludge COD contribution was found to be about 16 mgO<sub>2</sub>/l and would have, therefore, contributed only 2 % of the 14 % that was calculated using 72 h stored raw wastewater samples. Therefore, the observation of the RHCOD on day 4 was not completely due to the sludge. These results suggest that longer storage periods (> 24 h at 4 C) does promote some hydrolysis. Thus, NUR tests done with raw wastewater samples stored for 72 h could reveal an ‘apparent’ readily hydrolyzable COD fraction which would not have been observable with fresh samples.

The same trend was observed for the tests with primary settler effluent wastewater *i.e.* the RBCOD values did not show significant changes during storage (Table 5-3). Furthermore, it was observed that the tests with the primary settler effluent samples consistently produced lower RBCOD values than the tests with raw wastewater. This suggests the biological activity in the primary settler may have resulted in a slight reduction in the RBCOD fraction. A second biodegradable COD fraction, the RHCOD fraction, was revealed in all three of the tests conducted with the wastewater samples taken from the primary settler. It is probable that the retention of the raw wastewater in the primary settling tank enhances biological hydrolysis of the SBCOD fraction, thereby creating an intermediate biodegradable group which is rapidly hydrolyzable, *i.e.* RHCOD, which was observable in the 6 hour NUR batch test.

**Table 5-3: Comparison of RBCOD and RHCOD values after 0, 24, and 72 h of storage using raw wastewater and primary settler effluent samples (% of total COD).**

	Raw wastewater				Settler effluent samples			
	RBCOD		RHCOD		RBCOD		RHCOD	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%
0 h	71	11	–	–	54	8	72	13
24 h	77	11	–	–	65	9	75	11
72 h	75	9	79*	11*	64	9	73*	11*

\* - note that the 16mg/l (i.e. 2 %) of COD calculated from tests conducted with sludge samples only have been removed from the 72 h biodegradable COD values.

### 5.1.3.1 Denitrification rates

The first rates ranged between 4.7 and 7.2 mgN/gVSS.h (Table 5-4). No clear trend could be observed for the maximum specific denitrification rates for the studies with raw wastewater or primary settler effluent samples. However, the tests with the primary settler effluent did produce slightly higher specific denitrification rates. The second and third rates were found to be less variable and ranged between 2.0 to 2.5 and 1.3 to 2.0 mgN/gVSS.h, respectively. The third rates observed for both substrates (1.3 to 2.0 mgN/gVSS.h) were higher than the the endogenous denitrification rates of about 1.0 mgN/gVSS.h (30 to 100 % difference between  $K_3$  of raw wastewater and  $K_1$  of sludge)(see Table 5-2 and 5-4). These results suggest that the final rate observed for the NUR tests fed with wastewater was due to the utilization of slowly biodegradable COD of the substrate added.

**Table 5-4: Specific denitrification rates (mgN/gVSS.h) obtained from tests with stored samples collected from Evry WTP (24/11/97).**

Substrate	rate	Storage period		
		t0 (h)	t24 (h)	t72 (h)
raw wastewater	$k_1$	-5.3	-4.7	-5.1
	$k_2$	-	-	-2.3
	$k_3$	-2.0	-1.9	-1.5
Primary settler effluent samples	$k_1$	-5.0	-7.2	-6.6
	$k_2$	-2.1	-2.0	-2.5
	$k_3$	-1.4	-1.3	-1.3

## 5.2 THE IMPACT OF SLUDGE ACCLIMATIZATION ON WASTEWATER CHARACTERIZATION

The use of an 'external and unacclimatized' sludge *i.e.* sludge sampled from a different source to that of the wastewater sample may be used for certain NUR tests. This may become necessary when denitrifying sludge is absent or there are operational problems at wastewater treatment plants. This may also be necessary when characterizing wastewater from enhanced biological phosphorus removal (EBPR) plants. Sludges from EBPR plants contain higher proportions of polyphosphate accumulating organisms (PAO's). Thus, the aims of this experiment were to determine if raw wastewater could be characterized (using the NUR method) with an unacclimatized activated sludge (foreign biomass) sample and if denitrification rates are influenced by the origin of the sludge or the origin of the raw wastewater.

Four comparative tests were made between acclimatized and unacclimatized sludge (see Chapter 4, section 4.28.2). The total wastewater concentration for the different test wastewaters varied between 700 and 1132 mgO<sub>2</sub>/l (Table 5-5). The significant difference in the total COD concentrations for Boran WTP samples could be due to fact that Boran is a small treatment plant and therefore, unable to buffer any small perturbations in the COD load. The soluble fractions measured after filtration (S-f<sub>0.45</sub>) and coagulation (S-co) varied between 41 to 53 %, and 41 to 45 %, respectively. Wastewater from Boran (22/08/97) was tested with sludges from Artemps-Seraucourt WTP and Crespi©res WTP. The wastewaters from Boran and Gouvieux which were sampled on the 19/11/97 were interchanged and tested with Gouvieux and Boran sludge, respectively. The details from these tests are contained in Appendix IV, IV-A (Artemps 22/08/97), IV-B (Boran 22/08/97 ; Boran 19/11/97), IV-C (Crespi©res 22/08/97), IV-G (Gouvieux 19/11/97).

**Table 5-5: COD characterization of raw wastewater sampled from Boran and Gouvieux WTP for acclimatization tests (n.d. - not determined).**

Date	Substrate source	St	S-f <sub>0.45</sub>		S-co	
		mg/l	mg/l	%	mg/l	%
22/08/97	Boran	753	309	41	n.d.	n.d.
19/11/97	Boran	1132	553	49	467	41
19/11/97	Gouvieux	700	374	53	317	45

### 5.2.1 Comparison of biodegradable fractions using acclimatized and unacclimatized sludge

Of the four comparisons made with acclimatized and unacclimatized sludges, three of the tests (tests 1, 3, and 4) were found to be comparable (Table 5-6). The results of test 2 with Boran and Crespi©res, however, were found to be poorly comparable. In this case, tests done with the acclimatized sludge,

Boran, produced 9 % RBCOD and 25 % RHCOD. However, batch tests with the unacclimatized sludge from Crespières and raw wastewater from Boran produced a RBCOD fraction of 23 %, which was more than 2 times greater than the RBCOD fraction calculated with the acclimatized sludge of Boran. In addition, only one biodegradable fraction could be measured for the tests using the unacclimatized sludge of Crespières. It would appear that the unacclimatized Crespières sludge was capable of using the readily biodegradable COD and some of the readily hydrolyzable COD rapidly. Thus, the measured readily biodegradable COD appears to be a combination of the RBCOD and some of the RHCOD present in the raw wastewater sampled from Boran.

**Table 5-6: Comparison of RBCOD/RHCOD values calculated for wastewater from Boran using different sludges.**

Test	Substrate	Sludge source	% RBCOD		% RHCOD	
			mg/l	%	mg/l	%
1-(22/08/97)	Boran	Boran	72	9	189	25
		Artemps-Seraucourt	82	11	177	24
2-(22/08/97)	Boran	Boran	72	9	189	25
		Crespières	176	23	n.o.	
3-(19/11/97)	Boran	Boran	246	22	n.o.	
		Gouvieux	256	23	n.o.	
4-(19/11/97)	Gouvieux	Gouvieux	196	28	n.o.	
		Boran	217	31	n.o.	

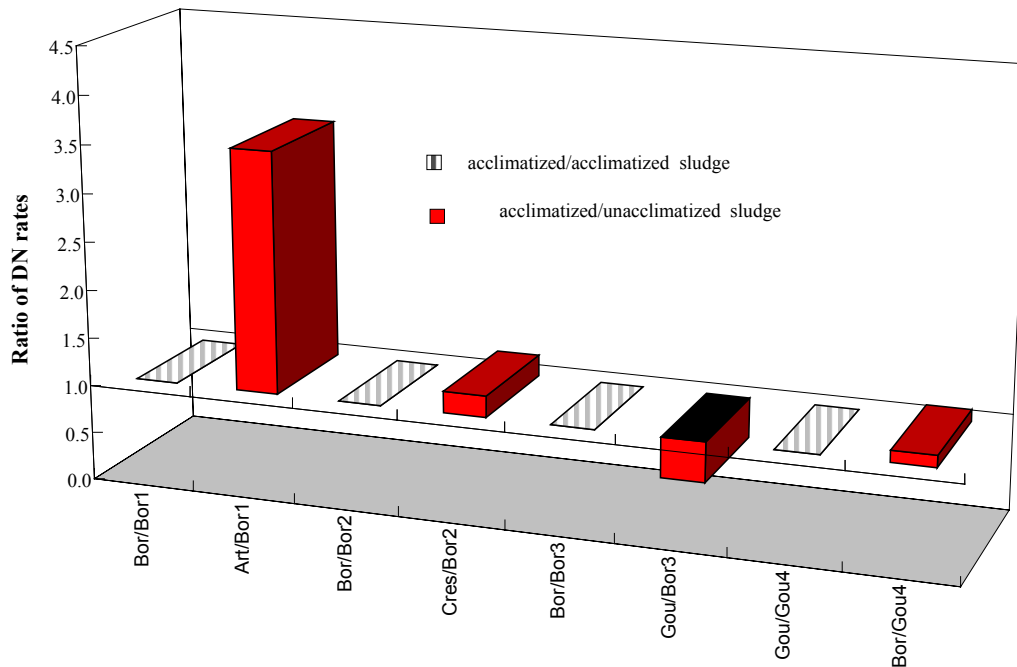
(n.o - not observable)

### 5.2.2 Denitrification rates

The rates obtained with the different sludges were variable. The maximum ( $k_1$ ), second ( $k_2$ ) and third ( $k_3$ ) rates varied between 5.8 to 3.2, 2.5 to 1.5 and 0.8 to 0.5 mgN/gVSS.h, respectively (Table 5-7). The ratios of the different rates of the acclimatized to the unacclimatized sludges were plotted in Figure 5-2. The results showed that none of the unacclimatized sludges produced rates that was comparable to the acclimatized sludges. In addition, some of the unacclimatized sludges *eg.* Artemps-Seraucourt and Boran produced higher rates than the acclimatized sludges (Table 5-7). This suggests that even though the wastewater quality may influences the rates to a certain extent, the magnitude of the rates are largely due to sludge characterization which are brought upon by plant operating conditions such as solids retention time, loading rates, and feeding regimes (continuous or intermittent). In addition, comparative tests between Boran (22/08/97) and Artemps (22/08/97) showed that although the rates ( $k_1$  and  $k_2$ ) measured with the two sludges were significantly different, the biodegradable fractions were comparable (see Table 5-6 and Table 5-7).

**Table 5-7 : Comparison of denitrification rates for acclimatized and unacclimatized sludges.**

Date	substrate source	sludge source	$k_1$	$k_2$	$k_3$
1-22/08/07	Boran	Boran	-3.2	-1.7	-0.8
1-22/08/97	Boran	Artemps-Seraucourt	<b>-11.2</b>	<b>-4.1</b>	<b>0.5</b>
2-22/08/97	Boran	Crespieres	-3.9	-1.5	-
3-19/11/97	Boran	Boran	-5.8	-2.5	-
3-19/11/97	Boran	Gouvieux	-3.4	-1.7	-
4-19/11/97	Gouvieux	Gouvieux	-3.3	-1.7	-
4-19/11/97	Gouvieux	Boran	-3.7	-2.4	-

**Figure 5-2: Ratios of denitrification rates of acclimatized to unacclimatized sludges (Bor -Boran, Art - Artemps-Seraucourt, Cres - Crespieres, Gou - Gouvieux).**

### **5.3 THE IMPACT OF SEPARATION TECHNIQUES ON RBCOD DETERMINATION**

It is hypothesized that the RBCOD fraction calculated by the biological tests (NUR, OUR) is equivalent to the 'truly soluble' COD fraction minus the inert fraction of raw wastewater. Thus, it may be accepted that if the soluble fraction of raw wastewater derived after coagulation or centrifugation was tested it

should give comparable results to the RBCOD values if the 'truly soluble' component consisted of RBCOD and inert COD.

Nine experiments were conducted with samples from various wastewater treatment plants (Appendix IV). The raw wastewater samples were separated by centrifugation and coagulation and the RBCOD was determined by the NUR tests. Table 5-8 lists the total COD concentrations and their RBCOD concentrations for the 9 tests.

**Table 5-8: Comparative tests between centrifuged and coagulated 'soluble' samples of raw wastewater.**

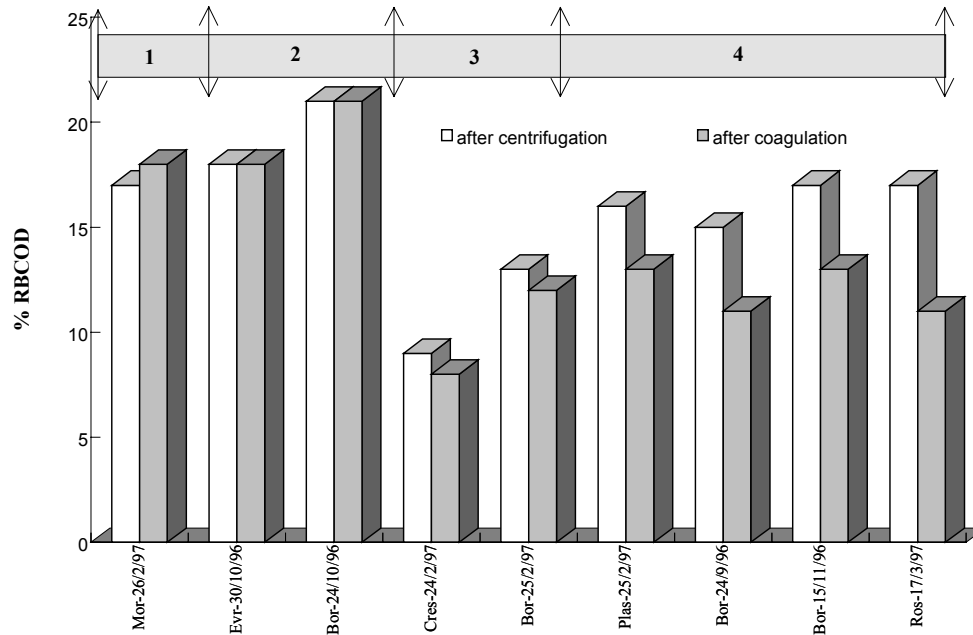
Group No.	Plant	Date	Total COD	RBCOD (mgO <sub>2</sub> /l)	
			St (mg/l)	centrifugation	coagulation
1	Morainvilliers	26/02/97	344	58	64
2	Boran	24/10/96	837	176	176
	Evry	30/10/97	587	106	106
3	Boran	25/02/97	707	93	84
	Crespieres	24/02/97	549	51	44
4	Plasir	25/02/97	691	108	89
	Boran	24/09/96	897	135	99
	Boran	15/11/96	727	124	94
	Rostock	17/03/97	953	161	105

Results obtained from the 9 tests were divided into 4 groups which seem to suggest two trends (Figure 5-3). The RBCOD fraction from centrifuged 'soluble' samples from Morainvilliers, Evry and Boran were found to be less than and equivalent to the RBCOD values of the coagulated 'soluble' samples (see Groups 1 and 2 in Figure 5-3). Consideration of the standard deviation of 1 for the RBCOD (%) values determined from reproducibility experiments suggested that the results were comparable *i.e.* there was no change in the RBCOD values derived from either centrifuged or coagulated samples. These results support the hypothesis that the RBCOD fraction of the influent raw wastewater is found in the truly soluble *i.e.* coagulated fraction of the wastewater. In other word, elimination of higher molecular weight compounds by the process of coagulation does not result in an underestimation of the RBCOD fraction because the RBCOD that is measured from the NUR test is part of the soluble component of raw wastewater and is not generated during the test.

The results that have been labelled Groups 3 and 4 showed that the RBCOD fraction derived from centrifuged 'soluble' samples were higher than that derived from coagulated 'soluble' samples (Figure 5-3). However, the results of Group 3 showed only a slight difference (1 % of total COD) between the 2 separation techniques. The results of Group 4 were more distinctive with a 3 to 6 % (of total COD)



difference between the 2 methods. These results suggest the RBCOD may consist of higher molecular weight compounds which are retained after centrifugation but removed after coagulation. Thus, the RBCOD is not always equivalent to the truly soluble fraction as suggested and demonstrated by Mamais *et al.* (1993). However, these results may also suggest that the process of coagulation may remove some of the low molecular weight biodegradable compounds resulting in a decrease in the RBCOD fraction. The observation of these two trends highlights once again the variability of the wastewater composition.



**Figure 5-3: Comparison of RBCOD values determined from raw wastewater samples after separation by centrifugation or coagulation.**

## 5.4 VARIATION IN WASTEWATER CHARACTERISTICS

Several factors such as seasonal changes, socio-economic conditions, temperature and sewer systems may influence wastewater characteristics. In this section, weekly and annual variations are presented. The results from Compiègne and Samaritaine which were monitored over a 7 day period and Boran which was monitored over the period of a year are discussed.

### 5.4.1 Weekly Variation

Four and three raw wastewater composite (24 h) samples were tested for Compiègne and Samaritaine, respectively. The results are presented in Table 5-9. There was no significant change in the total COD concentration measured for the Compiègne samples. COD analysis of the Samaritaine samples, however, showed a significant difference between the first (23/04/97) and second (25/04/97)

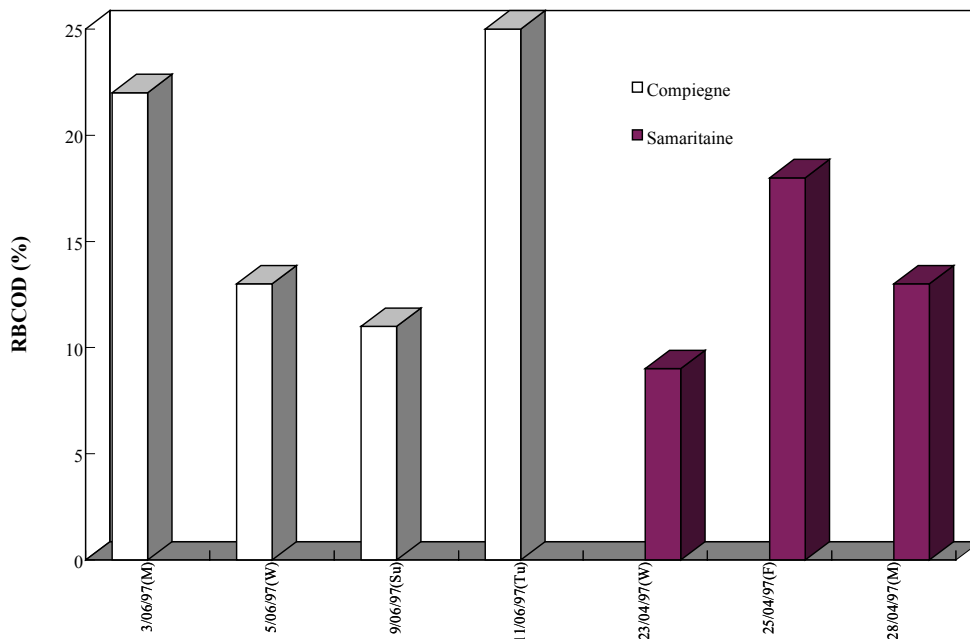
measurements. However, no distinct trend in the COD measurements could be observed for the Compiègne and Samaritaine tests.

Figure 5-4 shows the RBCOD results obtained from the NUR tests conducted on Compiègne and Samaritaine samples. The RBCOD varied between 11 and 25 %, and 9 and 18 % for Compiègne and Samaritaine, respectively. No specific trend could be ascertained for the Samaritaine tests from these results. The Compiègne results showed that the RBCOD concentration varied with time. The RBCOD content for Monday and Tuesday were found to be approximately two times that calculated for the Wednesday and Sunday samples (Table 5-9 and Figure 5-4). However, more tests would need to be done in order to establish a clear trend in the RBCOD content of raw wastewater samples taken from Compiègne and Samaritaine.

**Table 5-9: Weekly variation in total COD (St) and the RBCOD concentration.**

Compiègne WTP					Samaritaine WTP				
Date	Day	St (mg/l)	RBCOD		Date	Day	St (mg/l)	RBCOD	
			(mg/l)	%				(mg/l)	%
3/6/97	M	783	172	22	23/4/97	W	900	81	9
5/6/97	W	787	102	13	25/4/97	F	750	135	18
9/6/97	Su	883	97	11	28/4/97	M	720	94	13
11/6/97	Tu	817	204	25	-	-	-	-	-

(M - Monday; Tu - Tuesday; W-Wednesday; F-Friday; Su-Sunday)



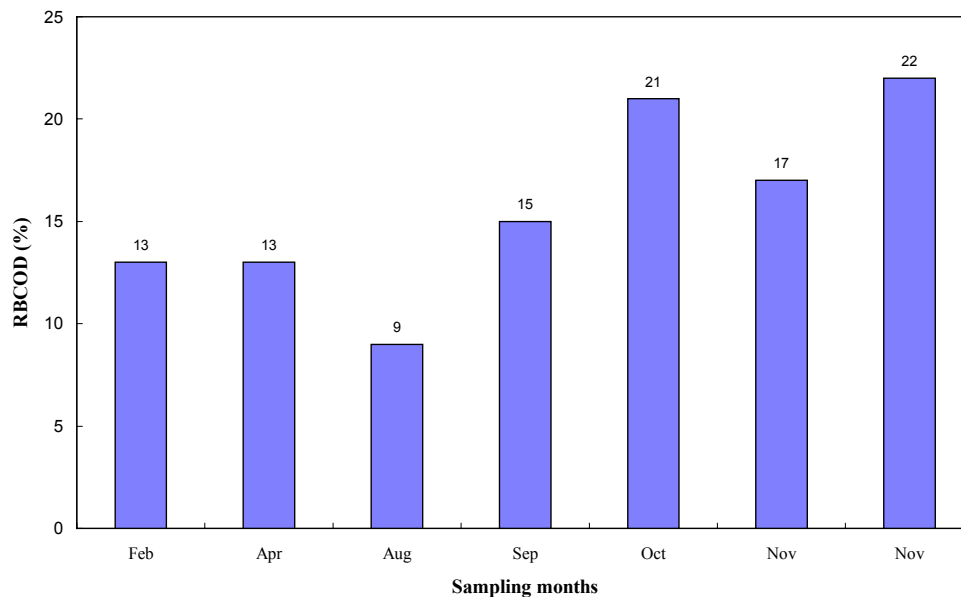
**Figure 5-4: Weekly variation in RBCOD fraction for Compiègne and Samaritaine.**

### 5.4.2 Annual Variation

Raw wastewater from Boran WTP was grab sampled and characterized, chemically and biologically, seven times between September 1996 and November 1997. The total COD concentration varied between 700 and 1100 mg/l for the 7 tests (Table 5-10) which showed that the raw wastewater concentration for Boran WTP was fairly concentrated and variable. The RBCOD fraction was found to vary between 9 and 22 % of the total COD. The RBCOD values are grouped by the month of the year in Figure 5-4. These results suggest that the higher RBCOD values ( $\geq 17\%$ ) are obtained in the latter part of the year *i.e.* between October and November.

**Table 5-10: Annual variation in total COD and RBCOD concentrations for Boran WTP between September 1996 and November 1997.**

Date	Month	St (mg/l)	RBCOD (mg/l)
24/9/96	September	897	135
24/10/96	October	837	176
15/11/96	November	727	124
25/02/97	February	707	93
2/04/97	April	1137	148
22/8/97	August	753	68
19/11/97	November	1132	249



**Figure 5-5: Annual variation in RBCOD (%) for Boran WTP from February 1996 to November 1997.**

## 5.5 SUMMARY

The storage of wastewater samples up to 72 h at 4 °C was shown to have no major effect on the determination of the RBCOD fraction *i.e.* the RBCOD fraction did not change during storage. The results obtained from the storage experiment also highlighted the advantage of a primary settler at the treatment plant since the tests with primary settler effluent samples revealed 2 biodegradable fractions in the 6 h tests as opposed to the single biodegradable fraction for raw wastewater samples, with the exception of the 72 h raw wastewater sample. In addition, storage of the sludge samples were shown to promote the hydrolysis of SBCOD in the 72 h sludge sample. This was manifested with the observation of a single phase for 0 h and 24 h samples, and 2 phases for the 72 h sample. This experiment showed that the accuracy and reliability of the data from NUR tests were not compromised with samples which had been stored up to 24 h.

Most of the tests showed that the readily biodegradable COD and readily hydrolyzable COD fractions determined with acclimatized and unacclimatized sludges were comparable. However, there was an exception, *e.g.* the unacclimatized sludge of Crespières gave RBCOD values that compared poorly to the results obtained with the acclimatized sludge of Boran. Therefore, this suggests that not all the sludges are compatible with different wastewaters.

The NUR tests using ‘soluble’ fractions derived from centrifugation and coagulation produced two trends. In the first case, the RBCOD values were found to be comparable which supports the premise that the RBCOD is found in the ‘truly soluble’ fraction, *i.e.* coagulated fraction, of raw wastewater. This also showed that the RBCOD measured by the NUR method came from the ‘soluble’ fraction of raw wastewater and was not generated during the 6 h batch test. In addition, the results also showed that the RBCOD determined from tests with the centrifuged ‘soluble’ sample was higher than that determined from the coagulated ‘soluble’ samples. This suggests that the process of coagulation may remove some low molecular weight readily biodegradable compounds with the coagulant.

The weekly RBCOD variation was found to be between 11 and 25 %, and 9 and 18 % for Compiègne and Samaritaine, respectively with no clear trend identified. These results showed that the RBCOD concentration should be monitored with time in order to ascertain a mean value. There was no significant change in the total COD concentration determined for the Compiègne samples while COD analysis of the Samaritaine samples showed a significant difference between the first and second measurements. This showed that while a global parameter like COD may not change significantly during the week, the biodegradable COD fraction can. A similar trend was observed for wastewater samples from Boran WTP which were monitored from September 1996 to November 1997. The RBCOD fraction was found to vary between 9 and 22 % of the total COD which compares well to the RBCOD expected range of 10 to 20 % of the total COD (Henze *et al.*, 1995). In addition, the results suggested that the higher RBCOD values ( $\geq 17$  %) were obtained in the latter part of the year *i.e.* between October and November.

# Chapter Six

## *ACETATE/RBCOD UTILIZATION UNDER ANOXIC CONDITIONS*

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This chapter is divided into 2 sections. The first section investigates the use of an experimental RBCOD substrate, acetate, in a denitrifying environment. Acetate was chosen as it is a simple, soluble compound which may be directly incorporated into the metabolic pathways via acetyl Co-A. The second section deals with polyphosphate accumulating organisms (PAO's) or denitrifying polyphosphate accumulating organisms (DPAO's) in denitrifying sludge and its influence on the determination of the RBCOD concentration of raw wastewater via the nitrate-N utilization rate (NUR) method.

### *6.1 ACETATE AS A REFERENCE SUBSTRATE*

Acetate, which is a readily biodegradable substrate, was tested with sludges from different sources as a reference for assessing the RBCOD determinations made from data obtained from NO<sub>x</sub> time profiles. The results from acetate fed reactors provide an important indicator of sludge activity and RBCOD utilization under anoxic conditions. The objective of this study was to assess the efficiency and accuracy of the NUR method by using acetate as a reference substrate for the readily biodegradable COD component of raw wastewater.

The results from the various NUR batch tests are presented in **Appendix III**. As discussed in **Chapter 4** denitrification kinetics with acetate revealed NO<sub>x</sub> time profiles with either two or three phases (see Figure 4-13). In those tests where only two phases were observed, the first phase was due to acetate utilization and the second phase was indicative of the utilization of slowly biodegradable substrates (see Figure 4-13). For the three phase NO<sub>x</sub> time profiles with acetate it was hypothesized that phase 1 was due to acetate utilization while phase 2 was due to the utilization of internally stored compounds. These storage products could arise from : (i) the synthesis of storage products from acetate which are subsequently utilized internally (rapid storage / utilization reaction) or (ii) the use of existing storage products whose utilization is triggered by the presence of acetate and/or the electron acceptor. Since no exogenous substrates other than acetate was added to the batch reactors, phase 3 was considered to be due to the utilization of endogenous products released by the bacterial cells or SBCOD attached to the sludge.

The data from NUR tests with acetate was interpreted and discussed in several ways by accepting that the NUR test was an accurate measure of the RBCOD concentration in a particular sample. Firstly, it was

possible to use the equation 4-7 in Chapter 4 to calculate the yield coefficient since the initial amount of acetate as COD was known. Secondly, one could assume that the yield coefficient for the different sludges was constant and thus, calculate the acetate consumed during denitrification. This was referred to as the acetate recovery or mass balance (%). For studies with acetate, two yield coefficients were used viz: 0.50 and 0.63 (mg O<sub>2</sub>/ mg O<sub>2</sub>) (aerobic yield). The yield coefficient of 0.50 mgO<sub>2</sub>/mgO<sub>2</sub> was chosen since it is a theoretical value derived on an energy consideration basis (Sozen *et al.*, 1998) and is fairly close to the value of 0.54 mgO<sub>2</sub>/mgO<sub>2</sub> measured by Sperandio *et al.* (1997) for acetate. The value of 0.63 mgO<sub>2</sub>/mgO<sub>2</sub> is the yield coefficient suggested by Henze *et al.*, (1995) for anoxic reactions involving activated sludge.

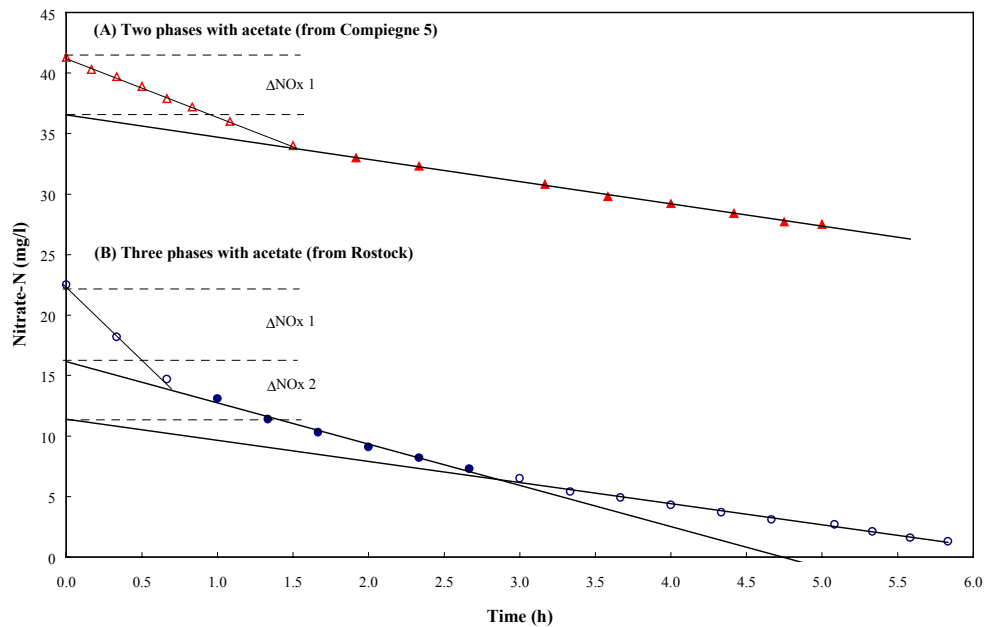


Figure 6-1: Typical Nitrate-N time profiles with acetate ( $T = 20^{\circ}\text{C}$ ,  $\text{pH} = 7.5$ ).

### 6.1.1 Estimation of yield coefficient

The yield coefficient can be estimated by modifying the equation 4-7 in Chapter 4 into equations 6-1a and 6-1b, where  $\Delta\text{NOx 1}$  or  $\Delta\text{NOx 2}$  refers to the amount of electron acceptor consumed and  $[\text{Ace}]$  refers to the concentration of acetate added at the start of the batch test.  $Y_{\text{HD}}^1$  refers to the yield coefficient calculated from using  $\Delta\text{NOx 1}$  while  $Y_{\text{HD}}^{1+2}$  refers to the yield coefficient from the sum of  $\Delta\text{NOx 1}$  and  $\Delta\text{NOx 2}$ . This was based on the assumption that phase 2 (rate 2) in a 3-phase acetate-NUR profile was linked to the presence of acetate (as COD) in the batch reactor.

$$Y_{\text{HD}}^1 = 1 - [(2.86 * \Delta\text{NOx 1}) / [\text{ace}]] \quad (6-1a)$$

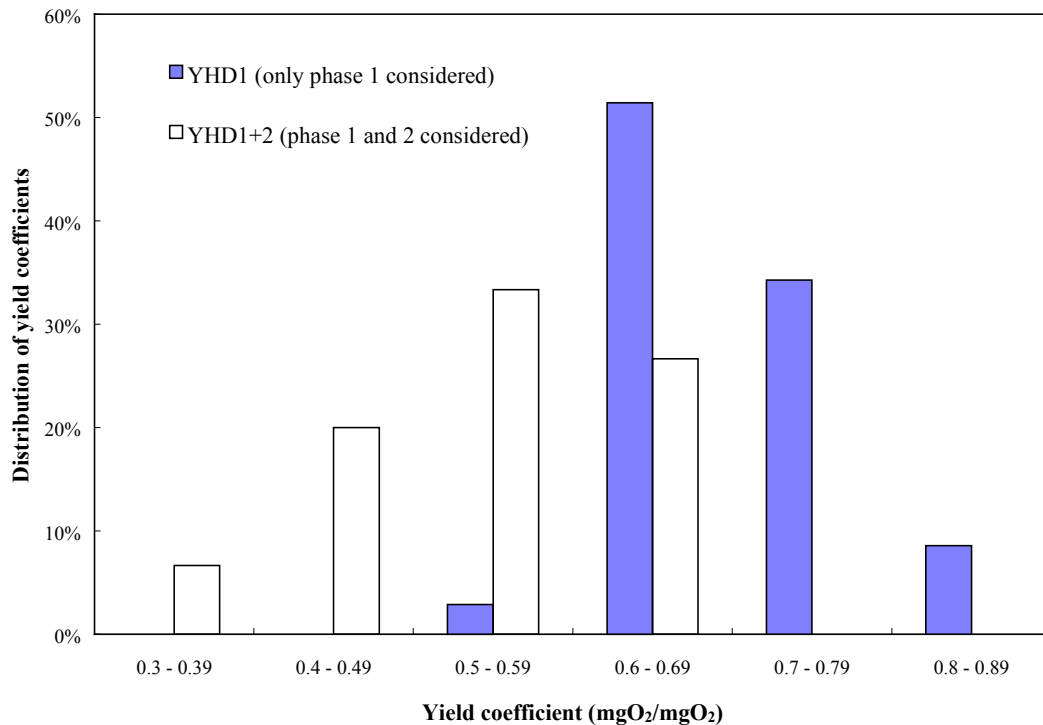
$$Y_{\text{HD}}^{1+2} = 1 - [(2.86 * \Delta\text{NOx 1+2}) / [\text{ace}]] \quad (6-1b)$$

The results obtained using equations 6-1 (a) and (b) are presented in Table 6-1. The variation in the results suggested that the yield coefficient is not constant for all types of activated sludges or that the acetate was not consumed solely by denitrifiers. In other words, acetate utilization was influenced by other factors. The frequency of distribution of the calculated yield coefficients ( $Y_{HD}^1$  and  $Y_{HD}^{1+2}$ ) are plotted in Figure 6-2. Majority of the  $Y_{HD}^1$  values were between 0.6 and 0.79 ( $\text{mg O}_2/\text{mg O}_2$ ) (Figure 6-2). The mean calculated  $Y_{HD}^1$  value (based on  $\Delta\text{NOx 1}$ ) was found to be 0.69 which is higher than the aerobic yield coefficient, 0.63  $\text{mgO}_2/\text{mgO}_2$ . These results suggest that the denitrifiers use some of the acetate that is available for denitrification and rest is used to replenish the stored reserves or may be accumulated. The accumulation and storage process are considered to be rapid (Majone *et al.*, 1999). This rapid accumulation or storage reaction is thought to be prevalent in biomass that has been growing under dynamic conditions. It is, however, also likely that the high yield coefficients calculated are due to the presence of polyphosphate accumulating organisms which take up and store some of the available acetate. This is supported by results obtained when both phase 1 and phase 2 are considered. The mean calculated  $Y_{HD}^{1+2}$  (based on  $\Delta\text{NOx 1} + \Delta\text{NOx 2}$ ) value, was found to be 0.54  $\text{mgO}_2/\text{mg O}_2$  which is lower than the aerobic yield coefficient, 0.63 ( $\text{mg O}_2 / \text{mg O}_2$ ). However, this value is closer to the anoxic yield coefficient values 0.50 and 0.54  $\text{mgO}_2/\text{mgO}_2$  cited in the literature (Sperandio *et al.*, 1997 ; Sozen *et al.*, 1998). The distribution frequency of these values varied from 0.5 to 0.69  $\text{mg O}_2/\text{mg O}_2$  (Figure 6-2). Thus, the calculated yield coefficient was found to be variable which suggests that the yield coefficient may not be constant for all the sludges tested.

**Table 6-1: The calculated yield coefficients for different sludges using acetate as an experimental readily biodegradable substrate (\* - enhanced biological phosphorus removal plants ; N/A - not applicable).**

Treatment Plant	$Y_{HD}^1$	$Y_{HD}^{1+2}$
Asnieres s/oise	0.72	N/A
Artemps-Seraucourt 1	0.62	0.44
Artemps-Seraucourt 2	0.69	0.57
Berwick	0.66	N/A
Boran 1	0.64	N/A
Boran 2	0.77	N/A
Boran 3	0.71	N/A
Boran 4	0.62	N/A
Boran 5	0.63	N/A
Boran 6	0.66	0.40
Boran 7	0.71	0.61
Boran 8	0.80	0.65
Boves	0.69	N/A
Brno	0.65	0.40
Compiègne 1*	0.80	N/A
Compiègne 2*	0.80	N/A
Compiègne 3*	0.73	N/A
Compiègne 4*	0.68	N/A
Compiègne 5*	0.73	N/A
Compiègne 6*	0.73	N/A
Creil 1	0.64	N/A
Creil 2	0.61	N/A
Cresprières 2	0.69	N/A
Gouvieux	0.62	N/A
Laon	0.79	0.61
Morainvilliers	0.54	N/A
Orense	0.60	N/A
Rostock	0.62	0.39
Samaritaine 1*	0.66	N/A
Samaritaine 2*	0.78	0.55
Samaritaine 3*	0.78	0.57
Thiverval 1*	0.68	0.58
Thiverval 2*	0.72	0.60
Villers sous St. Leu	0.78	0.58
Average	0.69	0.54
Standard deviation	0.07	0.08





**Figure 6-2: Frequency of distribution of the calculated yield coefficients with acetate as substrate.**

### 6.1.2 Acetate recovery

As discussed in **Chapter 4**, since acetate was the sole readily biodegradable substrate added, the first  $\Delta\text{NO}_x$  (*i.e.*  $\Delta\text{NO}_x 1$ ) was used to calculate the acetate recovery (percent acetate mass balance 1). However, in those cases where a second  $\Delta\text{NO}_x$  (*i.e.*  $\Delta\text{NO}_x 2$ ) could be determined it was used to calculate a second acetate recovery (percent acetate mass balance 2) since endogenous denitrification profiles revealed a single phase which showed that no COD contribution was made from the sludge. The second phase is hypothesized to be linked to the acetate that was added at the beginning of the experiment and is therefore, calculated as part of the initial amount of acetate acetate added to the reactor. This second (intermediate) phase hypothesis is similar to the one made by Majone *et al.* (1999) describing a tailing effect in the OUR profile and linking it to the acetate that was initially added.

These acetate recovery interpretations were made based on three assumptions :

- the NUR test is a reliable and accurate measure of the RBCOD concentration
- the yield coefficients, 0.50 or 0.63 mgO<sub>2</sub>/mgO<sub>2</sub>, used are correct and constant
- the interpretation of the NO<sub>x</sub> vs time curves is correct

Table 6-2 lists the acetate mass balances (recovery) for the different tests using a yield coefficient of 0.50 or 0.63. The percentage acetate recovery varied widely for the different types of activated sludges tested and the main observations are discussed below.

**Table 6-2: Acetate recovery 1 and 2 based on the use of constant yield coefficients, 0.50 and 0.63 (mg O<sub>2</sub>/ mg O<sub>2</sub>).**

Plant	Concentration		Y <sub>HD</sub> = 0.50			Y <sub>HD</sub> = 0.63			
	P	[Ace]	1 (%)	2 (%)	1+2 (%)	1 (%)	2 (%)	1+2 (%)	
Asnieres s/oise	11/9/97	4	50	55	0	-	74	0	-
Artemps	21/8/97	0	50	76	36	112	102	49	151
Artemps	22/8/97	1	50	62	25	87	83	33	117
Berwick	2/5/97	ND	50	68	0	-	92	0	-
Boran 1	22/10/96	ND	40	87	0	-	116	0	-
Boran 2	25/2/97	ND	70	72	0	-	97	0	-
Boran 3	1/4/97	ND	60	78	0	-	105	0	-
Boran 4	2/4/97	ND	70	79	0	-	106	0	-
Boran 5	3/6/97	0	50	77	0	-	104	0	-
Boran 6	9/6/97	0	50	74	0	-	99	0	-
Boran 7	11/6/97	0	50	67	54	121	90	72	162
Boran 8	17/7/97	3	50	59	20	79	79	27	106
Boran 9	31/7/97	7.5	50	40	30	70	53	40	93
Boran 10	22/8/97	3	50	46	0	-	61	0	-
Boran 11	29/8/97	4	50	58	0	-	78	0	-
Boves	4/9/97	3	50	62	0	-	84	0	-
Brno	1/6/97	ND	50	70	50	120	95	67	162
Compiègne 1*	3/6/97	7	50	39	0	-	53	0	-
Compiègne 2*	5/6/97	6.5	50	39	0	-	53	0	-
Compiègne 3*	9/6/97	6	50	54	0	-	73	0	-
Compiègne 4*	11/6/97	7	50	64	0	-	86	0	-
Compiègne 5*	28/8/97	6	50	54	0	-	73	0	-
Compiègne 6*	29/8/97	2	50	54	0	-	73	0	-
Creil 1	28/8/97	0	50	72	0	-	97	0	-
Creil 2	29/8/97	0	50	78	0	-	105	0	-
Cresprières 2	21/8/97	2	50	62	0	-	84	0	-
Gouvieux	11/9/97	ND	50	76	0	-	102	0	-
Laon	7/8/97	4	50	42	36	78	56	48	104
Morainvilliers	26/2/97	ND	70	92	0	-	123	0	-
Orense	18/5/97	ND	50	80	0	-	108	0	-
Rostock	17/3/97	ND	50	76	45	121	102	61	163
Samaritaine 1*	23/4/97	ND	50	67	0	-	91	0	-
Samaritaine 2*	25/4/97	ND	50	45	46	91	60	61	121
Samaritaine 3*	28/4/97	ND	50	44	41	85	60	55	115
Thiverval 1*	17/7/97	2	50	63	21	84	85	29	114
Thiverval 2*	31/7/97	6.5	50	55	25	80	74	34	108
Villers	10/9/97	6	50	44	40	84	59	54	113

(P - ortho-phosphate as P ; Ace - acetate concentration added as COD ; ND - not determined ; \* - EBPR plants)

### **6.1.2.1 Interpretation of data with a constant $Y_{HD}$ of 0.50**

The data were analyzed by considering  $NO_x 1$  and the sum of  $NO_x 1$  and 2 viz (Table 6-2). Three trends were observed :

1. < 100 % recovery (mass balance 1),
2. ca. 100 % recovery (mass balance 1 and 2), and
3. > 100 % recovery (mass balance 1 and 2)

- **100% recovery based on  $\Delta NO_x 1$**

None of the NUR results of acetate gave a mass balance of 100 % with a yield coefficient of 0.50 (Table 6-2 and Figure 6-3 ). Thus, it would seem that that the acetate available under anoxic conditions was not used solely by denitrifiers for denitrification. It is probable that polyphosphate accumulating organisms (PAO's) and / or denitrifying polyphosphate accumulating organisms (DPAO's) take up some of the available acetate for conversion to storage compounds like polyhydroxyalkanoates (PHA's). This is supported by observations (in Figure 6-4) which showed that denitrification and phosphorus release / uptake occurred simultaneously under anoxic conditions. The phosphorus release phase was found to coincide with the first rapid phase of denitrification while phases 2 and 3 corresponded with phosphorus uptake. These observations are indicative of the presence of PAO's which take up acetate-like compounds rapidly with a concomitant release of phosphorus to the bulk liquid. The acetate taken up is converted to PHA's. The phosphorus uptake seen in Figure 6-4 suggests that these are denitrifying polyphosphate accumulating organisms which are capable of using the stored PHA's during denitrification.

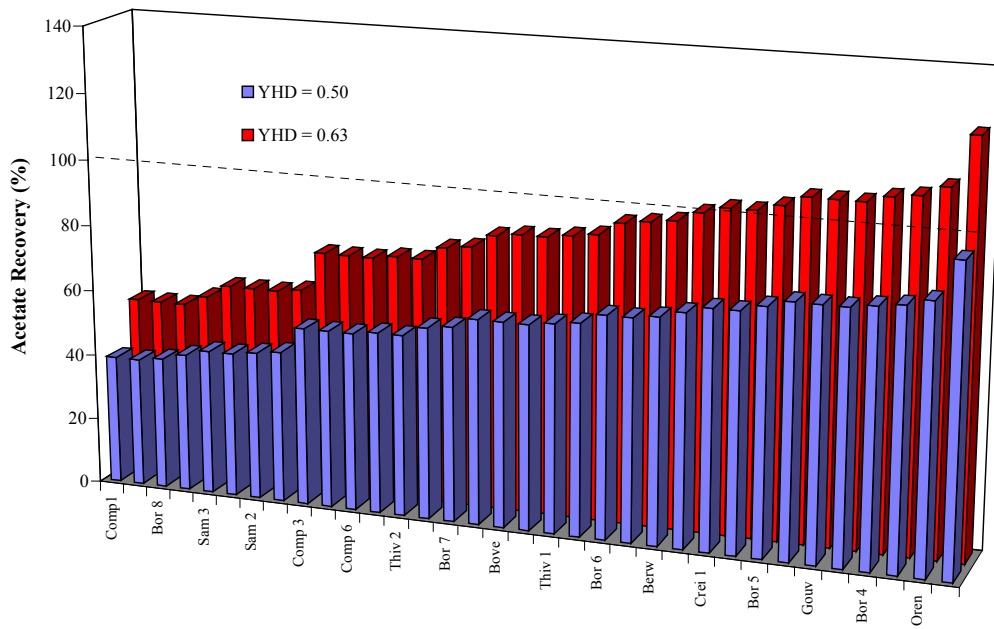


Figure 6-3: Acetate recovery based on  $\Delta NO_x$  1 for  $Y_{HD} = 0.50$  and  $0.63 \text{ mgO}_2/\text{mgO}_2$ .

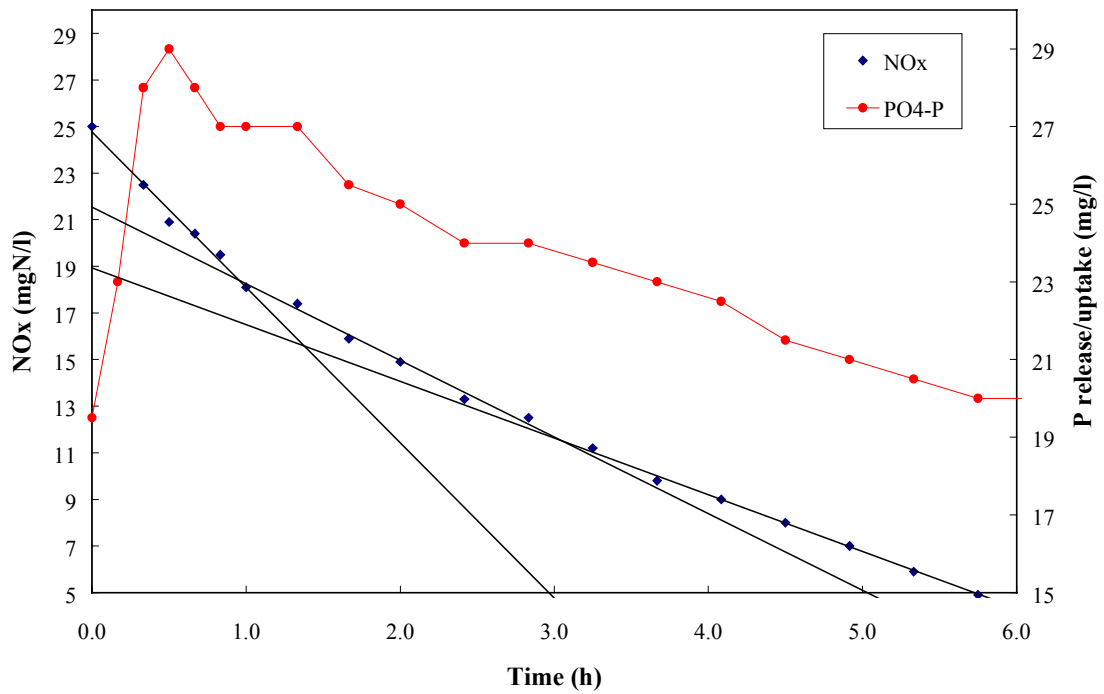


Figure 6-4 : Typical example of ortho-phosphate (as P) release and uptake with simultaneous denitrification (  $T = 20^\circ\text{C}$ ;  $\text{pH}=7.5$ ).

- Sum of acetate recoveries 1 and 2 based on  $\Delta NO_x$  1 +  $\Delta NO_x$  2

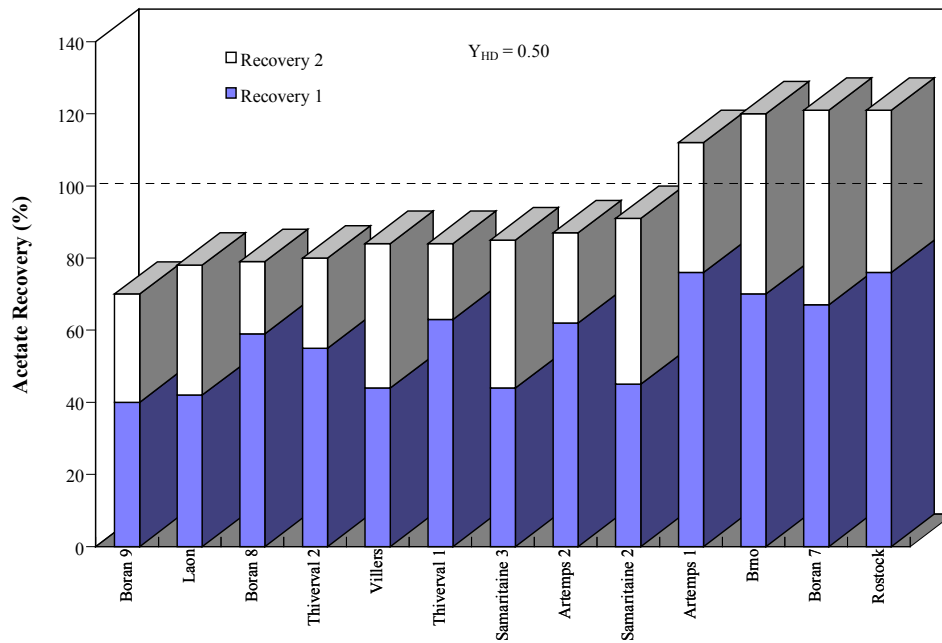
It was hypothesized that the second phase in a 3-phase denitrification profile was due to the utilization of internally stored compounds like polyhydroxyalkanoates. This utilization was thought to be linked to the presence of acetate in the reactor. Furthermore, it was postulated that during denitrification the acetate may be consumed by possibly 3 groups of bacteria viz : denitrifiers, denitrifying polyphosphate accumulating organisms and/or polyphosphate accumulating organisms. In the presence of nitrate the DPAO's sequestered the acetate and converted it to PHA's. The converted PHA's were then utilized during denitrification and corresponds to phase 2 (Figure 6-4). Two trends were observed for the sum of acetate recoveries 1 and 2 *i.e*  $< 100\%$  and  $> 100\%$  mass balance.

◆  $< 100\%$  recovery

Even though the  $\text{NO}_x$  1 and 2 were added, the acetate recovery for Artemps 2, Boran (8, 9), Laon, Samaritaine (2,3), Thiverval (1,2), and Villers was less than 100 % (Table 6-2 ; Figure 6-5). These results suggest that the acetate present in the reactor was sequestered by DPAO's or PAO's to produce storage compounds. In the case of denitrifying polyphosphate accumulating organisms the acetate taken up was not re-utilized for denitrification.

◆  $> 100\%$  recovery

Several tests such as Artemps 1, Boran 7, Brno, and Rostock produced acetate mass balances that were greater than 100 %. When  $\Delta\text{NO}_x$  1 +  $\Delta\text{NO}_x$  2 were added, most of tests gave mass balances of approximately 160 % *i.e.* 60% more acetate was calculated than was added. Table 6-2 clearly shows that the 60 % more acetate that was calculated was largely due to biodegradable COD that was calculated from phase 2 ( $\Delta\text{NO}_x$  2) results. Since almost 100 % of the acetate added could be accounted for in phase 1, the  $> 100\%$  recovery was possibly due to sludge contribution *i.e.* the sludge may have utilized existing storage products during denitrification.



**Figure 6-5: Acetate recovery 1 and 2 with a yield coefficient of 0.50 showing < 100 % and > 100 % mass balances for anoxic batch tests conducted with different sludges.**

### 6.1.2.2 Interpretation of data with constant $Y_{HD}$ of 0.63

With the use of the yield coefficient, 0.63  $\text{mgO}_2/\text{mgO}_2$ , the trends observed were similar to those observations made using a yield coefficient of 0.50  $\text{mgO}_2/\text{mgO}_2$  in equation 3-8. There was one additional observation viz: 100 % recovery was noted when using  $\Delta\text{NOx 1}$  values to calculate acetate recovery.

#### 1) 100 % recovery based on $\Delta\text{NOx 1}$

A mass balance of 100% was calculated for Artemps 1, Berwick, Boran (2, 3, 4, 5, 6), Brno, Creil (1, 2), Gouvieux, Orense and Rostock using  $\Delta\text{NOx 1}$  (Table 6-2 ; Figure 6-3). These results suggested that the activated sludge samples from these plants contained a higher proportion of denitrifiers and a smaller or insignificant proportion of polyphosphate accumulating organisms (PAO's). These PAO's were unable to compete with the denitrifiers for the available acetate. This inability to take up substrate for storage could also be explained in terms of 'biomass history'. Majone *et al.* (1996) reported that the bacterial response (i.e utilization/growth, accumulation or storage) may be due to the microbial composition as well as the physiological state of the bacteria. The latter is influenced by operating (dynamic) conditions imposed on the process.

#### 2) < 100 % recovery based on $\Delta\text{NOx 1}$

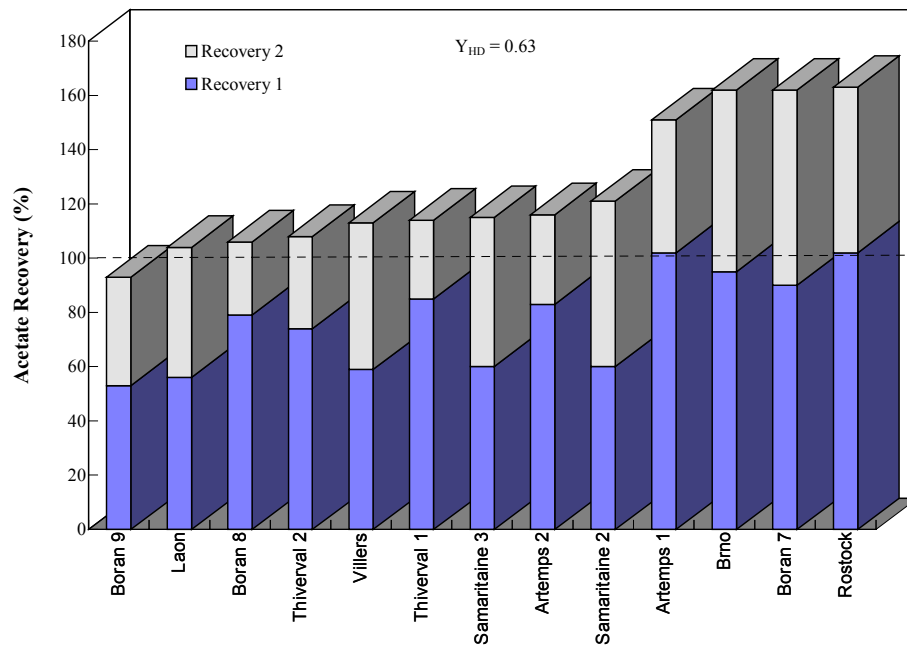
Kinetics with sludge from Boves (P release), Artemps 2 (P release), Asnieres (P release), Boran (7, 8, 9, 10, 11 - P release), Compiègne (1, 2, 3, 4, 5, 6 - P release), Samaritaine (2, 3 - P not determined), Thiverval (1, 2 - P release), and Villers (P release) resulted in a < 100 % acetate recovery (Table 6-2 ; Figure 6-3). In these cases, except for Samaritaine where ortho-phosphate (as P) was not determined, the activity of denitrifying polyphosphate accumulating organisms (DPAO's) and/or PAO's could account for the loss of acetate from the denitrification reaction. In addition, P release was not expected for Boves, Asnieres and Boran since these are not phosphorus removal plants i.e. these are non-EBPR plants. Thus, it would appear that even in non-EBPR systems, a proportion of PAO's were present which were able to compete with the denitrifiers for the available acetate or that the physiological state of the biomass brought about an accumulation or storage response.

**3) Sum of acetate recovery  $\cong$  100% recovery based on  $\Delta\text{NOx 1} + \Delta\text{NOx 2}$**

For those kinetics which produced three phases, acetate recovery 2 was calculated as a fraction of the acetate added to determine if a mass balance of 100 % was possible by taking the sum of acetate recovery 1 and 2. The sum of the acetate mass balances 1 and 2 was found to be approximately 100 % for Boran (8, 9), Laon, and Thiverval 2. These results seem to suggest that acetate may sometimes be diverted through three pathways, one for energy with the use of nitrates as electron acceptor, another for growth and the third is the production of storage compounds. Hence, there was < 100 % recovery with  $\Delta\text{NOx 1}$  but a 100 % mass balance when the sum of  $\Delta\text{NOx 1}$  and  $\Delta\text{NOx 2}$  was considered. However, the 100 % recovery with  $\Delta\text{NOx 1}$  and  $\Delta\text{NOx 2}$  suggests that the bacteria use storage products during denitrification. It was postulated that these storage products could arise from the synthesis of storage products from the acetate added to the reactor which are subsequently re-used when the acetate added becomes limiting (rapid synthesis / utilization reaction). This is substantiated with the observation from NUR profiles of a short 'intermediate' phase which follows the first rapid phase. This 'intermediate' phase appears to be similar to the 'tailing phenomenon' described for OUR tests done with acetate (Majone *et al.*, 1999). Both phosphorus release and phosphorus uptake was observed in several of these tests. Since it is known that polyphosphate accumulating bacteria release storage compounds for use with the electron acceptor  $\text{O}_2$  under aerobic conditions, it would seem likely that in the presence of the electron acceptor  $\text{NO}_3^-$  under anoxic conditions the same could apply. This is possible when denitrifying polyphosphate accumulating organisms are present (Meinhold *et al.*, 1999).

**4) Sum of acetate recovery 1 and 2 > 100 % based on  $\Delta\text{NOx 1}$  and  $\Delta\text{NOx 2}$**

The sum of recoveries 1 and 2 for Artemps (1, 2), Boran 7, Brno, Rostock and Samaritaine (2, 3), Thiverval 1 and Villers were greater than 100 % (Figure 6-6). As discussed in section 6.1.2.1 about 100 % of the acetate added could be accounted for in phase 1 which suggests that the biodegradable COD that was calculated in phase 2 could be due to the utilization of existing storage compounds present in the heterotrophic biomass (Fig 6-6).



**Figure 6-6 : Acetate recovery 1 and 2 with yield coefficient of 0.63 ( $\text{mgO}_2/\text{mgO}_2$ ).**

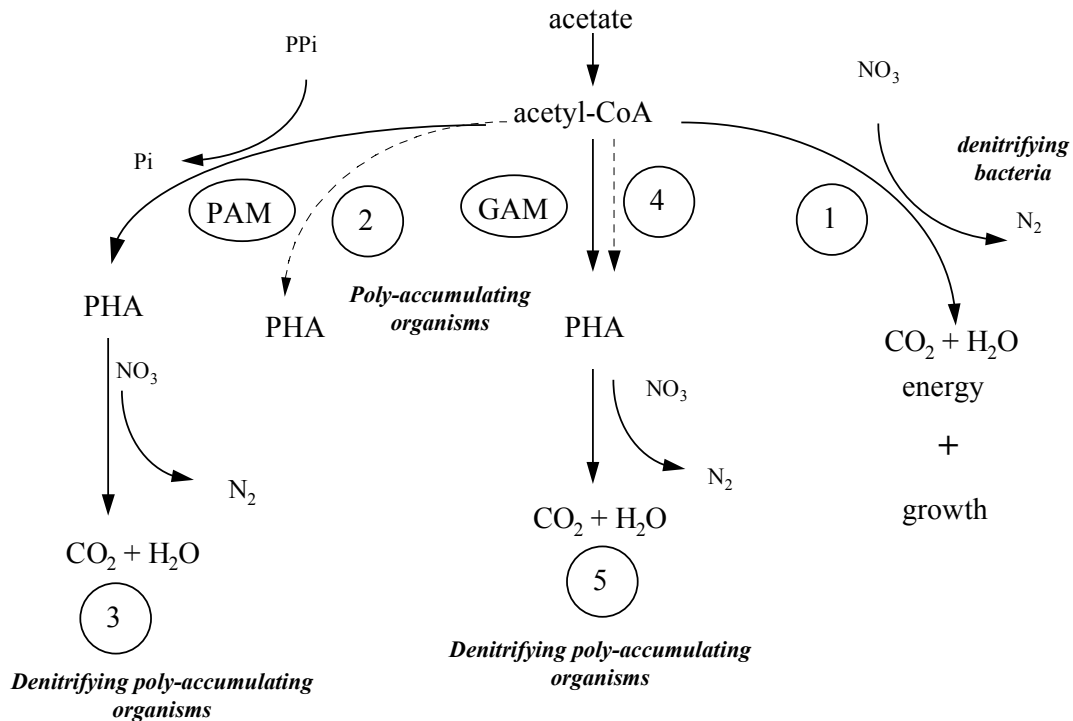
Based on these observations it was possible to interpret acetate utilization under anoxic conditions in the following way (see Figure 6-7):

- i.) Acetate was used exclusively for denitrification by denitrifiers *i.e.* where acetate mass balances were 100 % (1 in Figure 6-7). In this case, the sludge contained a significant proportion of denitrifiers and little or no polyphosphate accumulating organisms or that the bacteria did not require storage compounds.
- ii.) In cases where acetate recovery was < 100 %, it could be interpreted that acetate was used for denitrification and for the production of storage products like polyhydroxyalkanoates (PHA's). It is possible that these bacteria do not contain sufficient storage material and therefore, the acetate that is taken up is not utilized during denitrification but stored for future use (1, 2, and 4 in Figure 6-7). In addition, to the denitrifying bacteria these sludges probably contained a significant proportion of polyphosphate accumulating organisms but no denitrifying polyphosphate accumulating organisms.
- iii.) Results also suggest that acetate is used for denitrification and for polyhydroxyalkanoate production. These polyhydroxyalkanoate compounds are subsequently utilized during denitrification. The utilization of the stored compounds in the second denitrification phase is supported by the P uptake observed after the P release (Figure 6-4) (see step 1, 2 and 3, and 4 and 5 - Figure 6-7). Thus, the sum of the two mass balances is approximately 100 %. Thus, these sludges contained denitrifiers and denitrifying polyphosphate accumulating organisms which competed for the available acetate or



the physiological state of the biomass brought about an accumulation and / or storage response and the accumulated / stored compounds were re-used once the acetate became limiting.

- iv.) Some results suggest that all the acetate was used for denitrification. However, the bacteria also used existing storage compounds. Therefore, the sum of recovery 1 and 2 is greater than 100 %. This scenario could be due to the presence of denitrifying polyphosphate accumulating organisms which already have sufficient reserve material. Therefore, when an electron acceptor becomes available these storage compounds are utilized.



**Figure 6-7: Pathways of acetate utilization that may be possible in an anoxic system containing polyphosphate accumulating organisms, denitrifying PAO's, and denitrifiers.**

### 6.1.2.3 COD and P release correlations

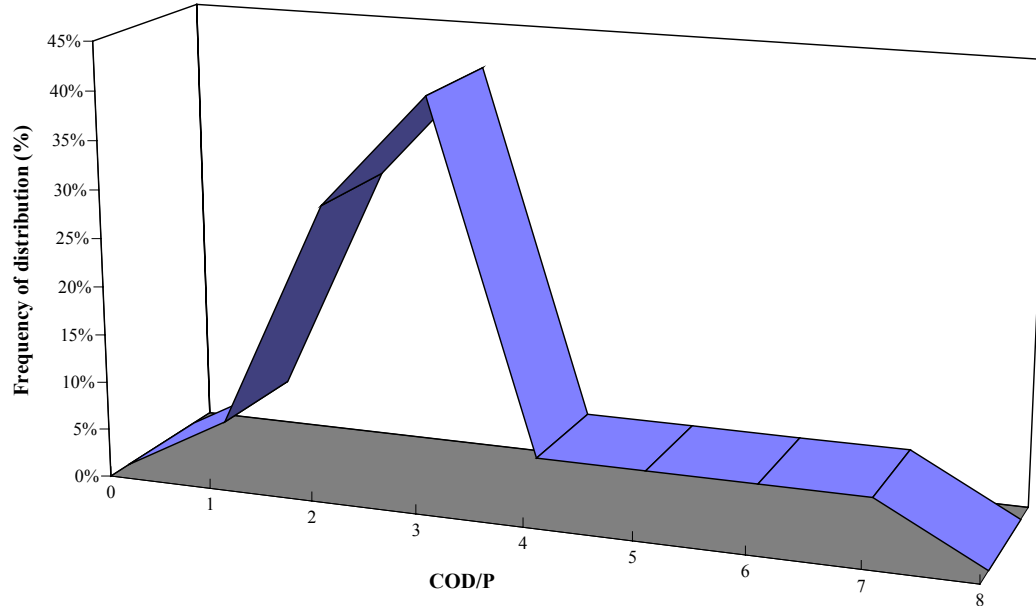
Since the concentration of acetate added to each reactor was known, the COD taken up by polyphosphate accumulating organisms could be found by the difference between the COD added and the COD recovered (i.e. COD consumed during denitrification) (Table 6-3). Consequently, the ratio of COD taken up to phosphorus (P) ratios were calculated. By plotting sequestered COD vs P release curves, a weak correlation of  $\text{COD}_{\text{seq}} = 2.9 \times \text{P release}$ ;  $r = 0.67$ ) was found between P release and COD consumed by PAO's which highlights the variability of these ratios. The average COD/P ratio was found to be  $3.5 \pm 1.5$  which correlates to the values 2 to 5 reported by Wentzel *et al.* (1986) (Table 6-3). Most of the COD/P ratios were between 2 and 4 (Figure 6-8).

Results also showed that the COD/P ratios were variable for individual plants. For example, Boran, a non-EBPR plant, gave COD/P ratios which ranged from 3.1 to 6.3 (mgO<sub>2</sub>/mgP). In addition, Compiegne, an EBPR plant, gave COD/P ratios ranging from 1.1 to 7.0 (mgO<sub>2</sub>/mgP). These are significantly different values for the same sludges. The pH could not be cited as a possible reason for the variability since the pH of the batch reactors were controlled at 7.5. The internal P content is cited as a factor which could contribute to this variability (Shuler and Jenkins, 1997). The variation in COD/P ratios could be linked to the energy source, polyphosphate and glycogen, used to drive the reaction. If more glycogen is expended for substrate uptake and conversion, then the amount of P released will be less while the amount of substrate taken up will remain the same. Thus, the COD/P ratio will decrease. If polyphosphates are mostly used to drive the substrate removal reaction then the COD/P ratio will increase. Therefore, glycogen or polyphosphate limitation may play a significant part in the amount of P released per mg COD taken up. The appearance of phosphorus in the bulk liquid is as a result of the degradation of the internal reserves of polyphosphates to provide the energy necessary for the production of polyhydroxyalkanoates. However, the dependency of polyP as an energy source can vary due to the balance between production and consumption of energy in the cell (Mino *et al.*, 1998 ; Brdjanovic *et al.*, 1998b). In addition, the indirect measurement of COD uptake could also explain the variation in COD/P ratios.

**Table 6-3: Comparison of P release and acetate (mgO<sub>2</sub>/l) recovery data using  $Y_{HD} = 0.63$  (mgCOD/mgCOD).**

	P release (mgP/l)	COD consumed (mgO <sub>2</sub> /l)	COD/P (mgO <sub>2</sub> / mgP)
Asnieres s/oise	4.0	13	3.25
Boran 2	3.0	19	6.33
Boran 3	4.0	11	2.75
Boran 7	3.0	10	3.33
Boran 8	7.5	23	3.07
Boves	3.0	8	2.67
Compiègne 1*	7.0	24	3.57
Compiègne 2*	6.5	24	3.69
Compiègne 3*	6.0	14	2.33
Compiègne 4*	7.0	7	1.14
Compiègne 5*	6.0	13	2.17
Compiègne 6*	2.0	14	7.00
Crespieres 2	2.0	8	4.00
Laon	4.0	22	5.25
Thiverval 1*	2.0	7	3.50
Thiverval 2*	6.5	13	2.00
Villers	6.0	20	3.50

\* Enhanced biological phosphorus removal (EBPR) plants



**Figure 6-8: Frequency (%) of the COD/P ratios (n=17).**

## 6.2 WASTEWATER CHARACTERIZATION IN BIOLOGICAL PHOSPHORUS REMOVAL AND DENITRIFICATION SYSTEMS

One of the main factors which influences the characterization of readily biodegradable COD in anoxic systems is the presence of polyphosphate accumulating organisms and denitrifying polyphosphate accumulating organisms which have the propensity to take up readily biodegradable COD (*i.e.*  $S_A$  fraction) with concomitant phosphorus release. In enhanced biological phosphorus removal (EBPR) systems this problem is increased due to the presence of higher numbers of PAO's which can influence biological wastewater characterization. In this investigation the activated sludges obtained from EBPR plants were referred to as bioP sludge while the non-EBPR or denitrification (DN) plant was referred to as non-bioP sludge. Thus, the objective of this study was to determine the impact of the bio-P sludge activity on wastewater characterization.

Two EBPR plants, Compiègne and Thiverval, were selected to study the impact of polyphosphate accumulating organism activity on RBCOD characterization. Sludge from Boran WTP was used as a non-bioP sludge for both tests. The total COD concentration of wastewater was less variable for Compiègne than Thiverval (Table 6-4). The total COD concentration for Thiverval (31/07/97) was approximately two times the COD concentration measured for the first test conducted on 17/07/97. Since Thiverval is a smaller plant it was likely that it was susceptible to small perturbations in the network whereas the high capacity of Compiègne was able to buffer any changes.

**Table 6-4: Wastewater characterization of bio-P plants, Compiègne and Thiverval.**

	Date	St	S-co	RBCOD				RHCOD			
		mg/l	%	mg/ l		%		mg/ l		%	
Compiègne 1 (M)	3/06	783	n.d.	145 <sup>a</sup>	172 <sup>b</sup>	18 <sup>a</sup>	22 <sup>b</sup>	n.o	–	n.o	–
2 (W)	5/06	787	23	70 <sup>a</sup>	104 <sup>b</sup>	9 <sup>a</sup>	13 <sup>b</sup>	94 <sup>a</sup>	142 <sup>b</sup>	12 <sup>a</sup>	18 <sup>b</sup>
3 (Su)	9/06	883	22	67 <sup>a</sup>	101 <sup>b</sup>	8 <sup>a</sup>	11 <sup>b</sup>	n.o	–	n.o	–
4 (Tu)	11/06	817	25	146 <sup>a</sup>	204 <sup>b</sup>	18 <sup>a</sup>	25 <sup>b</sup>	n.o	–	n.o	–
Thiverval 1 (W)	17/07	437	29	45 <sup>a</sup>	49 <sup>b</sup>	10 <sup>a</sup>	11 <sup>b</sup>	59 <sup>a</sup>	87 <sup>b</sup>	13 <sup>a</sup>	19 <sup>b</sup>
2 (W)	31/07	977	13	111 <sup>a</sup>	119 <sup>b</sup>	8 <sup>a</sup>	12 <sup>b</sup>	87 <sup>a</sup>	52 <sup>b</sup>	9 <sup>a</sup>	5 <sup>b</sup>

(<sup>a</sup> - bio-P sludge; <sup>b</sup> - non bio-P sludge, M - Monday, Tu - Tuesday, W - Wednesday, Su - Sunday)

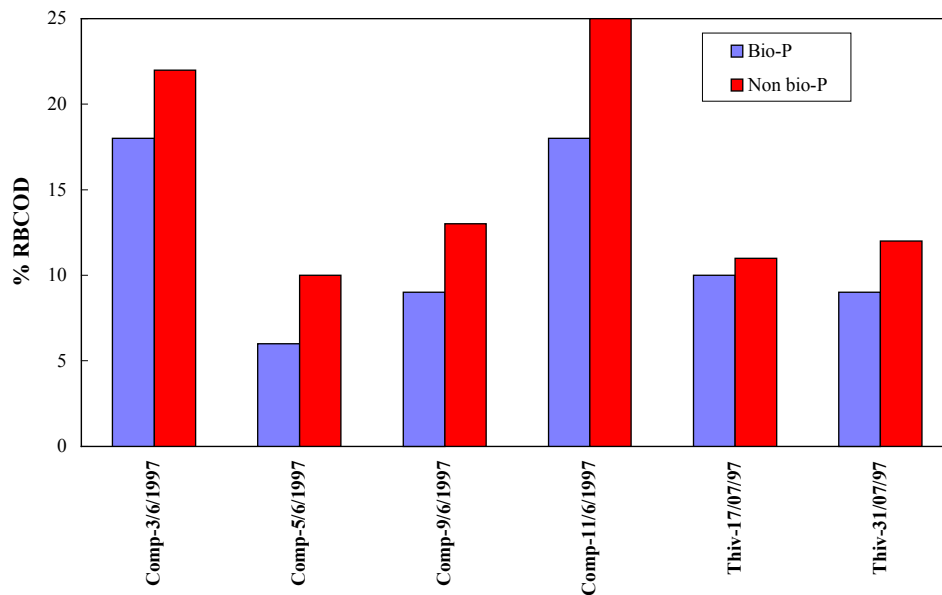
### 6.2.1 RBCOD fraction

Figure 6-9 clearly showed that that the non-bio P sludge resulted in higher RBCOD values than the bio-P sludge. Thus, the activity of polyphosphate accumulating organisms in the sludge from Compiègne and Thiverval resulted in an underestimation of RBCOD values. The difference between the RBCOD values derived using bio-P and non bio-P sludge was considered as the RBCOD fraction lost to PAO activity

under anoxic conditions. The RBCOD fraction of wastewater from Compiègne was found to be 8 to 18 % and 11 to 25 % of total COD with sludge from Compiègne and Boran, respectively (Table 6-4 ; Figure 6-9). This suggests that approximately 4 to 7 % of the RBCOD fraction of raw wastewater may be taken up by polyphosphate accumulating organisms.

This trend was also observed with tests conducted at Thiverval, where the difference in RBCOD between the 2 sludges ranged between 1 and 4 % (Table 6-4 ; Figure 6-9). One of the reasons for the lower RBCOD loss was that the acetate-like fraction made available to the bio-P bacteria was smaller for Thiverval 1 samples. This was confirmed with volatile fatty acid analysis of the raw wastewater sample which showed less than 10 mg/l of acetate as COD (Table 6-5). In all of the above tests, except Thiverval 1, phosphorus release and uptake was observed for the bio-P sludge. Similarly, no change in the P concentration was observed for the non bio-P sludges, except for the final test with Thiverval on the 31/07/97.

Phosphorus release of 1.5 mgP/l was observed for Boran for the test conducted on the 31/07/97. Sludge samples from Boran had previously not shown P release even in the presence of high concentrations of acetate. Enquiries into the plant operation revealed that there was a malfunction in the process control system which is required for switching the aeration on and off when nitrates are absent. Thus, it is possible that the creation of anaerobic conditions and the presence of RBCOD from the influent would have created conditions that were ideal for the enrichment of PAO's. Hence, there was a shift in population dynamics.



**Figure 6-9: Comparison of RBCOD fractions calculated using bio-P and non bio-P sludge with the NUR method.**

### 6.2.2 Correction of the RBCOD lost with P release and influent acetate data

It has been documented that polyphosphate accumulating organisms are only capable of using short chained fatty acids (VFA's) (Wentzel *et al.*, 1992). Therefore, the difference between the RBCOD values derived by bio-P and non bio-P sludge were compared to the acetate and VFA concentrations (acetate and propionate as COD) measured for the influent raw wastewater (Table 6-5). The acetate fraction was found to be fairly comparable to the RBCOD fraction lost. The VFA fraction (*i.e.* acetate and propionate) was less comparable. These preliminary results show that determination of the acetate fraction could be used to correct the underestimated RBCOD fraction when a bio-P sludge is used to characterize the wastewater by the NUR test. Further tests will need to be done to verify if this is the trend for all NUR tests conducted with EBPR sludges.

**Table 6-5: The wastewater fraction utilized by P removal organisms for P release under denitrifying conditions (% of total COD).**

Kinetic/Date	RBCOD Fraction lost to P release (%)		Measured acetate concentration (%)		Measured VFA concentration (%)	
	%	mgO <sub>2</sub> /l	%	mgO <sub>2</sub> /l	%	mgO <sub>2</sub> /l
1 - Com - 3/06/97	4	27	6	47	9	70
2 - Com - 5/06/97	4	34	5	39	5	39
3- Com - 9/06/97	3	34	3	26	3	26
4- Com - 11/06/97	7	58	5	41	7	57
5- Thiv - 17/17/97*	1	4	< 2	< 10	< 2	< 10
6 - Thiv - 31/17/97	4	48	4	39	4	39

(Com - Compiegne; Thiv - Thiverval; P - phosphorus as P; VFA - volatile fatty acid; \* - not considered)

### 6.2.3 Relationship between RBCOD lost to PAO's and P release

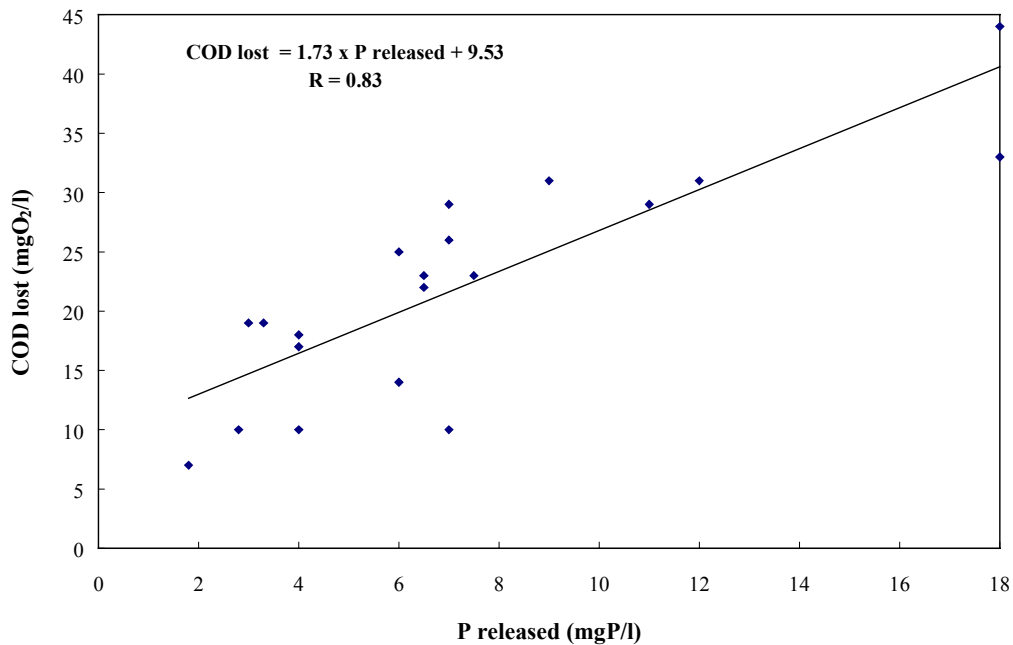
The RBCOD that is underestimated with EBPR sludges is equivalent to the concentration of RBCOD sequestered by the polyphosphate accumulating organisms that are present in the EBPR sludges. By using the measured phosphorus release values and then converting the RBCOD fraction lost to the polyphosphate accumulating organisms into COD (mgO<sub>2</sub>/l), the COD/P (mgO<sub>2</sub>/mgP) ratios were calculated (Table 6-6). The COD/P ratios varied between 1.4 to 4.1 with an average of 3.0. This compares well with the values, 2 to 5, cited by Mostert *et al.*, 1988 and Wentzel *et al.*, 1985. The phosphorus release vs COD lost results derived from the kinetics with acetate (see section 6.1) as well as in this study were combined and plotted in Figure 6-10. Figure 6-10 shows that the correlation coefficient (R=0.83) is improved by the addition of data from this study. However, the variation is still large. This variability could be due to the difference in the internal phosphorus content of the bacterial cells which is known to influence the acetate/VFA uptake (Schuler and Jenkins, 1997). The pH value is also known to influence the ratio between VFA uptake and P release (Van Loosdrecht *et al.*, 1997b). However, this factor would not have influenced the ratio as the pH was controlled at 7.5. The variability of the COD/P

ratios can also vary depending on the substrate. For example, Wentzel *et al.* (1985) cited ratios of 2 to 5 for acetate while Mostert *et al.* (1988) reported similar ratios for acetate but ratios of 3 to 14 for propionate and butyrate. Therefore, the use of the COD/P would not be an ideal method to estimate the amount of COD lost to polyphosphate accumulating organism activity due to the variability of the ratio.

**Table 6-6: Comparison of average COD/P ratios using different methods of calculation with data collected from kinetics with wastewater from Compiègne (COD in mgO<sub>2</sub>/l)**

Kinetic	Date	P release	RBCOD lost	COD/P
1 - Compiègne	3/06/97	12	31	2.6
2 - Compiègne	5/06/97	9	31	3.4
3 - Compiègne	9/06/97	18	62	3.4
4 - Compiègne	11/06/97	18	25	1.4
5 - Thiverval	31/17/97	7	29	4.1
average				3.0

(P - phosphorus as P).



**Figure 6-10 : Relationship between COD lost to polyphosphate accumulating organisms and P release.**

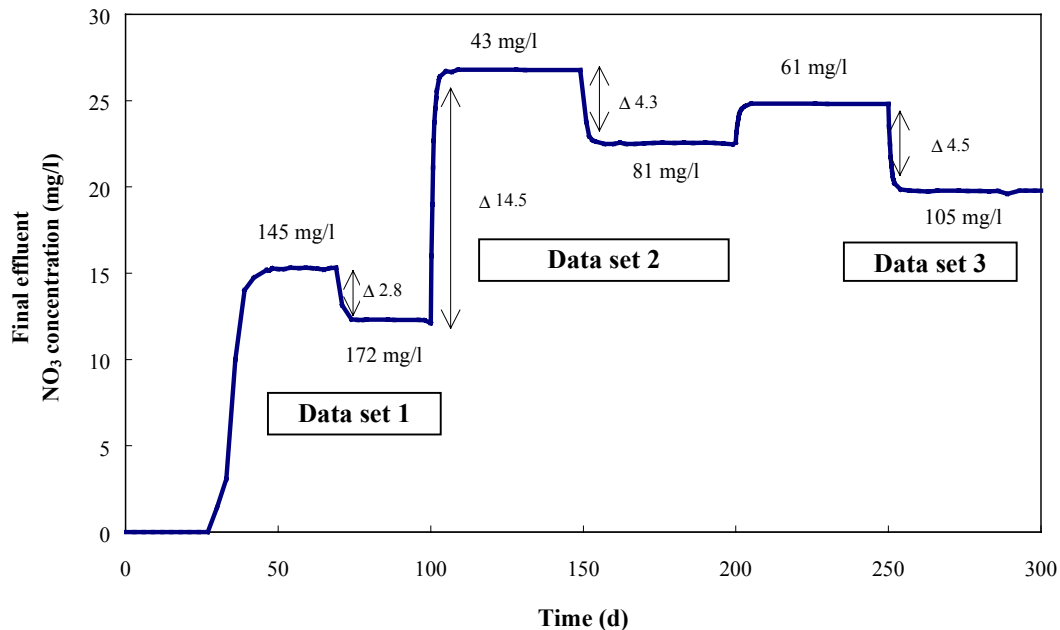
#### 6.2.4 Impact of RBCOD loss in a denitrification process

In order to assess the influence of the 4 to 7 % loss in RBCOD due to bio-P sludge activity, a simulation study was done using the IAWQ Activated Sludge Model I. The conditions of the simulation test are listed in Table 6-7. This simulation study was conducted to investigate how changes in the RBCOD

concentration can affect denitrification and thus, the final effluent quality. The simulation was done using a nitrification/denitrification system with 100% nitrification.

**Table 6-7: Conditions of simulation study using the IAWQ Activated Sludge model I**

	Conditions
Reactor volume	9 m <sup>3</sup>
Flow rate	0.5 m <sup>3</sup> /h
Air on/off	1.5 h
HRT	18 h (0.75d)
SRT	7.5 d



**Figure 6-11: Impact of RBCOD lost to polyphosphate accumulating organisms on final effluent quality using simulation studies (IAWQ Activated sludge Model I).**

The results from the simulation test are shown in Figure 6-11. The simulation also shows how the variation in the RBCOD concentration of the influent raw wastewater can also severely impact on the final effluent NO<sub>3</sub>-N concentration. For example, in data set 1 the RBCOD concentration made available to the denitrifying biomass was 145 mg/l (27 mg/l was lost to PAO's) but in data set 2 only 43 mg/l of RBCOD (38 mg/l was lost to PAO's) was available. This change was not due to a change in the PAO fraction or the total wastewater concentration, but was due to a significant variation (*i.e.* decrease) in the influent RBCOD concentration. Consequently, the final effluent NO<sub>3</sub>-N concentration increased from about 15 mg/l to about 25 mg/l (Figure 6-11). Therefore, a wastewater treatment process must be



operated in a manner which considers these variations in the influent RBCOD concentration without compromising the final effluent quality. Based on the simulation studies, the amount of  $\text{NO}_3^-$ -N denitrified was determined. The results show that approximately 0.1 mg  $\text{NO}_3^-$ -N was denitrified per mg of readily biodegradable COD consumed (Table 6-8).

**Table 6-8: The concentration of nitrogen denitrified with the available RBCOD**

Sludge Type	RBCOD conc.	Amount of N denitrified		
		Data set 1	Data set 2	Data set 3
EBPR	145	15.9		
non-EBPR	172	18.7		
EBPR	43		4.6	
non-EBPR	81		8.9	
EBPR	61			6.8
non-EBPR	105			11.3
$\Delta\text{N}$ (mg/l)		2.8	4.3	4.5
$\Delta\text{RBCOD}$ (mg/l)		27	38	44
mgN/mgRBCOD		0.10	0.11	0.10

### 6.3 SUMMARY

This chapter contains important observations as they provide some idea of how the sludge may react to the acetate and hence, RBCOD in the wastewater. Thus, there are three possible interpretations of the acetate results. Plants which showed < 100 % acetate show that there will probably be an underestimation of RBCOD values if the NUR test is done with the bio-P sludge. Plants which showed 100% recovery when acetate mass balances 1 and 2 were added, show that acetate like compounds may be sequestered for polyhydroxyalkanoate during phase one resulting in an underestimation of the RBCOD concentration. However, the sequestered compounds may be re-utilized during denitrification. This release may be dependent on the internal concentration of the storage compounds found in bacterial cells and on the physiological state of the biomass used for the tests. These are important observations as they show that RBCOD compounds, particularly the acetate fraction may not always be used exclusively for denitrification purposes under anoxic conditions. These interpretations will need to be considered when evaluating the RBCOD fraction of wastewater calculated using the NUR batch test method.

These interpretations were further substantiated in wastewater characterization experiments done on bio-P (EBPR) and non bio-P (non-EBPR) sludges. Tests with Compiègne and Thiverval wastewater clearly showed that the RBCOD fraction was underestimated when a bio-P sludge was used due to polyphosphate accumulating organism activity. This RBCOD fraction which was not available for

denitrification was found to be approximately 4 to 7% of the influent raw wastewater (9 to 33 % of RBCOD). The RBCOD lost to polyphosphate accumulating organisms was found to be fairly comparable to the acetate fraction. Thus, the fraction lost to PAO's can be roughly accounted for when conducting NUR tests with bio-P sludge by adding the influent acetate fraction to the RBCOD calculated. A weak correlation was found for the COD lost and P released. However, this COD/P ratio was variable and therefore, would not accurately account for the RBCOD loss in bio-P sludge. These tests confirmed the need to measure phosphorus during the denitrification batch test. Furthermore, a simulation of a nitrification/denitrification process with complete nitrification showed that approximately 0.10 mg  $\text{NO}_3^-$ -N was denitrified per mg of RBCOD consumed. Therefore, approximately 2.3 mg of RBCOD is required to remove 1 mg of  $\text{NO}_3^-$ -N.

# Chapter Seven

## ***WASTEWATER CHARACTERISTICS***

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Wastewater characterization is an important first step when evaluating the operation and efficiency of existing plants. It also provides useful information for the construction and operation of future plants. In addition, it accumulates useful input data for modelling studies which can then be used to simulate best and worst case scenarios with regard to biological processes. The objectives of this part of study were to:

- Characterize the wastewater by physical and chemical methods such as settling, centrifugation, filtration, and coagulation.
- Characterize the wastewater by a biological method, the NUR batch test.
- Compare wastewater fractions derived by a physico-chemical method (coagulation) with the biologically (NUR) derived fractions.
- Characterize the specific denitrification rate constants of wastewater, acetate, and sludge.

The wastewater characteristics presented here have been determined from several different wastewater treatment plants in Europe and South Africa, with the majority of the wastewaters characterized from France. The results from 4 South African wastewaters are presented separately in section 7.1. and collectively in section 7.2.

### ***7.1 PHYSICO-CHEMICAL CHARACTERISTICS OF WASTEWATERS***

Raw wastewater was fractionated by settling (2h) (S-ns), centrifugation (S-ce), filtration (S-f<sub>0.45</sub>) and coagulation (S-co). All concentrations are given as COD (mgO<sub>2</sub>/l) while the fractions are given as a percentage of the total COD concentration. Table 7-1 shows the characteristics of the different wastewaters.

The distribution of the raw wastewater COD concentrations and fractions (%) are plotted in Figure 7-1 and Figure 7-2. The total COD concentration varied significantly with a maximum and minimum values of 1157 and 176 mgO<sub>2</sub>/l, respectively. However, majority of the concentrations were found to be between between 700 and 1000 mgO<sub>2</sub>/l (Figure 7-1). Plotting of the distribution frequencies for the coagulated (S-

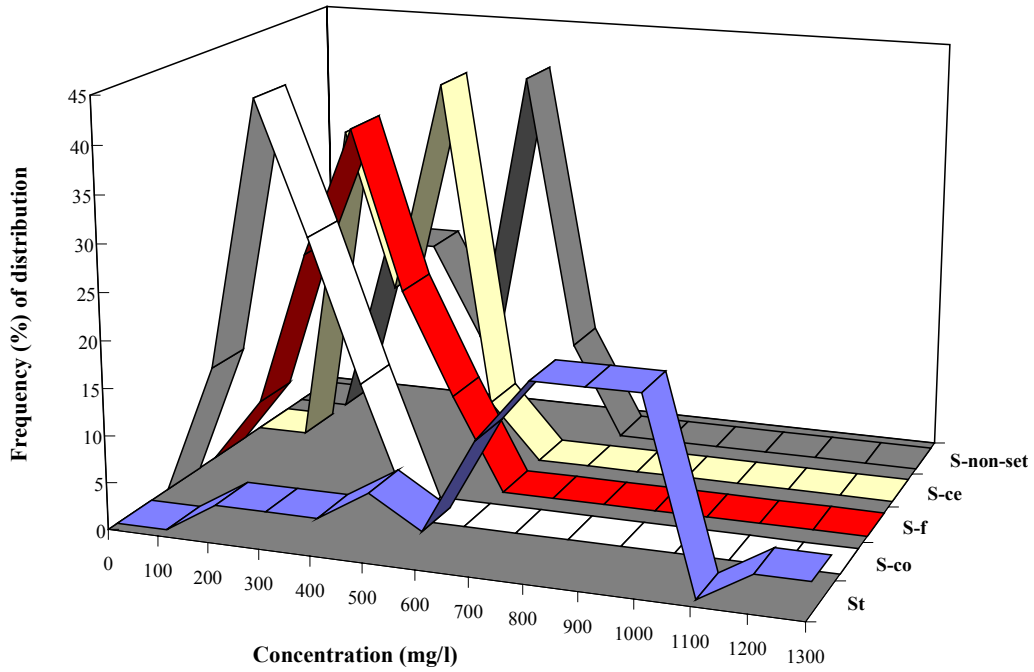
co), filtered (S- $f_{0.45}$ ), centrifuged (S-ce), and non-settleable (S-ns.) fractions of wastewater showed that the concentration for these fractions were approximately 100 to 200 mg/l, 200 to 300 mg/l, 200 to 400 mg/l, and 400 to 500 mg/l, respectively. Similarly, Figure 7-2 showed that the coagulated, filtered (0.45  $\mu\text{m}$ ), centrifuged, and non-settleable 'soluble' fractions were found to be  $26 \pm 8$ ;  $34 \pm 10$ ;  $38 \pm 15$ ; and  $58 \pm 17$  % of the total COD concentration, respectively. These results and trends were expected since coagulation was considered to be the most efficient of the methods tested for the separation of the soluble and particulate components of wastewater. Coagulation was followed by filtration, and centrifugation with settling being the least effect of the methods used. It is important to bear in mind that the results obtained are not only dependent on the separation process but also on the protocol used for the separation technique. For example, the results obtained for samples that had been separated by coagulation and filtration would have been more comparable if the final step in the coagulation protocol *i.e.* filtration had been removed (see Chapter 4, section 4.1.4). Similarly, the soluble fractions measured after filtration or centrifugation would have been less comparable if a lower centrifuge speed had been used.

The results from the 4 South African plants showed that the total COD concentrations were fairly concentrated ranging between 624 and 957  $\text{mgO}_2/\text{l}$  (Table 1). The non-settleable fraction was found to be about 50 % of the total wastewater. The filtered and coagulated COD concentration for the South African wastewaters ranged between 248 to 268  $\text{mgO}_2/\text{l}$ , and 139 to 241  $\text{mgO}_2/\text{l}$ , respectively. The average filtered and coagulated fractions were found to be 33 and 25 % of the total COD concentration. These results were similar to the overall characteristics of the European wastewater samples. In addition, the results obtained from the 4 South African samples were less variable than the European ones. The limited variability of the different fractions determined from South African wastewater samples was partly due to the limited number of samples tested. Another factor which probably influenced the results was the fact that the samples were collected from treatment plants with similar characteristics e.g. plant capacity 100 000 to 300 000 population equivalents, all the samples were taken from plants connected to separate sewers (Table 7-1).

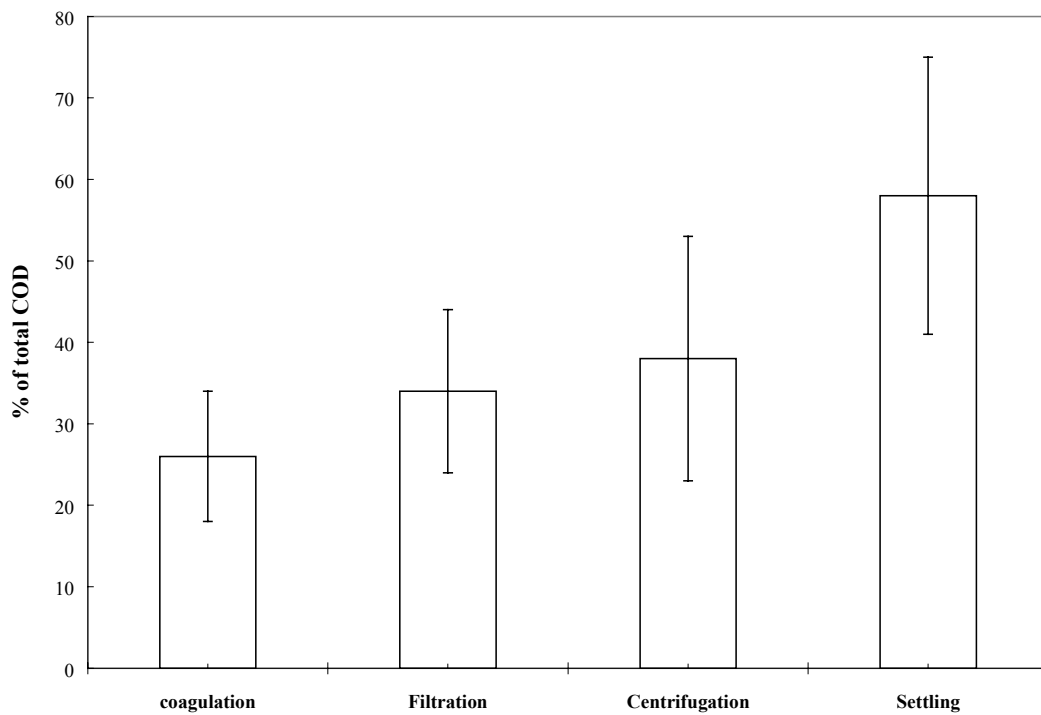
Table 7-1: Characterization of wastewater by physico-chemical methods (mgO<sub>2</sub>/l).

Plant	St	S-ns.		S-ce		S-f <sub>0.45</sub>		S-co	
	mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l
Crespieres 26/02/97	176	n.d.	n.d.	49	86	31	54	33	58
Brno	250	n.d.	n.d.	n.d.	n.d.	40	100	32	80
Morainvilliers 26/02/97	344	n.d.	n.d.	49	168	48	165	41	141
Orense	407	n.d.	n.d.	n.d.	n.d.	32	130	17	70
Thiverval 17/07/97	437	60	264	n.d.	n.d.	32	142	29	127
Crespieres 24/02/97	549	n.d.	n.d.	57	313	39	214	31	170
Thiverval 23/07/97	627	48	300	24	153	25	158	24	153
Laon	652	n.d.	n.d.	n.d.	n.d.	41	267	27	176
Boran 29/08/97	670	n.d.	n.d.	12	80	12	40	6	18
Plaisir	691	n.d.	n.d.	32	221	30	207	25	173
Boran 25/02/97	707	n.d.	n.d.	65	459	57	403	50	353
Samaritaine 28/04/97	720	63	453	n.d.	n.d.	35	252	26	187
Samaritaine 25/04/97	750	76	567	n.d.	n.d.	42	315	28	210
Boran 22/08/97	753	n.d.	n.d.	41	308	41	n.d.	n.d.	n.d.
Compiègne 3/06/97	783	76	596	n.d.	n.d.	35	274	n.d.	n.d.
Compiègne 5/06/97	787	42	329	n.d.	n.d.	29	229	23	180
Boves	813	n.d.	n.d.	42	341	40	325	31	252
Gouvieux	817	n.d.	n.d.	42	343	36	294	27	221
Compiègne 11/06/97	817	68	553	n.d.	n.d.	35	283	25	208
Creil	853	n.d.	n.d.	44	375	45	384	28	239
Compiègne 9/06/97	883	61	536	n.d.	n.d.	29	256	22	191
Morainvilliers 24/02/97	891	n.d.	n.d.	30	267	26	232	20	178
Samaritaine 23/04/97	900	69	620	n.d.	n.d.	40	360	24	216
Berwick	913	n.d.	n.d.	n.d.	n.d.	51	466	41	374
Villers sous St. Leu	923	n.d.	n.d.	43	397	41	378	31	286
Rostock	953	n.d.	n.d.	30	286	27	257	24	229
Thiverval 31/07/97	977	22	213	16	152	15	143	13	128
Artemps-Seraucourt	980	n.d.	n.d.	n.d.	n.d.	42	412	32	314
Asnières	1183	n.d.	n.d.	16	189	15	177	12	142
Compiègne 28/08/97	1257	n.d.	n.d.	31	390	29	364	24	302
Darvil *	957	50	482	n.d.	n.d.	28	268	25	241
Kwa-Mashu *	869	51	447	n.d.	n.d.	29	251	26	224
Northerns *	704	56	396	n.d.	n.d.	36	252	29	208
Southerns *	624	57	356	n.d.	n.d.	39	248	22	139

(\* - South African treatment plants; n.d. - not determined)

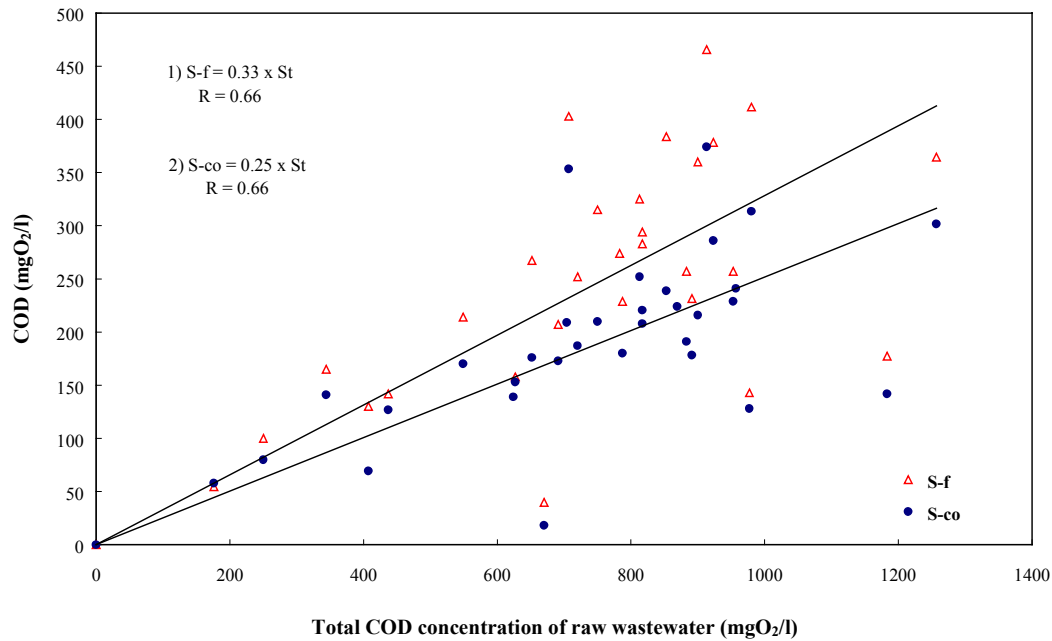


**Figure 7-1: Distribution frequencies of the raw wastewater and the non-settleable, centrifuged, filtered and coagulated concentrations.**



**Figure 7-2: Distribution of the 'soluble' fractions of raw wastewater which were determined after coagulation, filtration, centrifugation and settling tests.**

Fairly good linear relationships were found between the total COD concentration and the filtered and coagulated fractions. The 0.45  $\mu\text{m}$  filtered (S-f) and coagulated (S-co) fraction were found to be 33 and 25 % of the total COD concentration, respectively (Figure 7-3). Good correlations were found between the soluble fractions, S-ce, and S-f and S-co. Figure 7-4 shows that the coagulation and filtration method includes about 28 and 9 % less solids/colloids, respectively, than centrifugation. Thus, centrifugation and filtration were fairly similar in terms of threshold limits (Figure 7-4). In addition, a good correlation was also found between the S-f and the S-co fraction. The coagulated fraction was found to be approximately 76 % of the filtered fraction *i.e.* the coagulant takes out about 24 % more of the colloids that pass through a 0.45 $\mu\text{m}$  filter (Figure 7-5).



**Figure 7-3: Relationship between total COD, and filtered and coagulated COD concentrations ( $n = 28$ ).**

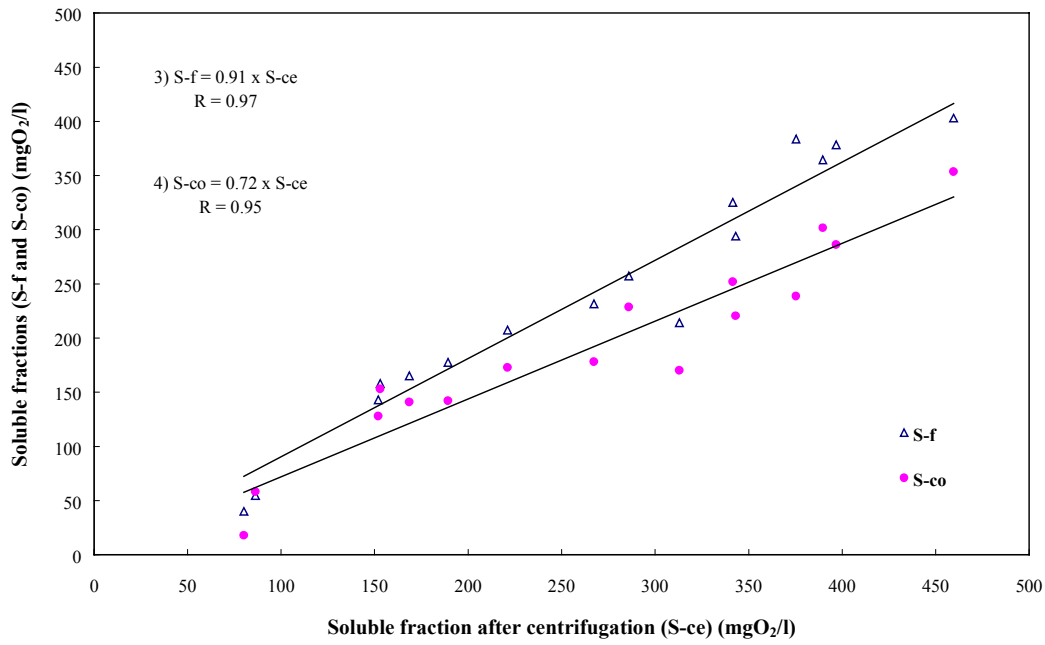


Figure 7-4: Relationships between the 'soluble' concentrations (derived by centrifugation, filtration or coagulation) ( $n = 17$ ).

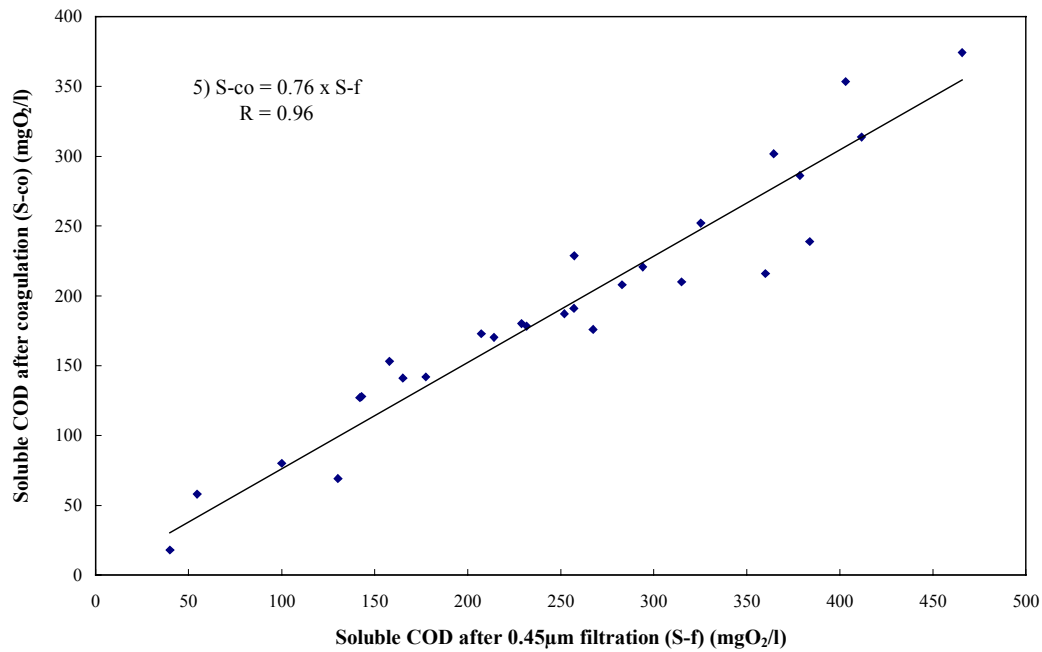


Figure 7-5: Correlation between the filtered and coagulated COD concentrations ( $n = 28$ ).



## 7.2 BIOLOGICAL CHARACTERISTICS

The use of NUR tests allowed for the observation and monitoring of the biokinetic response of the denitrifying bacteria in the presence of available organic carbon in the raw wastewater samples tested. This allowed for the determination of a biodegradable component of raw wastewater. It was also possible in certain tests to calculate a second biodegradable component of raw wastewater. This second biodegradable was termed the readily hydrolyzable component of wastewater or the 'storage' fraction. The basis for this classification is discussed in more detail in sub-section 7.2.2.

### 7.2.1 The RBCOD fraction

Table 7-2 lists the results obtained from NUR tests done on different wastewaters. In several of the tests the raw wastewater was separated by settling, centrifugation, filtration or coagulation and the 'soluble' component was used as the substrate. The RBCOD fraction derived from NO<sub>x</sub>-N vs time profiles varied between 7 and 25 % with an average of 13 % (Table 7-2 and Figure 7-6). Frequency distributions curves of the RBCOD concentrations showed that most of the samples contained between 40 to 120 mgO<sub>2</sub>/l of readily biodegradable organic matter (Figure 7-7).

These readily biodegradable values (n = 40) were represented as a fraction of the total COD and divided into three groups *i.e.*

- **Group 1** : < 10 % of total raw wastewater COD concentration (St)
- **Group 2** : Between 10 to 20 % of St
- **Group 3** : Between 20 to 30 % of St

The distribution of RBCOD fractions were plotted in Figure 7-7. Less than 5 % of the 40 samples tested contained RBCOD fractions greater than 20 % of the total COD. A fairly high number (30 %) of tests contained RBCOD fractions which were less than 10 % of the total COD concentration. Majority of the samples (65 %) tested gave values between 10 and 20 % (of total COD). This compares well with the values of 10 to 20 % of total COD cited by Henze *et al.*, (1995). It is important to note that 35 % of the samples did not fall within this range. This significant variability highlights the need to characterize the wastewaters of different plants independently for use in simulation studies. This variability in wastewater RBCOD fractions could be due to a number of factors such as type of sewer system, climatic conditions of the region, and dietary habits of the community from which the treatment plant receives its wastewater.

Less than 10 % RBCOD was calculated for 11 of the samples tested. These low RBCOD fractions could also be as a result of loss of RBCOD to polyphosphate accumulating organisms which sequester

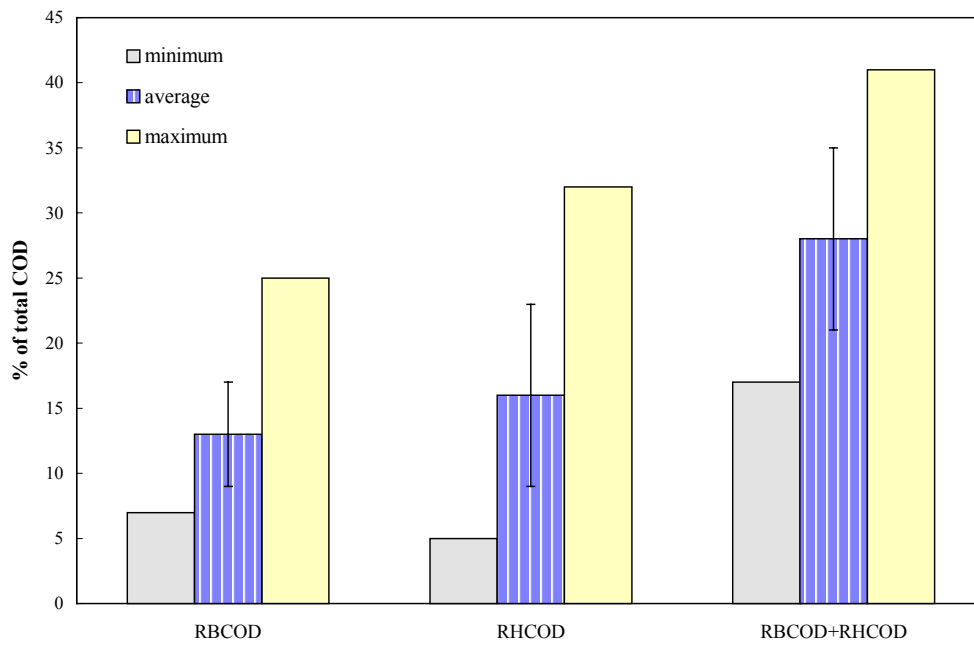
RBCOD for the production of storage compounds with concomittant P release. This could not be verified for the first three plants since phosphorus analysis was not conducted. No P release was observed for tests done on samples from Asnieres, Northernns, Kwa-Mashu, and Southernns WTP. However, P release of 2 and 3 mgP/l was observed for Boves and Villers, respectively, suggesting polyphosphate accumulating organism activity. Using the COD/P ratio of 2 and 5 mgO<sub>2</sub>/mgP, the amount of RBCOD lost to polyphosphate bacteria was estimated to be between 1 and 2 % of the total COD. Consideration of these values leads one to conclude that the RBCOD values compare well to those cited by Henze *et al.*, (1995) (Table 7-2), *i.e.* between 10 and 20 %.

The phosphorus release patterns for the French Wastewater Treatment Plants differed from Darvil WTP, the one South African EBPR plant that was tested which showed P removal capabilities. For all the French WTP's tested, simultaneous denitrification and phosphorus release was observed (see Figure 6-4). However, for Darvil WTP the P release was sequential *i.e.* P was released only after all the nitrates-N had been consumed (see Appendix IV, IV-D). It is possible that the French Treatment Plants are operated and configured in such a way as to promote the growth of denitrifying polyphosphate accumulating organisms while the South African plant, Darvil has a significantly higher proportion of polyphosphate accumulating organisms which do not compete with the denitrifiers for available RBCOD. It is also possible that operating conditions such as loading rates and feeding regimes may be responsible for the culturing of different microorganisms which show different P release patterns. Majone *et al.* (1996) reported that biomass fed intermittently were more likely to accumulate and store substrate as a form of competitive or survival mechanism brought about by dynamic conditions such as concentration gradients. Thus, a storage response may not be completely due to the presence of polyphosphate accumulating organisms but may be brought about by ordinary heterotrophs as well.

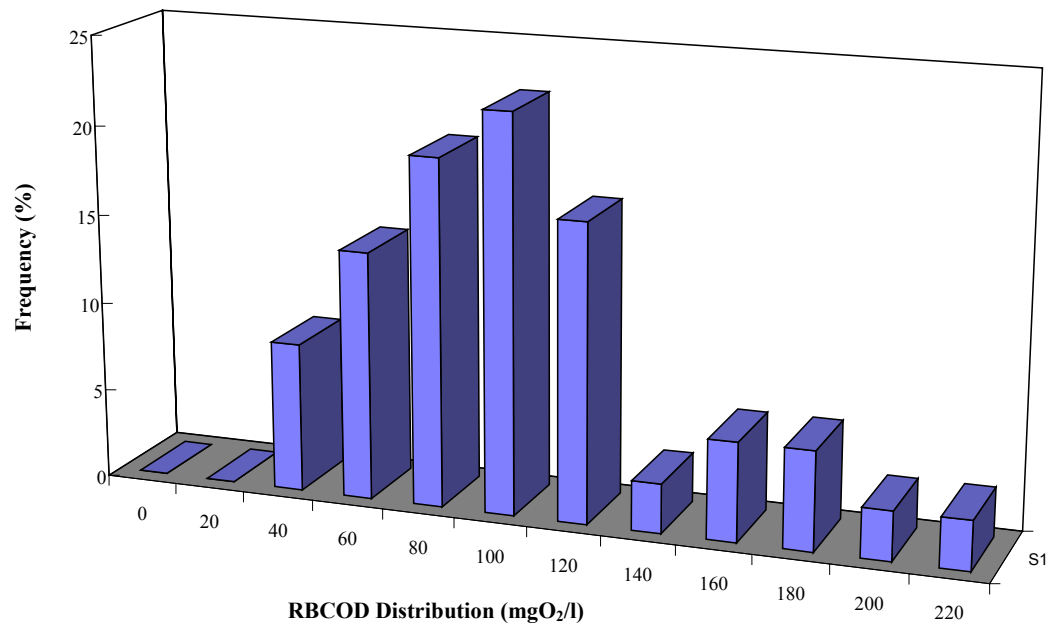
**Table 7-2: Characterization of the readily biodegradable and readily hydrolyzable COD components of different wastewaters using the NUR method.**

Plant	Substrate	St	RBCOD (1)		RHCOD (2)		1+2
		mgO <sub>2</sub> /l	%	mgO <sub>2</sub> /l	%	mgO <sub>2</sub> /l	%
Crespieres 24/02/97	ww-cent	549	9	51	–	–	–
	ww-coag		8	44	–	–	–
Morainvilliers 24/02/97	ww-cent	891	7	65	15	137	22
Morainvilliers 26/02/97	ww-cent	344	17	58	–	–	–
	ww-coag		18	64	–	–	–
Boran 25/02/97	ww-cent	707	13	93	–	–	–
	ww-coag		12	84	–	–	–
Plaisir	ww-cent	691	16	108	–	–	–
	ww-coag		13	89	–	–	–
Rostock	ww-cent	953	17	161	18	176	35
	ww-filt		19	186	15	140	34
	ww-coag		11	105	12	112	23
Orense	ww	407	19	79	22	88	41
	ww-coag		7	29	26	108	33
Brno	ww	250	13	34	24	59	37
	ww-coag		12	31	32	79	34
Samaritaine <sup>BP</sup> 23/04/97	ww	900	9	79	–	–	–
	ww-non-set.		9	80	–	–	–
Samaritaine <sup>BP</sup> 25/04/97	ww	750	19	146	10	72	29
	ww-non-set.		17	125	11	83	28
Samaritaine <sup>BP</sup> 28/04/97	ww	720	11	86	28	200	39
	ww-non-set.		15	110	26	189	41
Laon	ww	652	15	98	12	78	27
Artemps	ww	980	15	108	17	108	32
Creil	ww	853	20	145	–	–	–
Boves	ww	813	18	148	–	–	–
Villers	ww	923	9	80	13	120	22
Asnières	ww	1183	9	95	13	154	22
Gouvieux	ww	817	13	90	14	106	24
Compiègne <sup>BP</sup> 3/06/97	ww	783	22	172	–	–	–
Compiègne <sup>BP</sup> 5/06/97	ww	787	13	102	18	142	31
Compiègne <sup>BP</sup> 9/06/97	ww	883	11	97	–	–	–
Compiègne <sup>BP</sup> 11/06/97	ww	817	25	204	–	–	–
Compiègne <sup>BP</sup> 28/08/97	ww	1257	11	75	–	–	–
Thiverval <sup>BP</sup> 17/07/97	ww	437	11	48	14	55	25
Thiverval <sup>BP</sup> 31/07/97	ww	977	12	119	5	52	17
Darvil *	ww	958	14	135	14	138	28
Kwa-Mashu *	ww	869	8	71	12	105	20
Northerns *	ww	704	7	48	13	88	20
Southerns *	ww	624	7	42	7	41	14

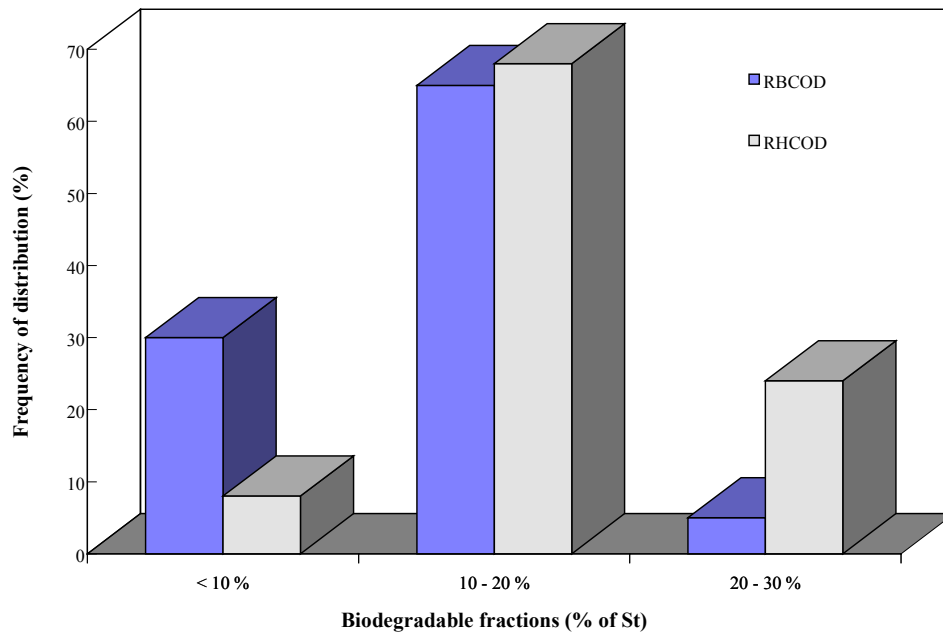
(\* - South African treatment plants; ww - raw wastewater; ww-non-set. - non-settleable component after 2 h settling test; ww-cent - centrifuged component; ww-filt - filtered component; ww-coag - non-coagulated component; BP - biological phosphorus removal plant)



**Figure 7-6:** Comparison of average, minimum and maximum values of the biodegradable fractions derived by the NUR method ( $n = 40$  for RBCOD values and  $n = 24$  for RHCOD values).



**Figure 7-7:** Frequency of distribution of the RBCOD concentrations from different wastewater samples ( $n = 40$ ).



**Figure 7-8: Distribution of the RBCOD (n=40) and ‘intermediate’ RHCOD (n=24) fractions of raw wastewater measured by NUR tests.**

### 7.2.2 The RHCOD fraction

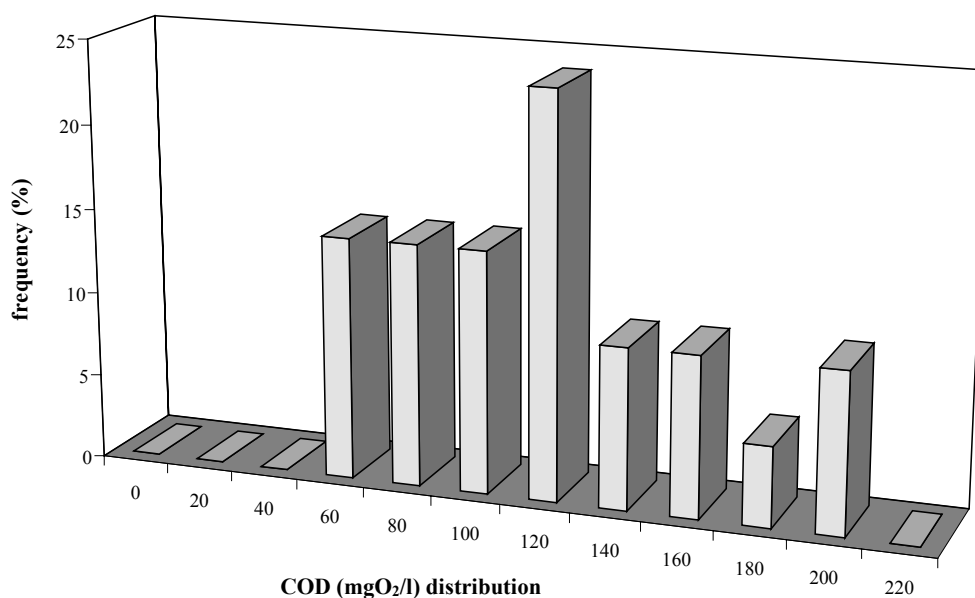
As with the acetate fed tests, some of the NUR batch tests revealed 3 distinctive phases. This made it possible to calculate a second biodegradable COD fraction. The second biodegradable COD fraction, which was calculated for 24 of the 40 samples tested, varied significantly between 5 and 30 % with an average of 16 % (Table 7-2). The biodegradable COD concentration, related to phase 2 in  $\text{NO}_x(t)$  profiles, was found to range between 60 - 200 mg/l (Figure 7-9). A distribution diagram, Figure 7-10 shows that most of the values fell between 10-20 % of the total COD. Only 5 % of the samples (n = 24) had less than 10 % of biodegradable COD. However, about 29 % of the tests gave biodegradable COD values greater than 20 % of the total COD.

This ‘intermediate’ phase which allowed for the calculation of the second biodegradable fraction can be explained in the following ways :

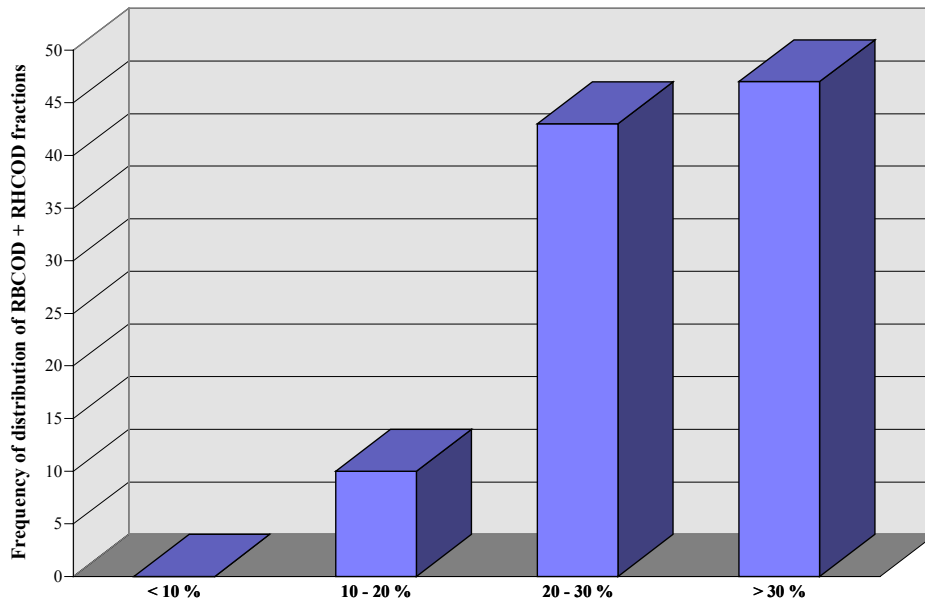
1. It could form part of the slowly biodegradable COD of the influent wastewater. Most of these values do not compare well to the SBCOD fraction which is considered to make up about 30 to 60 % of the total COD concentration of wastewater (Henze *et al.*, 1995). Since this second phase lasted for about 2 to 3 h and the biodegradable COD fractions calculated from the NUR tests were far lower than expected, this fraction could be classed as a readily hydrolyzable fraction (RHCOD) of the slowly biodegradable group of compounds found in raw wastewater.

2. It could also be that this second biodegradable COD fraction was part of the RBCOD and the intermediate phase was in fact a *residual phase* of phase 1. Thus, the RBCOD and the second biodegradable COD values were added and grouped into 4 categories : < 10 % ; 10 to 20 % ; 20 to 30 % and > 30 % (Figure 7-10). The majority of the values were > 20 % while only 10 % of the values were between 10 and 20 % of the total COD, the expected range for RBCOD. This suggests that either French wastewaters have unusually high RBCOD concentrations, or that the NUR test measures an intermediate fraction of the raw wastewater *i.e.* the readily hydrolyzable fraction. The suggestion that the second phase is a residual phase of phase 1 is supported by the observations made with the acetate fed reactors (see Chapter 6) where an intermediate phase was also observed. Similarly, it could be postulated that some of the RBCOD fed to the biomass was used directly for energy and growth while some of the RBCOD was accumulated or stored. These accumulated and stored compounds become available to the bacteria once the RBCOD concentration becomes limiting. This re-use of accumulated or stored compounds is supported by work done by Majone *et al.* (1999) where a 'tailing phenomenon' was described for OUR tests done with acetate. This 'tailing phenomenon' was linked to a storage response because of the high observed yields.

The second explanation for the observation of the intermediate (residual) phase seems more likely. However, it is also probable that the second biodegradable fraction could not be calculated for all the kinetics because either the duration of the second phase may have been longer than the 6 hour test or the COD fraction causing phase 2 may have been too small to detect. However, these results do suggest that the NUR method may be able to show an intermediate fraction which could be the readily hydrolyzable fraction of SBCOD or a storage fraction of the RBCOD component of wastewater.



**Figure 7-9: Frequency of distribution of the RHCOD concentrations (n = 24).**



**Figure 7-10: Distribution of sum of RBCOD and RHCOD fractions.**

### 7.2.3 The 'SBCOD' component of raw wastewater

If the first explanation of the intermediate fraction is accepted then while the NUR test may be able to calculate part of the SBCOD, in the form of the readily hydrolyzable fraction, it is however, unable to measure the whole SBCOD component of raw wastewater. Raw wastewater comprises biodegradable COD, unbiodegradable COD and active biomass (as COD). By taking into account the raw wastewater fractions listed in Table 3-1, we find that approximately 20 to 40 % of the raw wastewater is composed of unbiodegradable (soluble and particulate) and active biomass fractions. Therefore, the remaining COD should make up the biodegradable fraction of raw wastewater. Hence, for raw wastewater samples which fall into Group 1 i.e. 0 to 10 % RBCOD, the SBCOD component probably makes up 50 to 80 % of total COD. For raw wastewater samples which comprised 10 to 20 % RBCOD (Group 2), the SBCOD could comprise between 40 to 70 % of the total COD. In those cases where the RBCOD made up 20 to 30 % (Group 3) of the total COD, the SBCOD could form approximately 30 to 60 % of the wastewater concentration.

## 7.3 COMPARABILITY OF RBCOD CONCENTRATIONS DERIVED BY COAGULATION AND THE NUR METHOD

According to a method outlined by Mamais *et al.* (1993) the 'truly soluble' biodegradable fraction (S<sub>s</sub>) can be found by the difference between the soluble fraction of the influent after coagulation (S-co) and

the inert fraction ( $S_i$ ) (see equation 7-1). The inert soluble fraction can be determined by measuring the COD concentration of an effluent sample taken from a reactor with a SRT  $>3$  days. Coagulation of this fraction would then give the inert soluble fraction. Mamais *et al.* (1993) showed that this method which was used for the calculation of the readily biodegradable fraction gave values comparable to the RBCOD fraction determined by the oxygen utilization rate method.

$$S_s = S_{-co} - S_i \quad (7-1)$$

Since the coagulated fraction of the wastewater as well as the soluble inert ( $S_i$ ) fraction was known, it was decided to test this approach. Since the plants tested were considered to be operated at SRT's greater than 10 days, the soluble fraction of the sludge can be considered as the inert soluble fraction of the effluent. The method used here differs from that of Mamais *et al.* (1993) in the following ways:

- Ferric chloride and not zinc hydroxide was used as the coagulant,
- the  $S_i$  fraction was filtered through  $0.45\mu\text{m}$  filters and not coagulated, and
- the RBCOD fraction was determined by the NUR method and not the OUR test.

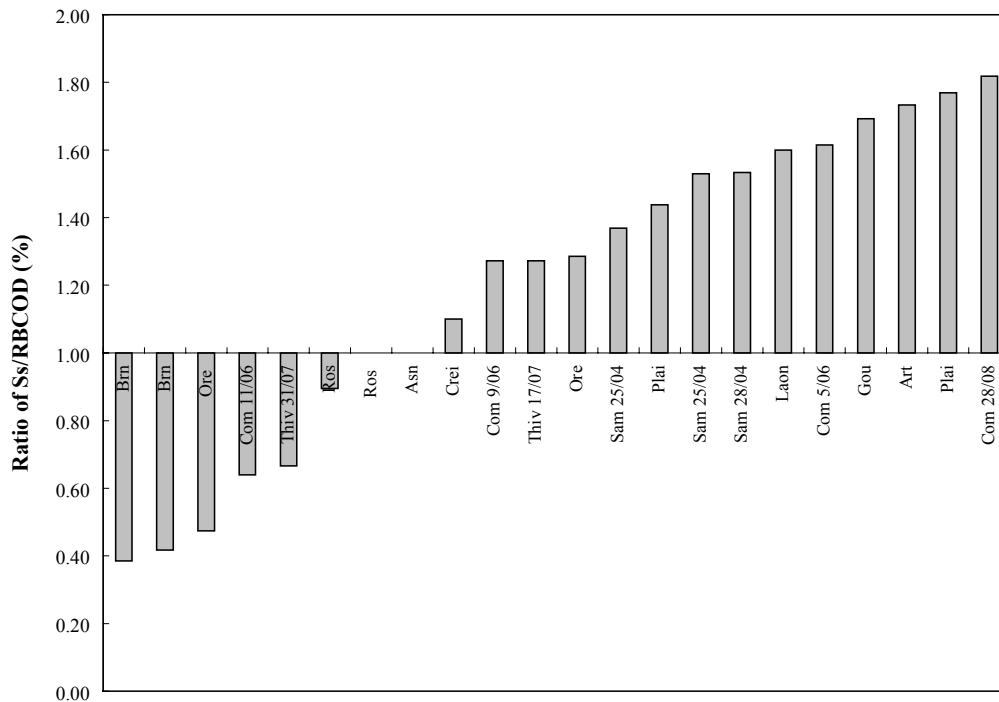
A comparison of RBCOD results from the biological tests with those derived by the method of Mamais *et al.*, (1993) ( $S_s$ ) did not correlate well (Table 7-3). Figure 7-11 represents these results as a ratio of the RBCOD determined by chemical means to the RBCOD determined by the NUR method ( $S_s / \text{RBCOD}$ ) where the value 1 shows comparability between the 2 methods. Only 4 of the RBCOD batch test values were found to be fairly comparable to the  $S_s$  values. Some of the ratios were  $< 1$  which showed that the RBCOD determined by the NUR tests were greater than the values determined by coagulation. Majority of the values were  $> 1$  which showed that the chemical method gave higher RBCOD values than the biological anoxic batch test method. There was also no correlation between the  $S_s$  values and the RHCOD or a combination of the RBCOD and RHCOD fractions (Table 7-3). Thus, if one accepts that the three differences outlined above did not affect the rationale nor the results, it would seem that this approach cannot be applied to all wastewaters due to the variability of wastewater composition.



**Table 7-3: Comparison biological fractions determined by coagulation (Ss) and the NUR method (RBCOD and RHCOD).**

Plant	Ss		RBCOD		Ss/RBCOD	RHCOD	1+2
	%	mgO <sub>2</sub> /l	%	mgO <sub>2</sub> /l		%	%
Brno	5	13	13	34	0.38	24	37
Brno	5	13	12	31	0.42	32	34
Orense	9	37	19	79	0.47	22	41
Compiègne 11/06	16	135	25	204	0.64	–	–
Thiverval 31/07	8	78	12	119	0.67	5	17
Rostock	17	162	19	186	0.89	15	34
Rostock	17	162	17	161	1.00	18	35
Asnières	9	95	9	95	1.00	13	22
Creil	22	190	20	145	1.10	–	–
Compiègne 9/06	14	128	11	97	1.27	–	–
Thiverval 17/07	14	82	11	48	1.27	14	25
Orense	9	37	7	29	1.29	26	33
Samaritaine 25/04	26	195	19	146	1.37	10	29
Plaisir	23	159	16	108	1.44	–	–
Samaritaine 25/04	26	195	17	125	1.53	11	28
Samaritaine 28/04	23	166	15	110	1.53	26	41
Laon	24	156	15	98	1.60	12	27
Compiègne 5/06	21	162	13	102	1.62	18	31
Gouvieux	22	180	13	90	1.69	14	24
Artemps	26	255	15	108	1.73	17	32
Plaisir	23	159	13	89	1.77	–	–
Compiègne 28/08	20	180	11	75	1.82	–	–
Morainvillier 24/02	13	115	7	65	1.86	15	22
Morainvillier 26/02	34	117	18	64	1.89	–	–
Morainvillier 26/02	34	117	17	58	2.00	–	–
Samaritaine 28/04	23	166	11	86	2.09	28	39
Crespieres 24/02	19	104	9	51	2.11	–	–
Crespieres 24/02	19	104	8	44	2.38	–	–
Villier	27	249	9	80	3.00	13	22
Boves	25	203	18	148	3.57	–	–
Boran 25/02	48	339	13	93	3.69	–	–
Boran 25/02	48	339	12	84	4.00	–	–

Ss - fraction determined after coagulation; RBCOD - fraction determined from NUR tests



**Figure 7-11: Comparative ratios of biological fractions determined by coagulation (Ss) and the NUR method (RBCOD).**

## 7.4 DENITRIFICATION RATES

Denitrification batch kinetics generally produced two or three rates which depended on the substrate used, the biomass activity and the test conditions. The results from these tests were combined and evaluated in this section. All results can be found in **Appendix III** and **Appendix IV**.

### 7.4.1 Maximum specific denitrification rates

Table 7-4 shows the range of maximum denitrification rates calculated with either wastewater or acetate. The range for the two substrate, acetate and raw wastewater, was fairly similar (Appendix VI). The variation in the  $k_1$  values, 2.6 to 9.3 mgN/gVSS.h and 2.6 to 8.3 mgN/gVSS.h, with acetate and wastewater, respectively, highlights the influence of plant operating conditions such as solids retention time, and type of substrate made available to the bacteria in the influent raw wastewater.

Several tests produced atypical denitrification rates. The maximum specific denitrification rate with sludge from Brno was considered to be far higher ( $k_1 = 14.2$  mgN/gVSS.h) than the other tests conducted with acetate. It appears that this sludge is highly acclimatized to acetate as a substrate. Atypical observations were also made with tests conducted with raw wastewater samples from Rostock,

Orense, and Berwick (Table 7-4). Rostock and Orense produced high first rates  $>13$  mgN/gVSS.h. These rates were of short duration (20-30 min) (see **Appendix IV**, Tables O1, R1, R2, and R3). In addition, Rostock revealed 4 phases as opposed to the 3 that were normally observed in the 6 hour test. Brno, Rostock and Orense are all European wastewater treatment plants which were located outside France and had to be stored during transit to the laboratory. Therefore, one factor which could explain these observations is the storage of these samples which was for about 3 to 5 d. It is possible that during transport and storage (*i.e.* dynamic conditions), the bacteria accumulated and/or stored organic compounds that were taken up from the bulk liquid. When conditions became favourable there was a rapid uptake of nitrates from the bulk liquid. Hence, the high denitrification rates. Grau *et al.* (1982) and Daigger and Grady (1982) reported that both accumulation and storage are rapid responses which may be brought about by dynamic conditions such as starvation. Majone *et al.* (1996) hypothesized that in high starvation (low OUR) conditions accumulation is dominant while at low starvation (high OUR) conditions storage is dominant since the latter is more energy consuming.

Berwick was also considered as an atypical case since only a single phase was observed even though the 'soluble' fraction ( $S-f_{0.45}$ ) was not limiting at 374 mgO<sub>2</sub>/l (41%) (see Table 7-1). The specific denitrification rate obtained with raw wastewater from Berwick WTP was 1.6 mgN/gVSS.h, which is low (Table 7-4). It is likely that the industrial wastewater received from the beverage industries (orange and whisky) may have had an inhibitory effect on the bacteria or that the wastewater consisted of only slowly biodegradable COD. However, high maximum denitrification rates with acetate ( $k_{1 \text{ acetate}} = 4.5$  mgN/gVSS.h) as substrate showed that the activity of the bacteria was not the cause of this single phase (see **Appendix III**, Table B1). Thus, it appears that the raw wastewater from Berwick contains limiting concentrations of RBCOD but a significant concentration of slowly biodegradable substrates.

**Table 7-4: Range of maximum specific denitrification rates (mgN/gVSS.h) and atypical maximum specific denitrification rates.**

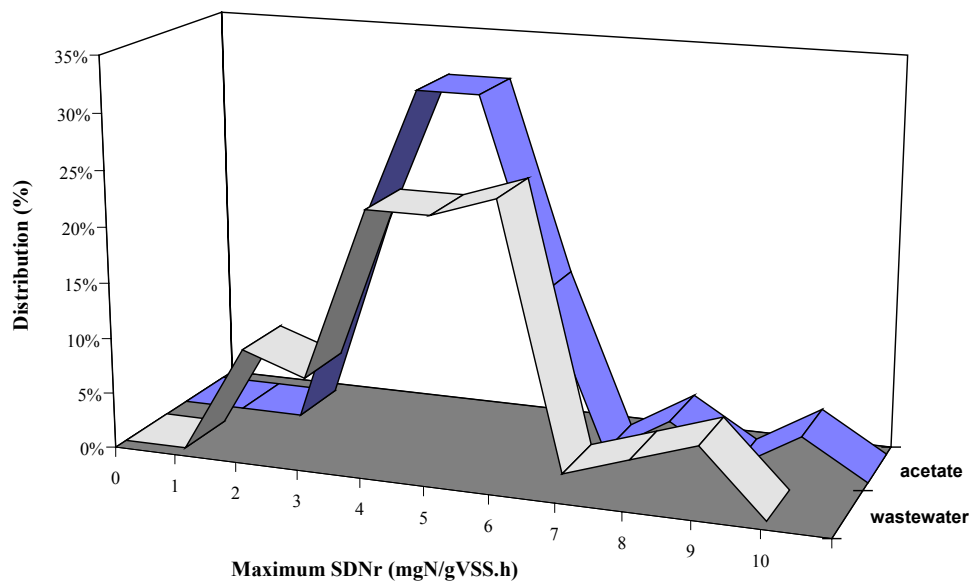
Substrate	Range	Atypical rates
acetate	2.6 - 9.3	Brno (14.2)
wastewater	2.6 - 8.3	Rostock (13-18) Orense (21) Berwick (1.6)

#### 7.4.2 Distribution frequency of denitrification rates

The majority of the sludges tested produced  $k_1$  values between 4 and 5 mgN/gVSS.h, and 4 and 6 mgN/gVSS.h for acetate and wastewater, respectively (Figure 7-12). The distribution range was wider

for wastewater than for acetate. Acetate is a single simple compound and the rates obtained would be largely due to sludge activity and biomass history. However, the maximum specific rate obtained with raw wastewater is controlled to a large extent by both the characteristics of the sludge and the composition of the raw wastewater sample being tested. Since raw wastewater is composed of different compounds of varying biodegradability, a wider range of specific denitrification rates with a greater overlap between the second and third rates observable in the NUR test would be expected.

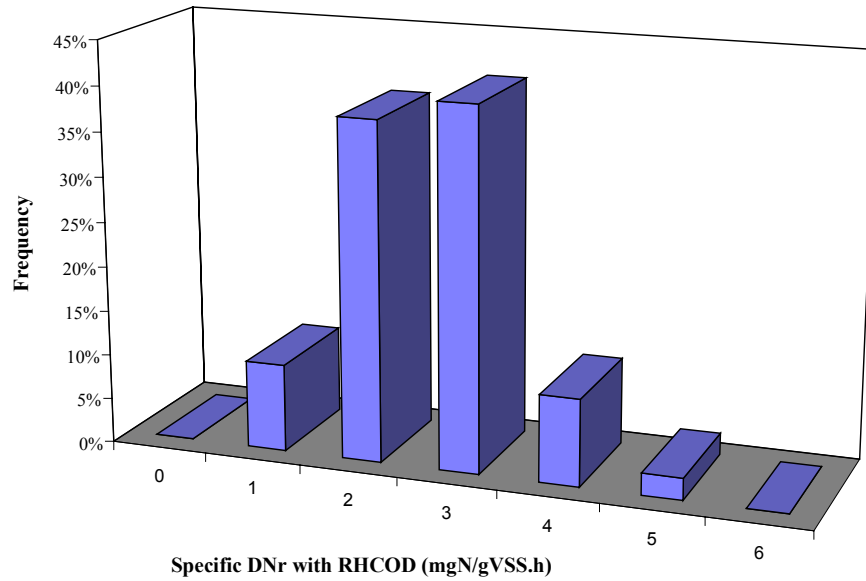
Determination of the frequency of distribution of the maximum specific denitrification rates from tests with acetate and wastewater showed that about 84 % of the maximum specific denitrification rates were between 3 and 6 mgN/gVSS.h. Only 6 % of the samples were found to have maximum specific denitrification rates less than 3 mgN/gVSS.h, while 10 % of the maximum denitrification rates were greater than 6 mgN/gVSS.h.



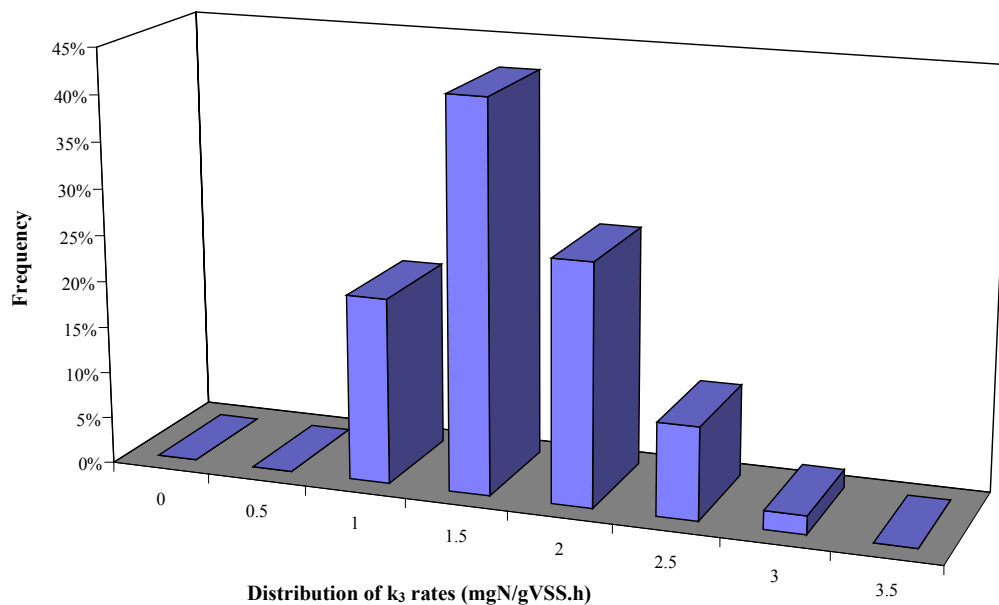
**Figure 7-12: Frequency of distribution of the maximum denitrification rates for acetate and wastewater.**

The second rate ( $k_2$ ) or the second phase in the NO<sub>x</sub>-N profile was considered to be due to the readily hydrolyzable fraction of wastewater or sludge. About 78 % of the rates calculated were found to lie in the range 2 to 3 mgN/gVSS.h (Figure 7-13). Less than 10 % of the samples gave values below 2 mgN/gVSS.h and only 12 % were above 3 mgN/gVSS.h. These results suggest that the intermediate rate lies between 2 and 3 mgN/gVSS.h. The third rate ( $k_3$ ) was considered to be due to the slowly biodegradable fraction and endogenous products and most of the rates (68 %) were found to be less than 1.5 mgN/gVSS.h (Figure 7-14). However, a significant number were found to be between 2 and 3 mgN/gVSS.h. In this case it is also possible that there may be an overlapping of hydrolytic rates where

phase 2 ( $k_2$ ) hydrolytic products may still be exerting its influence on  $k_3$  values. The variation and range suggests that the SBCOD components of the wastewater samples are complex and variable in composition and concentration. Therefore, there was an overlap between rate 2 ( $k_2$ ) and rate 3 ( $k_3$ ).



**Figure 7-13: Distribution of second denitrification rates ( $k_2$ ) for all samples (i.e. acetate and wastewater combined) ( $n = 85$ ).**

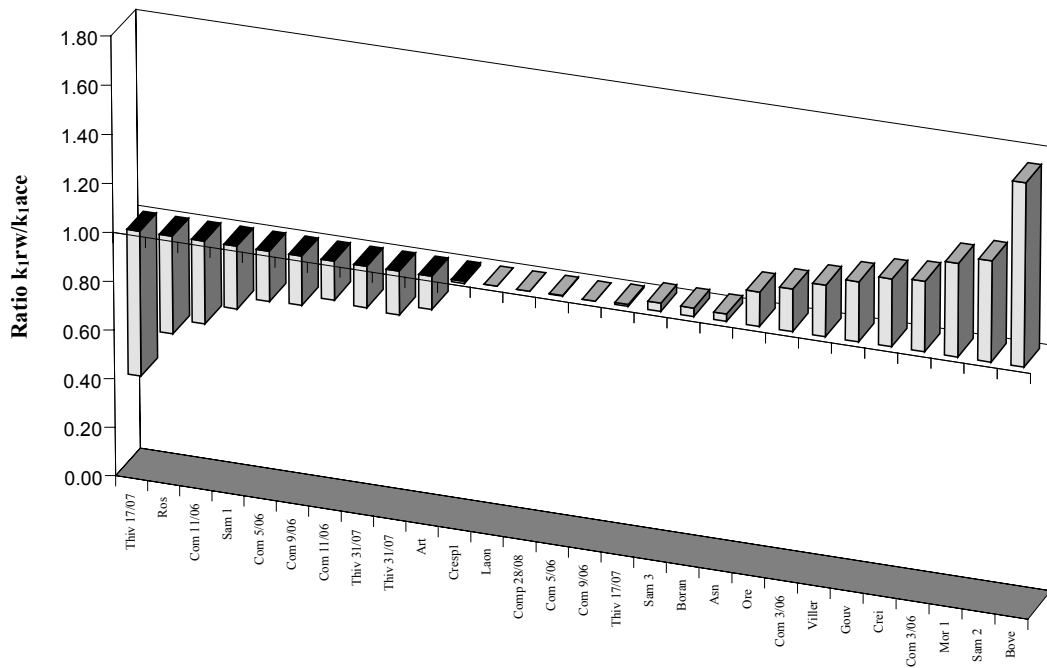


**Figure 7-14: Frequency of distribution of the third denitrification rates ( $k_3$ ) obtained from denitrification kinetics with acetate and raw wastewater ( $n = 50$ ).**

### 7.4.3 Acetate as a reference for rates obtainable with RBCOD?

A preliminary study was done with 4 different concentrations of acetate viz : 40, 100, 200 and 400 mg/l as COD (see Appendix II, II.3.4.1). The results showed that an increase in acetate concentration from 40 mg/l to 400 mg/l did not result in an increase in the specific denitrification rates. It was therefore, decided that for all the future NUR tests the use of approximately 50 mg/l acetate as COD was sufficient to give the maximum specific denitrification rate.

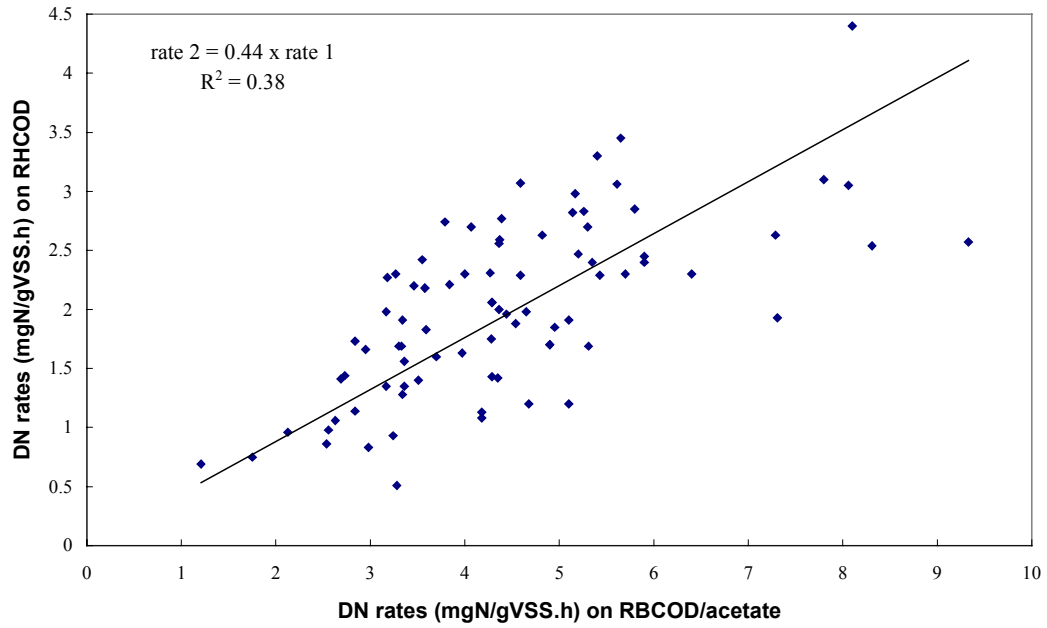
A plot of the ratio of  $k_1$  of wastewater to  $k_1$  of acetate was made (Figure 7-15) to determine if the maximum specific denitrification rates with acetate were comparable to the maximum specific denitrification rates with raw wastewater. 21 % ( $n = 6$ ) of the tests produced comparable rates for raw wastewater and acetate. In these cases, acetate could be used to mimic the maximum specific denitrification rate constants of raw wastewater. It also suggested that these sludges were exposed to substrates similar to acetate. Approximately 43 % of the tests produced a ratio greater than 1 which shows that these bacteria use some other compounds (possibly with acetate) which gives higher denitrification rates. Several of the tests ( $n = 10$ ) produced ratios that were lower than 1 suggesting that the acetate fraction was not high in these wastewaters. These results show that a single simple compound like acetate cannot be used as an efficient substitute for RBCOD which is more complex in composition.



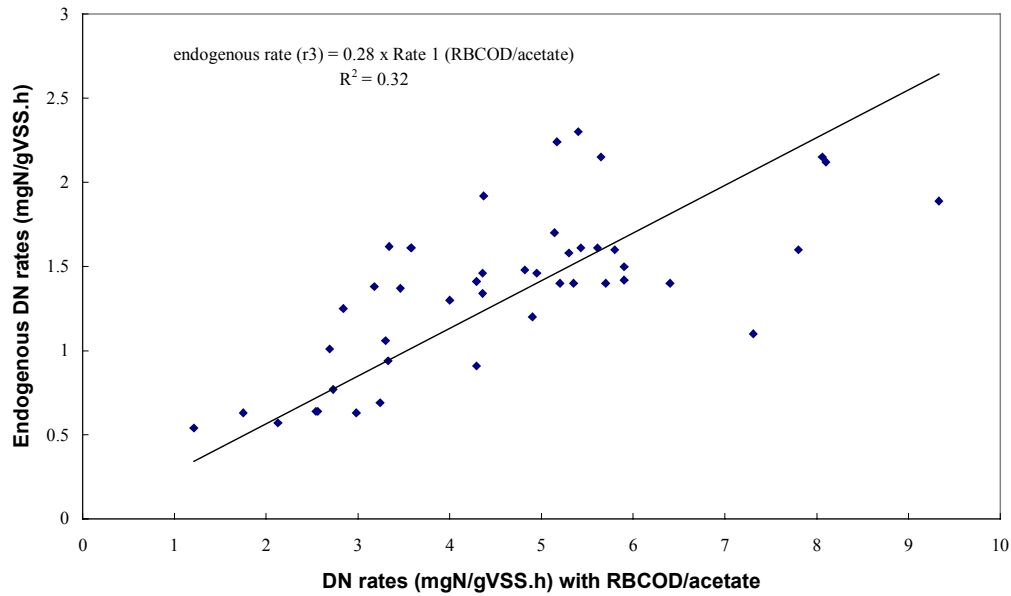
**Figure 7-15: Ratio of the maximum denitrification with wastewater ( $k_{1rw}$ ) and acetate ( $k_{1acc}$ ) for the samples tested.**

#### 7.4.4 Relationships between the different denitrification rates

Fairly weak correlations were found between rate 1 and rates 2 and 3 (see Figure 7-16 and Figure 7-17). Since hydrolysis is considered to be the rate limiting reaction, it can be said that the rate of hydrolysis of intermediate SBCOD compounds *i.e.* the readily hydrolyzable fraction is approximately 44 % of the rate of utilization of RBCOD. Furthermore, the rate of hydrolysis of the SBCOD/endogenous products is 28 % of the rate of utilization of RBCOD. Figure 7-18 shows that the endogenous denitrification rate is about two-thirds the rate of hydrolysis of the readily hydrolyzable fraction. These results could be used to estimate the slower denitrification rates ( $k_2$  and  $k_3$ ) in a particular system for a particular type of wastewater.

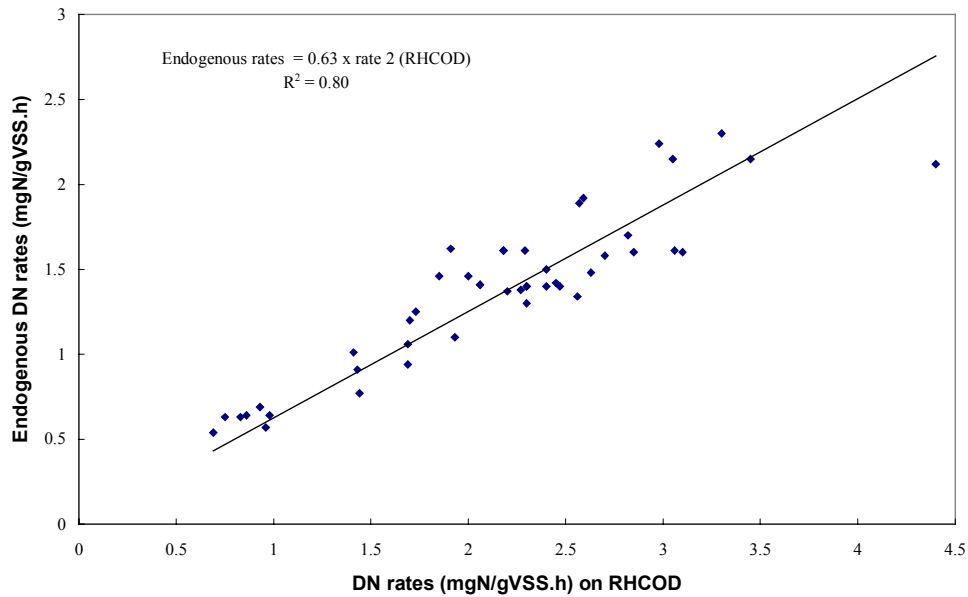


**Figure 7-16: Correlations between rate 1 and rate 2 obtained from tests with raw wastewater and acetate (DN -denitrification).**



**Figure 7-17: Correlations between rate 1 and rate 3 obtained from tests with raw wastewater and acetate (DN - denitrification)**





*Figure 7-18: Correlation between rate 2 and rate 3 (DN - denitrification).*

## 7.5 SUMMARY

Several correlations (strong and weak) were made between the total COD and soluble fractions. Most of the raw wastewaters tested were fairly concentrated with total COD concentrations ranging between 700 and 1000 mgO<sub>2</sub>/l. Fairly good linear relationships were found between the total COD and the filtered and coagulated COD fractions. The filtered and coagulated COD fractions were found to be 33 and 25 % of the total COD. Correlation plots also showed that centrifugation may include between 28 and 9 % more colloids / solids than coagulation and filtration (0.45 μm).

No correlation was made between the fractions determined by the physico-chemical methods and the biological method. No trend could be found between the S<sub>s</sub> fraction (determined by a coagulation method) and the RBCOD fraction (determined from NUR tests) suggesting that the rationale and approach proposed by Mamais *et al.* (1993) cannot be applied to all wastewaters. In this case, it appears that the variability in the wastewater composition and the efficiency of the physico-chemical techniques may have contributed to the incomparability of the results.

The RBCOD fraction determined from different wastewater samples varied between 7 and 25 % which highlighted the need to characterize wastewaters independently to obtain accurate input data for simulation studies. A second biodegradable fraction varied between 5 and 30 %. This intermediate fraction could have arisen from the utilization of a readily hydrolyzable component of SBCOD of wastewater or from the utilization of storage compounds that had been produced from the influent RBCOD fraction. The latter explanation is supported by the results obtained in batch tests done with

acetate. It should be noted that this second biodegradable fraction was not classed as total SBCOD since it was found to be lower than those values cited by the Henze *et al.* (1995) for SBCOD fractions (*i.e.* 30 to 60 %) in raw wastewater.

The maximum denitrification rates ( $k_1$ ) were found to be variable but within the range 3 to 6 mgN/gVSS.h. This variability was influenced by the wastewater composition and sludge activity. The second and third rates were less variable at 2 to 3 mgN/gVSS.h and 1.5 mgN/gVSS.h, respectively. The latter two rates highlighted the difference in the hydrolysis rates for different slowly biodegradable COD substrates. The rate of hydrolysis of the SBCOD was found to be about 37 % lower than the rate of hydrolysis of the readily hydrolyzable fraction of SBCOD. The rate of utilization of the RHCOD fraction was found to be about 44 % of that of RBCOD utilization.

# Chapter Eight

## ***CONCLUSIONS and RECOMMENDATIONS***

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One of the aspects of this study was to assess the experimental approach adopted for the realization of the nitrate-N utilization rate (NUR) batch tests. This was dependent on the analysis and interpretation of the NUR profiles. Two types of profiles were observed for raw wastewater during the 6 h batch test. Some tests with raw wastewater revealed 2 phases while others produced 3 phases. The first phase was due to the utilization of the readily biodegradable COD of raw wastewater while the latter phase was due to the utilization of slowly biodegradable COD present in the influent raw wastewater and sludge. In the case of 3-phase NUR profiles, phase one was once again attributed to readily biodegradable COD consumption. However, phase 2 was thought to reflect the utilization of an intermediate, readily hydrolyzable fraction (RHCOD) present in the influent raw wastewater. The final phase (phase 3) was due to a combination of slowly hydrolyzable substrates of SBCOD from the raw wastewater and the sludge endogenous products.

In the case of acetate-fed reactors (based on the S/X ratio of 0.02) 2 phases were expected. However, as was the case with raw wastewater, both 2- and 3-phase NUR profiles were observed. For 2-phase NUR profiles, the first phase was considered to be due to acetate utilization while phase 2 was due to the utilization of slowly biodegradable COD provided by bacterial death and lysis and residual organic matter from the influent. Three-phase NUR profiles, however, present a more complicated scenario. Phases 1 and 3 may be explained in terms of the utilization of acetate and SBCOD substrates from the sludge, respectively. Phase 2 however, was hypothesized to be due to one of 2 factors : i) the utilization of internally stored compounds present in the original mixed liquor seed, or, ii) some of the exogenous acetate was rapidly accumulated and / or converted to storage compounds by ordinary heterotrophs or denitrifying polyphosphate accumulating organisms which subsequently utilize the storage compounds during denitrification. The second hypothesis was supported by endogenous profiles which revealed a single phase. These observations suggested that the second phase was acetate-linked. This reaction could, therefore, be triggered by the presence of acetate but only in some.

The results obtained for acetate-fed NUR tests were used to formulate several conclusions on acetate utilization under anoxic conditions. Firstly, it was concluded that for some of the wastewaters and sludges tested, acetate was used exclusively for denitrification by denitrifiers *i.e.* where acetate mass balances were 100 %. In this case, the sludge contains a significant proportion of denitrifiers and little or no polyphosphate accumulating organisms or that the physiological state of the biomass is such that rapid accumulation or storage is not required. Secondly, in the cases where the acetate mass balances were found to be < 100 %, it can be concluded that the acetate could have been used for denitrification as well

as for the production of storage products like polyhydroxyalkanoates. It is possible that some of the bacteria found in the mixed liquor sequester the acetate in order to replenish the reserves of storage compounds. These sludges probably contained denitrifying bacteria as well as a significant proportion of polyphosphate accumulating organisms. Thirdly, tests showed acetate mass balances were 100 % when the 2 biodegradable fractions from the NUR test were calculated. These results suggest that acetate could be used for denitrification and for polyhydroxyalkanoate synthesis by denitrifying polyphosphate accumulating organisms. The acetate that the DPAO's take up is re-utilized during denitrification. This utilization in the second denitrification phase is supported by the observation of phosphorus uptake. Thus, these sludges contain denitrifiers and denitrifying polyphosphate accumulating organisms which compete for the available acetate. Finally, in cases where the acetate mass balances were > 100 %, it was concluded that all the acetate was used for denitrification and the excess COD that was calculated was as a result of the use of existing storage compounds.

The observations made with NUR data using acetate as a substrate were important as they provided some idea of how the sludge may react to the readily biodegradable COD of wastewater. There were 4 possible interpretations of these results. In those cases where 100 % acetate recovery was noted, the RBCOD determination can be considered to be reliable since the denitrifiers would have been the dominant group of bacteria. Plants which showed < 100 % recovery show that there will probably be an underestimation of RBCOD values. Plants which showed 100 % recovery when acetate mass balances 1 and 2 were added show that acetate compounds may be sequestered during phase one resulting in an underestimation of the RBCOD concentration. However, the sequestered fraction may be released internally and will be utilized (in phase 2) when nitrates are present. If this hypothesis is true, then the correct RBCOD concentration would be to combine the results from phase 1 and phase 2. Acetate tests showing > 100 % recovery showed that denitrifiers may use existing storage compounds which would thus, result in an overestimation of the RBCOD fraction. These are important observations as they show that RBCOD compounds, particularly the acetate fraction was not always used exclusively for denitrification purposes under anoxic conditions but could be used for accumulation or storage. These interpretations will need to be considered when determining the RBCOD fractions of wastewater calculated using this biological method.

The use of NUR tests allowed for the observation and monitoring of the biokinetic response of the denitrifying bacteria in the presence of available organic carbon in the raw wastewater samples tested. This allowed for the determination of a readily biodegradable component of raw wastewater. The RBCOD fraction determined from different wastewater samples varied between 7 and 25 % which highlighted the need to characterize wastewaters independently to obtain accurate input data for simulation studies. However, majority of the results fell with the 10 to 20 % of the total COD group, which was expected.

It was also possible in certain tests to calculate a second biodegradable component of raw wastewater. The intermediate fraction was found to vary between 5 and 30 % of the total COD concentration. This second

biodegradable was considered to be part of the readily hydrolyzable component of wastewater or the storage fraction based on 2 hypotheses.

- Since this second phase lasted for about 2 to 3 h and the biodegradable COD fractions calculated from the NUR tests were far lower than expected, this fraction was classed as a readily hydrolyzable fraction (RHCOD) of the SBCOD found in raw wastewater. The slowly biodegradable COD fraction of raw wastewater is reported to comprise 30 to 60 % of the total COD. However, these results do suggest that the NUR method may be able to differentiate between an intermediate readily hydrolyzable fraction and the slowly hydrolyzable fraction for some wastewaters. While the NUR test is able to calculate part of the SBCOD, in the form of the readily hydrolyzable fraction, it is however, unable to measure the whole SBCOD component of raw wastewater.
- It could also be that this second biodegradable COD fraction was part of the RBCOD and the intermediate phase was in fact a *residual phase* of phase 1. Combination of phase 1 and phase 2 values showed that the majority of the RBCOD were > 20 % while only 10 % of the values were between 10 and 20 % of the total COD, the expected range for RBCOD. This suggests that either French wastewaters have unusually high RBCOD concentrations, or that the NUR test measures an intermediate fraction of the raw wastewater *i.e.* the readily hydrolyzable fraction. The suggestion that the second phase is a residual phase of phase 1 is supported by the observations made with the acetate fed reactors where an intermediate phase was also observed. It was, therefore, postulated that some of the RBCOD fed to the biomass was used directly for energy and growth while some of the RBCOD was accumulated or stored. These accumulated and stored compounds become available to the bacteria once the RBCOD concentration becomes limiting.

A major objective of this study was to characterize the wastewater by physical and chemical methods. Raw wastewater was fractionated by settling (2h) (S-non-set), centrifugation (S-ce), filtration (S-f<sub>0.45</sub>) and coagulation (S-co). Several correlations (strong and weak) were made between the total COD and soluble fractions. The filtered (0.45 µm) and coagulated fractions were found to be approximately 33 and 25 % of the total COD, respectively. Studies also showed that filtration (0.45 µm) and coagulation included about 9 and 28 % less colloids (solids) than centrifugation. Furthermore, in a comparative study, no distinctive correlation was made between the fractions determined by the physico-chemical method suggested by Mamais *et al.* (1993) and the biological method *i.e.* no trend could be found between the biodegradable COD results obtained by coagulation (Ss) and the readily biodegradable COD fraction determined by the NUR tests which could suggest that the rationale and approach proposed by Mamais *et al.* (1993) cannot be applied to all wastewaters. In this case, it appears that the variability in the wastewater composition and the efficiency of the physico-chemical techniques may have contributed to the poor comparability of the methods.

Denitrification batch kinetics generally produced two or three rates which depended on the substrate used, the biomass activity and the test conditions. The maximum denitrification rates ( $k_1$ ) were found to be variable but within the range 3 to 6 mgN/gVSS.h. This variability is influenced by the wastewater quality and the activity of the sludge. The second rate ( $k_2$ ) or the second phase in the NO<sub>x</sub>-N profile was considered to be due to the readily hydrolyzable fraction of wastewater or sludge. About 78 % of the rates calculated were found to lie in the range 2 to 3 mgN/gVSS.h. Less than 10 % of the samples gave values below 2 mgN/gVSS.h and only 12 % were above 3 mgN/gVSS.h. These results suggest that the intermediate rate lies between 2 and 3 mgN/gVSS.h. The third rate ( $k_3$ ) was considered to be due to the slowly biodegradable fraction and endogenous products. Most of the  $k_3$  rates (68 %) were found to be less than 1.5 mgN/gVSS.h. However, a significant number were found to be between 2 and 3 mgN/gVSS.h. In this case it is also possible that the utilization of hydrolytic products of phase 2 ( $k_2$ ) may still be exerting its influence on  $k_3$  values. The variation and range suggests that the SBCOD components of the wastewater samples are complex and variable in composition and concentration. Therefore, there was an overlap between rate 2 ( $k_2$ ) and rate 3 ( $k_3$ ). The rate of hydrolysis of the SBCOD (endogenous and wastewater) was found to be about 37 % slower than the rate of hydrolysis of the readily hydrolyzable fraction.

In order to better understand the anoxic process and wastewater characterization several secondary experiments were done to investigate the influence of various factors on the accuracy of the results. The studies done with acetate showed that the results obtained by the NUR method may be influenced by the presence of polyphosphate accumulating organisms or denitrifying polyphosphate accumulating organisms. Therefore, tests were done with sludges obtained from the enhanced biological phosphorus removal plants (bio-P), Compiègne and Thiverval. The results clearly showed that the readily biodegradable COD fraction was underestimated by about 4 to 5 % (of the total COD) when a bio-P sludge was used. Furthermore, the RBCOD lost to polyphosphate accumulating organisms was found to be fairly comparable to the acetate fraction. Thus, the fraction lost to PAO's can be roughly accounted for when conducting NUR tests with bio-P sludge by adding the influent acetate fraction to the RBCOD fraction calculated. A weak correlation was found for the COD lost to PAO's and P release associated with COD sequestration. This COD/P ratio was variable and therefore, will not provide an accurate estimation of the RBCOD underestimation. These tests confirmed the need to measure phosphorus during the NUR batch test.

Several of the wastewater and sludge samples had to be stored prior to the NUR test. It was, therefore, necessary to do a preliminary study to determine the effect of storage at 4°C on the biodegradable fractions found in wastewater. Samples were collected from Evry Wastewater Treatment Plant and stored for 0, 24, and 72 h prior to the NUR test. The storage of raw wastewater samples up to 72 h at 4 °C did not compromise the determination of the readily biodegradable COD fraction which comprised about 9 % of the total COD. The results with the primary settler effluent samples revealed 2 biodegradable fractions in the 6 h NUR batch tests as opposed to the single biodegradable fraction which was calculated for raw

wastewater samples, with the 72 h raw wastewater sample being the one exception. The raw wastewater sample that had been stored for 72 h revealed 2 biodegradable fractions which suggests that longer storage periods ( $\geq 72$  h) could foster hydrolysis even at 4 °C or that the longer starvation periods triggers the utilization of existing storage products. In addition, in order to ascertain if the sludge may have contributed to the biodegradable fractions calculated, sludge samples were stored for 0, 24, and 72 h. NUR tests were conducted with the stored sludge samples *i.e.* no exogenous substrate was added. A single phase was observed for sludge samples that had been stored for 0 h and 24 h. However, 2 phases were observed for sludge samples stored for the 72 h and the sludge contribution for the test done with the 72 h sample was found to be 16 mgO<sub>2</sub>/l (*i.e.* 2 % of the total COD). This experiment showed that the accuracy and reliability of the data from NUR tests was not compromised for samples stored up to 24 h.

Tests were also done to determine if the use of an unacclimatized sludge would yield inaccurate biodegradable COD results. Most of the tests showed that the biodegradable COD fractions determined with acclimatized and unacclimatized sludges were comparable with one exception, Crespières. Biodegradable COD results obtained with the unacclimatized sludge of Crespières and the acclimatized sludge of Boran were incomparable. Tests with the acclimatized sludge of Boran revealed 2 biodegradable fractions while tests with the unacclimatized sludge of Crespières revealed a single fraction. Therefore, it would appear that not all the sludges are compatible with different wastewaters.

NUR tests using 'soluble' fractions derived from centrifugation or coagulation were shown to reduce two trends. In the first case, the readily biodegradable COD values obtained from wastewater samples that had been through either the process of centrifugation or coagulation were found to be comparable. These results support the premise that the RBCOD is found in the 'truly soluble' fraction, *i.e.* coagulated fraction, of raw wastewater. However, in one case (Plasir) the results also showed that the RBCOD determined from tests with the centrifuged 'soluble' samples were higher than that determined from the coagulated 'soluble' samples. This suggests that the readily biodegradable COD may not be limited to the 'truly soluble' component of wastewater but may be composed of intermediate molecular weight compounds which are retained by centrifugation but removed by coagulation. However, it could also suggest that the process of coagulation may remove some low molecular weight readily biodegradable compounds with the coagulant, ferric chloride, resulting in an underestimation of the readily biodegradable COD fraction.

Since the wastewaters characterized were done on grab or 24 h composite samples taken at a particular time, it was necessary to assess the weekly and annual variations that may occur for a particular wastewater. The weekly RBCOD variation was found to be between 11 and 25 %, and 9 and 18 % for Compiègne and Samaritaine, respectively with no clear trend identified. These results showed that the readily biodegradable COD concentration should be monitored with time in order to ascertain a mean value. There was no significant change in the total COD concentration determined for the Compiègne samples while COD measurements of the Samaritaine samples showed a decrease between the first and

second measurements. This showed that while a global parameter like COD may not change significantly during the week, the biodegradable COD fraction can. A similar trend was observed for wastewater samples from Boran Wastewater Treatment Plant which were monitored from September 1996 to November 1997. The RBCOD fraction was found to vary between 9 and 22 % of the total COD. In addition, the results suggested that the higher RBCOD values ( $\geq 17\%$ ) were obtained in the latter part of the year *i.e.* between October and November.

The NUR method was an effective tool for the characterization of municipal wastewaters. However, the major disadvantage lies in the off-line procedure which requires liquid samples to be taken at specific time intervals in order to follow NO<sub>x</sub> utilization. This characterization method should gain more use once an effective electrode or method is found which is able to follow the kinetics automatically. In addition, the NUR method showed that the characterization was necessary since there was a significant variation in the RBCOD content of wastewaters. Since this project analyzed several wastewaters from plants of similar and differing characteristics, the biodegradable fractions (RBCOD and RHCOD) data presented here can be used to do sensitivity analysis using the activated sludge models I and II to assess process efficiency and operation. Unfortunately, the rate constants determined cannot be used in these models as they are a function of the total VSS concentration and not the active biomass concentration.

The NUR method also allowed for the calculation of a second biodegradable fraction which was considered to be due to the utilization of either : 1) a readily hydrolyzable fraction of the slowly biodegradable COD of wastewater, or 2) the storage fraction that had been produced from the rapid uptake of RBCOD. These 2 hypotheses needs to be validated since it will have a major impact on the way current respirometric techniques are used as a characterization tool. In addition, the validation of the rapid accumulation / storage hypothesis will influence the way wastewater processes are modelled in the future.

This study also showed that certain factors need to be considered when assessing the data obtained from NUR tests. One of the major factors is the impact of polyphosphate accumulating organisms and denitrifying polyphosphate accumulating organisms under anoxic conditions. This is particularly evident in systems which contain a significant acetate fraction. The presence of a significant proportion of PAO's in the mixed liquor seed will result in the underestimation of the readily biodegradable COD fraction.



# Chapter Nine

## *RECOMMENDATIONS*

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This project analyzed several wastewaters from plants of similar and differing characteristics. The biodegradable fractions (RBCOD and RHCOD) data presented here can be used to do sensitivity analysis using the activated sludge models I and II to assess process efficiency and operation. Unfortunately, the rate constants determined cannot be used in these models as they are a function of the total VSS concentration and not the active biomass fraction.

These studies revealed a second biodegradable fraction, the readily hydrolyzable COD fraction. Future experiments could look at validity of this fraction. Is this fraction part of the RBCOD fraction or is it an intermediate fraction? The percentages RHCOD obtained are far too small to have this fraction labelled as the SBCOD of wastewater. Another aspect that needs to be investigated is whether this fraction is observable with the OUR test.

Investigations into acetate utilization provided some interesting observations and questions. One of the important aspects of this part of the study was the choice of yield coefficient. The acetate recovery results were significantly changed when a lower anoxic  $Y_{HD}$  of 0.50 was chosen as opposed to the aerobic value of 0.63. Therefore, there needs to be some standardization of the anoxic yield coefficient for NUR tests. Another significant observation was the presence of an intermediate phase which was hypothesized to be due to the utilization of acetate that had been sequestered by polyphosphate accumulating organisms. In other words, there is a secondary utilization of the sequestered acetate. Thus, this hypothesis of secondary utilization during denitrification needs to be validated. In addition, the question of the different bacterial groups needs to be investigated. Is there a differentiation between denitrifying PAO's and PAO's in anoxic sludge?

Experiments with bio-P sludge clearly showed that RBCOD values determined by bio-P sludge were lower than those determined by non bio-P sludge. Results also showed that this loss of RBCOD to PAO's activity may be comparable to the influent wastewater acetate concentration. However, further studies need to be done to confirm this relationship.



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# ***APPENDIX I***

## ***DESCRIPTION AND CHARACTERISTICS OF TREATMENT PLANTS***

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Samples from a total of 23 different plants were tested, 15 of which were French WTP, 4 were South African and the remaining four were from various European countries (Britain, Germany, Spain and the Czech Republic). Four South African plants which are located in the Natal-Durban region were also tested.

Table I-1 lists the different plants, their capacity, the type of wastewater treated, the distribution system, the presence or absence of primary settlers and the biological processes employed. The majority of the plants treat only municipal wastewater. However, some wastewater treatment plants do treat small proportions of industrial waste. Table I-2 lists the experimental conditions in the batch tests. They include the volumes used as well as the COD/N and S/X ratios used in the tests. In addition, three typical examples of French plants of small (< 10 000 p.e), medium (40 000 p.e.) and large (220 000 p.e.) capacity are presented in Figures 1, 2 and 3.

**Table 1: Description of the different wastewater treatment plants tested**

Plant	Country	Capacity (p.e)	Type of wastewater	Distribution system	Primary settler	Biological process
Asnières s/oise	France	42 000	municipal	separate	+	Carbon and ammonia removal
Berwick	England	13 390	municipal and reject from beverage industry (orange juice and whisky)	pseudo-separate	+	Carbon removal
Boran s/oise	France	3 000	municipal	separate	-	Carbon and nitrogen removal
Boves	France	2 500	municipal	combined	-	Carbon and ammonia removal
Brno	Czech Republic	600 000	70% municipal and 30% industrial (unidentified)	combined	+	Carbon removal
Compiègne	France	220 000	municipal with some reject from industries	combined	-	Carbon, nitrogen and phosphorus removal
Creil	France	110 000	municipal and some industrial	pseudo-separate	+	Carbon and nitrogen removal
Cresprières	France	1 500	municipal	combined	-	Carbon and ammonia removal
Gouvieux	France	10 000	municipal	combined	-	Carbon and nitrogen removal
Laon	France	40 000	municipal	combined	+	Carbon and nitrogen removal
Morainvilliers	France	13 000	municipal	1/3separate; 2/3 combined	-	Carbon and nitrogen removal
Orense	Spain	170 000	municipal and a low percentage of abattoir wastewater in the mornings	combined	+	Carbon removal (nitrogen removal occurs but not controlled)
Plaisir	France	42 000	municipal	separate	+	Carbon removal
Rostock	Germany	170 000	municipal	pseudo-separate	+	Carbon and nitrogen removal
Samaritaine	France	40 000	municipal	separate	-	Carbon , nitrogen and phosphorus removal
Thiverval-Grignon	France	12 000	municipal	separate	-	Carbon and nitrogen removal (P-chemical removal)
Artemps-Seraucourt	France	1 500	municipal	separate	-	Carbon removal
Villers sous St. Leu	France	500 ?	municipal	combined	-	Carbon and phosphorus removal

0.1,2,3 - refers to the number of days the samples were stored; \* - storage time varies between 0 to 3 days, p.e. - population equivalent

**Table 2: Experimental conditions of the batch tests conducted**

Date	Plant	V <sub>ww</sub> (L)	V <sub>x</sub> (L)	V <sub>t</sub> (L)	V <sub>d</sub> (L)	1/D.F	COD <sub>t</sub> /N	COD <sub>s</sub> /N	COD <sub>t</sub> /X	COD <sub>s</sub> /X
24/02/97	Crespières	0.73**	1.1	1.61	0.00	2.21	11.3	4.4	0.08	0.03
26/02/97	Crespières	0.60**	1.1	1.61	0.00	2.68	2.7	0.8	0.01	0.004
24/02/97	Morainvilliers	0.70**	1.1	1.61	0.00	2.24	18.0	4.7	0.14	0.04
26/02/97	Morainvilliers	0.80**	1.1	1.61	0.00	2.01	6.8	3.3	0.09	0.04
25/02/97	Boran s/oise	0.50	1.1	1.61	0.00	3.22	9.6	5.4	0.11	0.06
25/02/97	Plaisir*	0.60**	1.1	1.61	0.00	2.68	11.2	3.3	0.13	0.04
17/03/97	Rostock(Germany)	0.50	1.1	1.61	0.00	3.22	11.8	3.2	0.12	0.03
02/05/97	Berwick(England)	0.70**	1.0	1.46	0.00	2.09	19.0	9.7	0.16	0.08
15/05/97	Orense(Spain)	0.50**	1.0	1.46	0.00	2.92	4.8	1.6	0.07	0.02
15/05/97	Brno(Czech Republic)	0.40	1.0	1.46	0.05	3.65	2.4	1.0	0.07	0.02
23/04/97	Samaritaine 1 <sup>BP</sup>	0.35	1.0	1.46	0.10	4.17	7.7	3.0	0.09	0.03
25/04/97	Samaritaine 2 <sup>BP</sup>	0.35	1.0	1.46	0.10	4.17	6.4	2.7	0.07	0.03
28/04/97	Samaritaine 3 <sup>BP</sup>	0.40	1.0	1.46	0.05	3.65	7.0	2.5	0.08	0.03
7/08/97	Laon	0.35	1.0	1.41	0.05	4.02	6.2	2.6	0.07	0.03
21/08/97	Seraucourt-Le-Grand	0.30	1.0	1.41	0.10	4.70	8.7	3.7	0.11	0.05
28/08/97	Creil	0.30	1.0	1.41	0.10	4.70	5.8	2.6	0.07	0.03
28/08/97	Compiègne <sup>BP</sup>	0.30	1.0	1.41	0.10	4.70	10.3	3.0	0.12	0.04
4/09/97	Boves	0.30	1.0	1.41	0.10	4.70	6.7	2.7	0.06	0.03
10/09/97	Villers	0.30	1.0	1.41	0.10	4.70	8.2	3.3	0.05	0.02
11/09/97	Asnieres s/oise <sup>CP</sup>	0.30	1.0	1.41	0.10	4.70	6.6	1.0	0.18	0.03
11/09/97	Gouvieux	0.30	1.0	1.41	0.10	4.70	7.3	2.6	0.05	0.02
3/06/97	Compiègne <sup>BP</sup>	0.40	1.0	1.41	0.00	3.53	7.0	2.7	0.18	0.07
5/06/97	Compiègne <sup>BP</sup>	0.40	1.0	1.41	0.00	3.53	7.5	2.2	0.10	0.07
9/06/97	Compiègne <sup>BP</sup>	0.35	1.0	1.41	0.05	4.03	7.3	2.2	0.08	0.05
11/06/97	Compiègne <sup>BP</sup>	0.35	1.0	1.41	0.05	4.03	6.8	2.4	0.08	0.05
17/07/97	Thiverval <sup>BP</sup>	0.30	1.0	1.41	0.10	4.70	3.4	1.1	0.06	0.01
31/07/97	Thiverval <sup>BP</sup>	0.40	1.0	1.41	0.00	3.53	10.3	1.5	0.08	0.01

\*The sludge from Boran was used to test the wastewater from Plaisir since the sludge was not suitable; \*\*In the cases where more than 0.5 l were added the total volume was maintained by concentrating the sludge by settling; <sup>BP</sup> - biological phosphorus removal plant; <sup>CP</sup> chemical phosphorus removal plant.

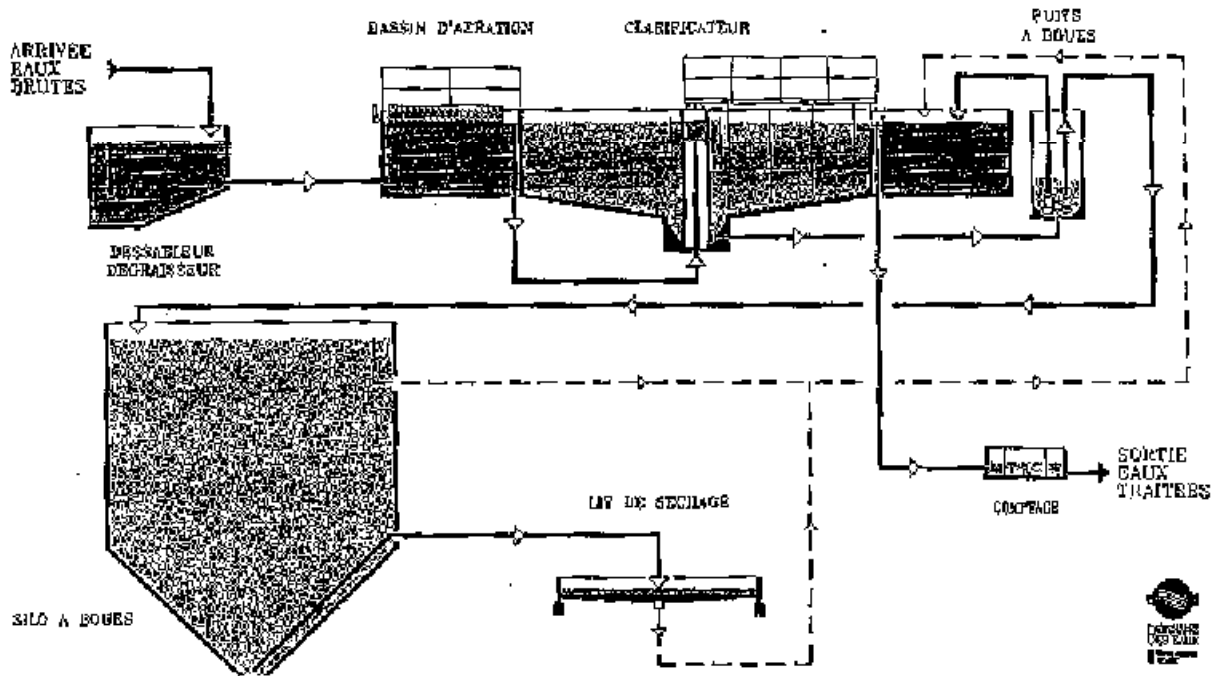


Figure 1: Plants schematics of Artemps-Seraucourt WTP with a capacity of 1 500 p.e.

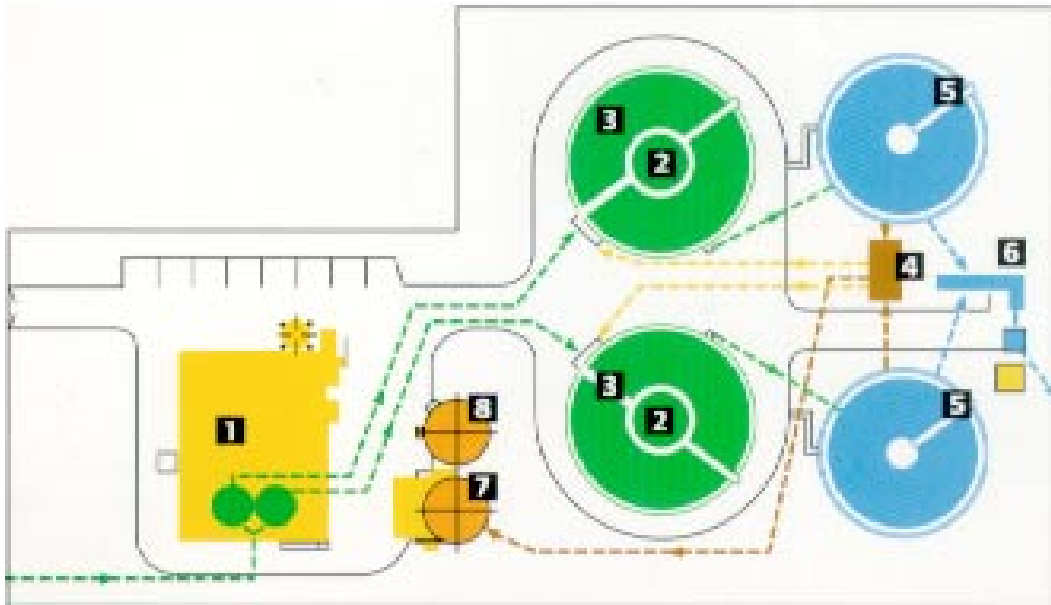


Figure 2: Plants schematics of Samaritaine WTP with a capacity of 40 000 p.e.

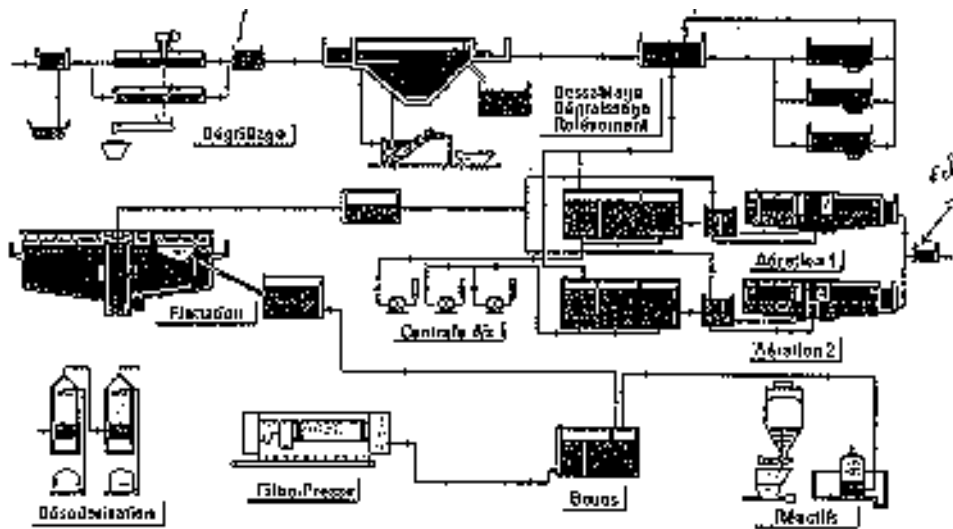


Figure 3: Plants schematics of Compiègne WTP with a capacity of 220 000 p.e.

# ***APPENDIX II***

## ***DEVELOPMENT OF METHODS FOR ANALYSIS AND BATCH TESTS***

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**Appendix II** discusses all the secondary experiments conducted to improve and understand analytical techniques and the NUR batch tests.

### ***II.1 OPTIMIZATION OF ANALYTICAL TECHNIQUES***

#### ***II.1.1 Chemical Oxygen Demand (COD)***

COD is an important analytical tool since much of the characterization of wastewater is based on this measurement. The method used in this study was the colorimetric method outlined in Standard Methods. This section shows a typical calibration curve, the theoretical and experimental values for sodium acetate as COD. In addition, preliminary tests were conducted to determine possible dilution factors which could be used for concentrated raw wastewater and sludge samples so that COD analysis would be representative of the samples collected.

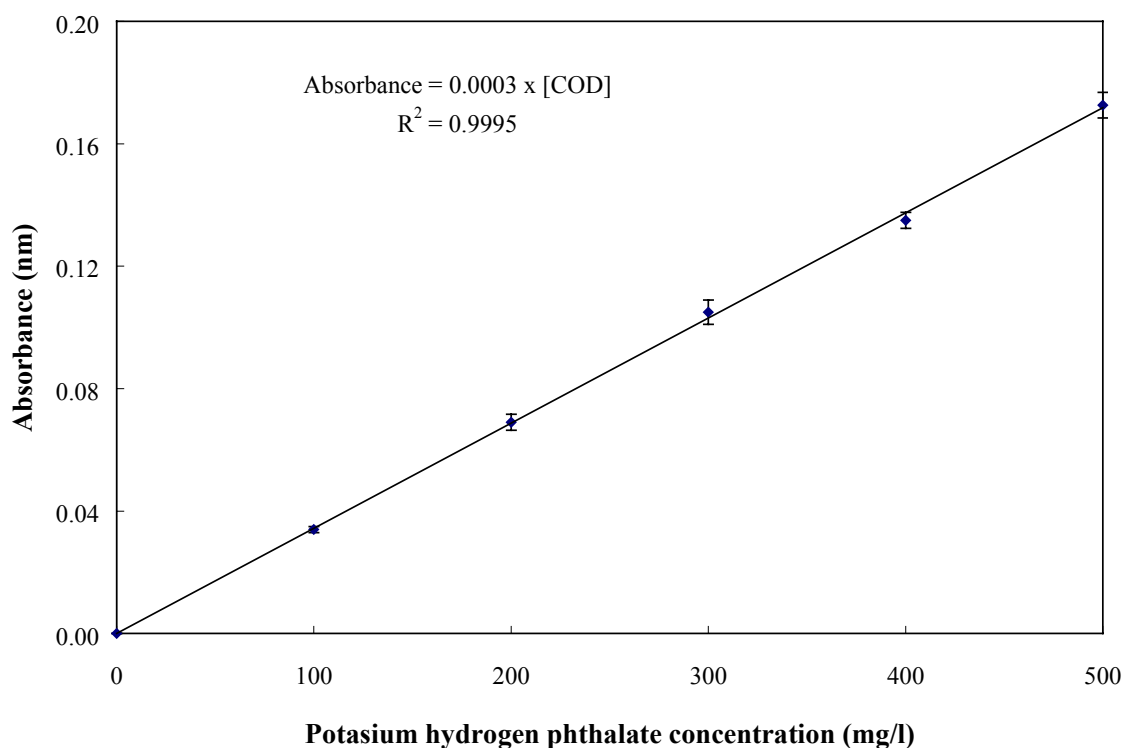
##### ***II.1.1.1 The COD calibration curve***

COD calibration curves were constructed using potassium hydrogen phthalate (PHT) as the standard. A stock PHT solution of 500 mgO<sub>2</sub>/l was made and a COD calibration test ranging from 0 to 500 mgO<sub>2</sub>/l was done. The standard solutions were measured in triplicate. An example of the COD calibration data set and curve are presented in Table II-1 and Figure II-1. A linear plot was observed for the above range. The equation of the line was found to be  $Y = 0.0003 x$ ,  $r^2 = 0.99$ . Thus,

$$\text{COD (mgO}_2\text{/l)} = \text{Absorbance}/0.0003 \quad (\text{II-1})$$

**Table II-1: An example of calibration data with PHT (SD-standard deviation ; cv-coefficient of variation)**

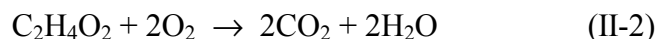
Concentration mgO <sub>2</sub> /l	Absorbance (600 nm)					
	1	2	3	average	SD	cv
0	0.000	0.000	0.000	0.000	0.000	0.000
100	0.035	0.033	0.034	0.034	0.001	2.941
200	0.067	0.072	0.068	0.069	0.003	3.834
300	0.101	0.105	0.109	0.105	0.004	3.810
400	0.137	0.136	0.132	0.135	0.003	1.960
500	0.168	0.176	0.174	0.173	0.004	2.411



**Figure II-1: An example of a COD calibration curve with potassium hydrogen phthalate as standard.**

### **II.1.1.2 The chemical oxygen demand (COD) of sodium acetate**

Since all acetate concentration values are given as COD in this study, it was necessary to determine the conversion factor of sodium acetate (mg/l) as COD (mgO<sub>2</sub>/l). Analytical and theoretical methods were used to calculate the chemical oxygen demand of hydrated sodium acetate (CH<sub>3</sub>COONa.3H<sub>2</sub>O, MW = 136). The stoichiometric conversion of acetic acid as mgO<sub>2</sub>/l was derived by first writing the oxidation reaction for acetic acid as follows:



The theoretical oxygen demand (TOD) sodium acetate can be calculated by using the following formula:

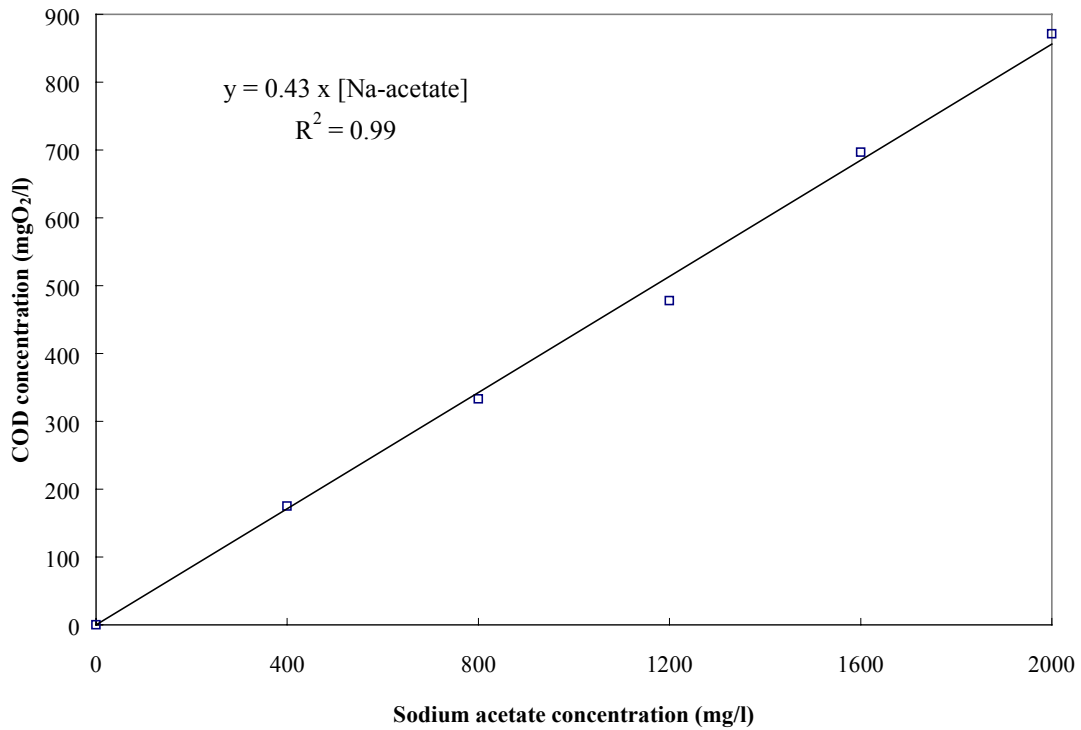
$$\begin{aligned} \text{COD} &= \{[4(\text{nC}) + (\text{nH}) - 2(\text{nO})] 8\} / \text{MW}_{\text{Na-acetate}} \\ &= \{[12-4] 8\} / 136 \\ &= 64/136 \\ &= 0.47 \text{ (mgO}_2\text{/mg Na-Ace)} \end{aligned}$$

A calibration curve of sodium acetate (mg/l) was plotted against sodium acetate (mg/l) as COD (Table II-2 ; Figure II-2). Acetate as COD was found to be 0.43 x sodium acetate concentration. This value (0.43) compares favourably with the value 0.47 derived theoretically. The percentage accuracy of the measured (experimental) and calculated (theoretical) values (0.88/0.97\*100) is 91 %. According to the standard methods the accuracy of the COD method ranges between 90 to 100 %.

**Table II-2: Data for the sodium acetate vs COD calibration curve (conc.-concentration)**

Na-acetate conc. (mg/l)	ABSORBANCE (600 nm)						COD measured (mgO <sub>2</sub> /l)
	1	2	3	average	sd	CV	
0	0.000	0.000	0.000	0.000	0.0000	0.00	0.0
400	0.050	0.055	0.054	0.053	0.0026	4.99	177
800	0.101	0.099	0.100	0.100	0.0010	1.00	333
1200	0.141	0.145	0.144	0.143	0.0021	1.45	478
1600	0.212	0.207	0.208	0.209	0.0026	1.27	697
2000	0.260	0.262	0.262	0.261	0.0012	0.44	871

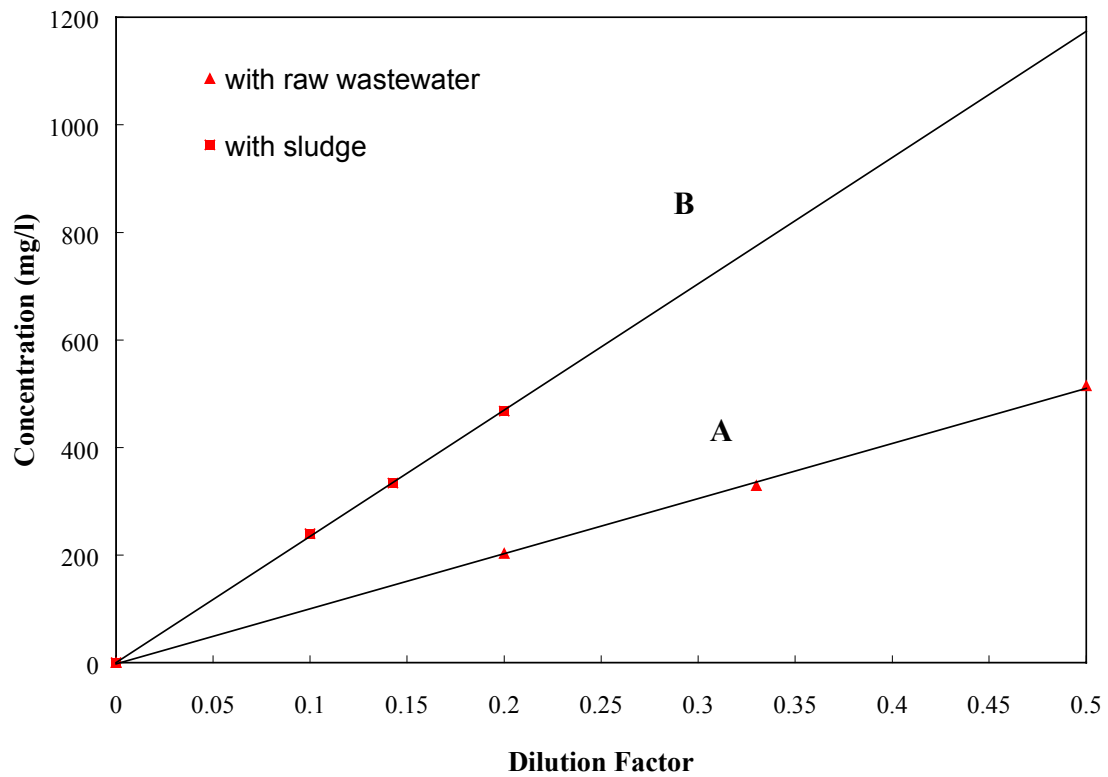




**Figure II-2 : Calibration curve to derive the COD to acetate conversion factor ( $n=3$ ; and the CV (%) is less than 10 for all points).**

### **II.1.2 Dilution factors used for raw wastewater and sludge samples for COD analysis**

Raw wastewater and especially sludge samples are fairly concentrated and fall outside the COD calibration range of 0 to 500 mg/l. It was therefore, necessary to test different dilution factors to ensure that the accuracy of the measurement was maintained. Dilution factors 1/5 (0.20), 1/3 (0.33), and 1/2 (0.50) were tested for raw wastewater (Figure II-3 ; (A)). The measurements were found to be linear over this range of dilution factors. Generally, raw wastewater was diluted 1 in 2. Similarly, dilution factors, 1/10 (0.10), 1/7 (0.15), and 1/5 were tested for sludge samples (Figure II-3 ; (B)). A dilution of 1 in 10 (0.10) was chosen for all subsequent COD analyses with sludge samples.



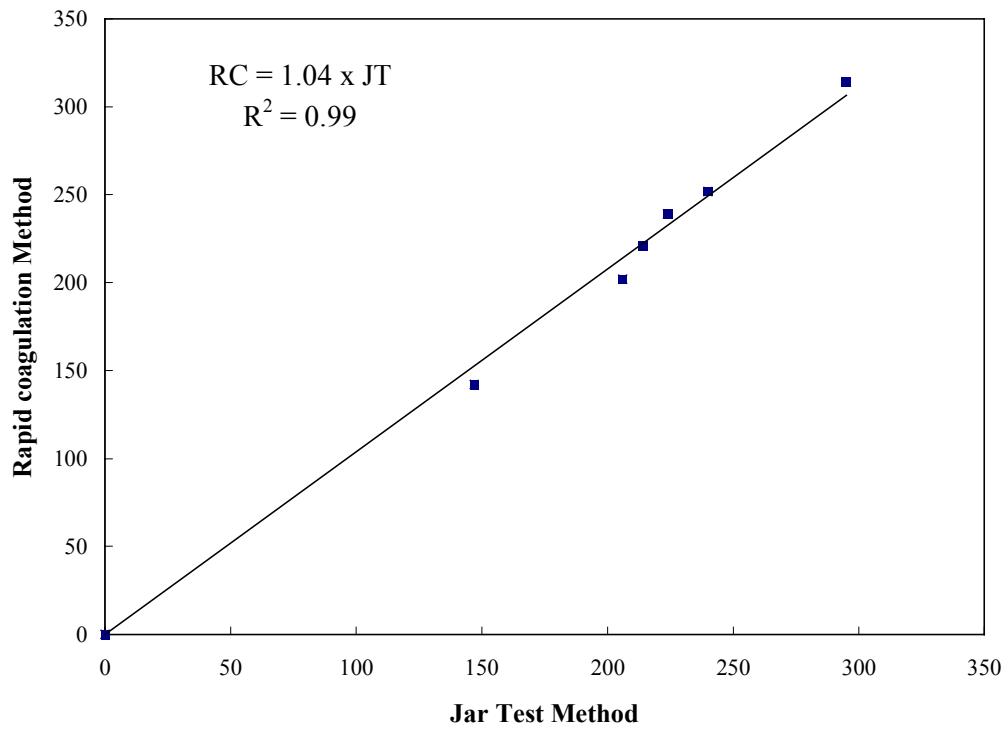
*Figure II-3: Testing of a range of dilution factors for concentrated raw wastewater and sludge samples.*

### ***II.1.3 Coagulation tests***

The rapid coagulation (RC) method was tested against the jar test (JT) method in order to shorten the coagulation procedure. The latter method was limiting since it required 1 l of raw wastewater, a 12 min mixing time and a 30 min or longer settling period. The rapid coagulation method shortened the mixing period to 1 min manual mixing and substituted the settling step with a centrifugation step. These two methods were compared using raw wastewater from 6 different treatment plants (Table II-3). The soluble COD (S-co) results were plotted and a linear curve was found and is expressed in equation II-3 (Figure II-4). The results showed that the 2 methods were fairly comparable (see Table II-3). This implied that the jar test method can be adequately substituted by the rapid coagulation method.

**Table II-3: Comparison of soluble COD (mgO<sub>2</sub>/l) (S-co) results using the Jar test and Rapid coagulation method.**

Plants	S-co (mgO <sub>2</sub> /l)	
	Jar Test	Rapid coagulation
Artemps	295	314
Asnières	147	142
Boves	240	252
Creil	224	239
Gouvieux	214	221
Boran	206	202



*Figure II-4: Relationship between jar test and rapid coagulation method*

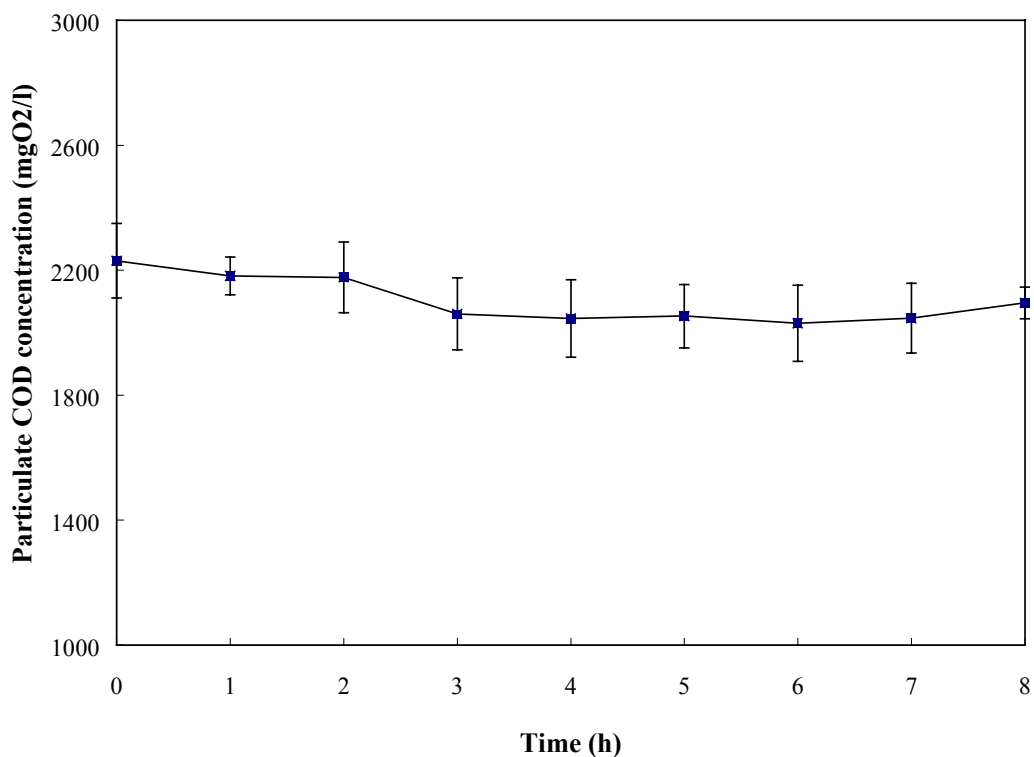
$$COD_{S(RC)} = 1.04 \times COD_{S(JT)} \quad (II-3)$$

## ***II.2 BIOMASS GROWTH DURING THE BATCH TEST***

This preliminary test was done to investigate if biomass growth occurred at S/X ratios of about 0.07. The results showed that there was a slight decrease in the particulate COD concentration (Table II-5 ; Figure II-5). However, it must be noted that the standard deviations for the analysis of these particulate substrates are quite high. Thus, these results do confirm that no nett growth occurred during the 8 h batch test.

***Table II-4 : COD measurements taken from 5 reactors operated under identical batch experimental conditions for 8 h (sd - standard deviation).***

<b>Time (h)</b>	<b>Mixed liquor total COD (mgO<sub>2</sub>/l)</b>						
	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>average</b>	<b>sd</b>
0	2384	2417	2384	2311	2100	2339	87
1	2150	2278	2278	2300	2167	2271	60
2	2033	2278	2333	2211	2033	2198	110
3	2100	2256	2100	2067	1933	2091	110
4	2233	2087	2000	2150	1916	2077	120
5	2384	2067	2067	1990	1933	2088	170
6	2150	1900	2033	1984	2200	2053	120
7	2033	2150	1967	2000	2233	2076	110
8	2150	2144	2033	2033	2300	2132	110



*Figure II-5: Change in particulate COD concentration during an 8h batch test (n=5).*

### ***II.3 NUR BATCH TESTS***

Several secondary experiments were carried out to understand and optimize the NUR batch test. These included the analysis of redox, pH and S/X data.

#### ***II.3.1 Redox potential under anoxic conditions***

Facultative organisms are able to use different electron acceptors such as oxygen, nitrates and nitrites. They use these acceptors in preferential sequence with oxygen being the first choice followed by nitrates and nitrites. Redox potential allows one to differentiate between the type of electron acceptor used. When oxygen is present the redox potential is high. Once oxygen is depleted, nitrates and nitrites are utilized and the redox drops to a lower value. This value decreases even further once oxygen, nitrates and nitrites are no longer present denoting the presence of anaerobic conditions.

During experimentation redox data was collected from most of the tests. Thus, data was analyzed to determine the usefulness of redox either as a monitoring or analytical tool or both. The discussions that follow look at some of the more interesting results and observations.

### II.3.1.1 Relationship between redox potential and denitrification profiles

An attempt was made to determine if redox potential profiles could be used to study denitrification rates and thus, substrate utilization. Figure II-6 shows the redox drop with a constant denitrification rate observed for tests where no exogenous substrate was added *i.e.* sludge only. Figure II-7 shows the redox potential and NO<sub>x</sub> curves with a readily biodegradable substrate (acetate). The break in the redox potential curve does not match the break point of the NO<sub>x</sub> curve. Thus, the redox profiles for tests with and without substrate addition were similar. These results showed that redox potential profiles produced typical trends which did not mimic the type of biodegradable COD used.

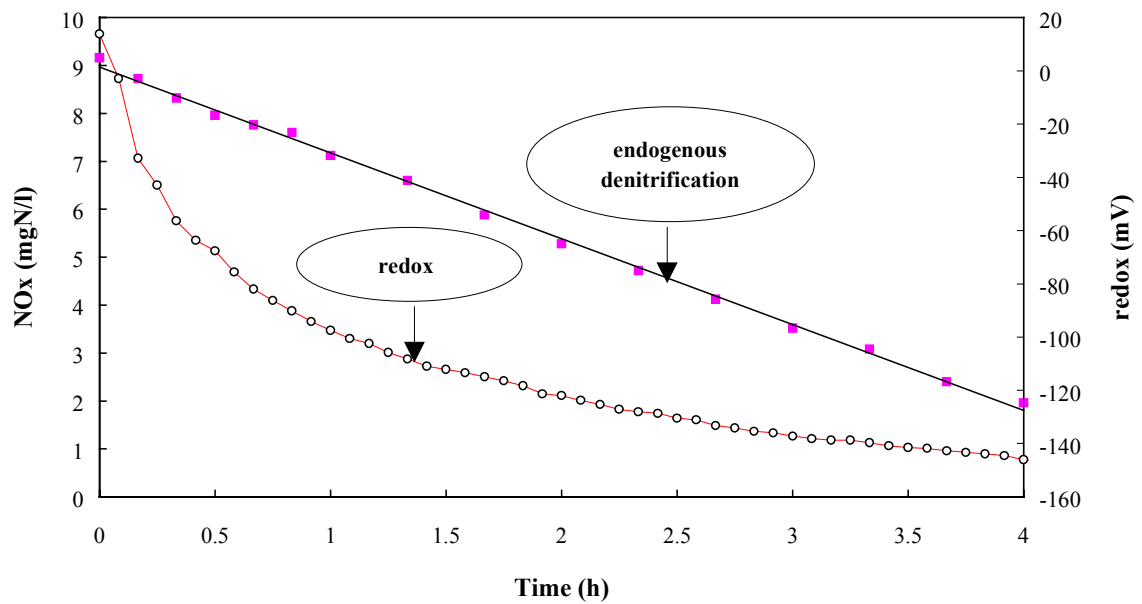
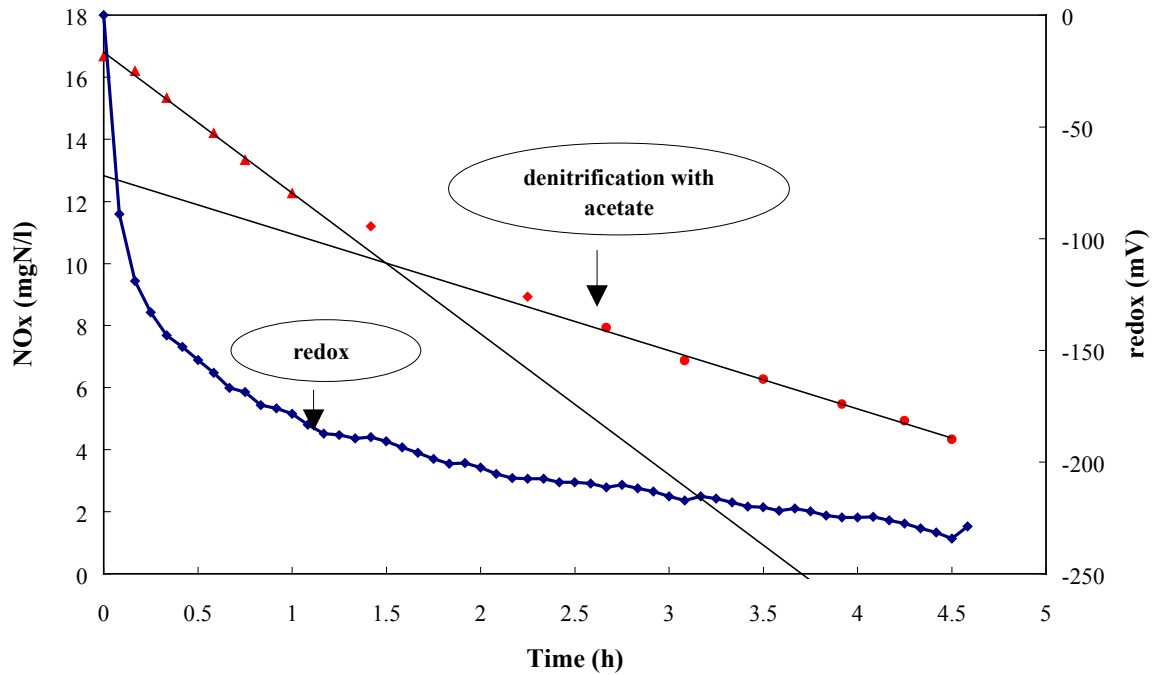


Figure II-6 : Redox potential and endogenous denitrification profiles ( $T = 20^{\circ}\text{C}$ ;  $\text{pH} = 7.5$ )



*Figure II-7: Redox potential and NO<sub>x</sub>-N utilization curves with acetate (T = 20°C; pH = 7.5)*

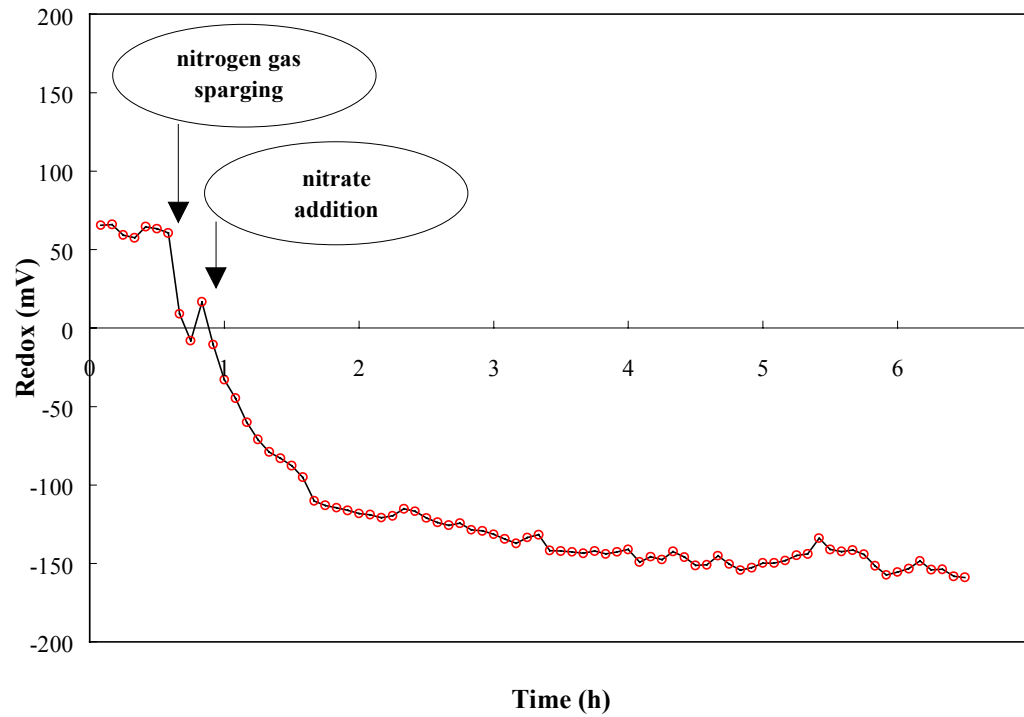
### ***II.3.1.2 Redox as a monitoring tool***

Figure II-8 highlights a typical redox potential curve prior to and after the addition of nitrates for denitrification (note that the values represented in Figure II-8 are observed / recorded values using a hydrogen standard electrode). Figure II-8 shows a period of stability when no oxygen or nitrogen was sparged into the reactor. Once nitrogen was sparged into the reactor the redox potential began to drop rapidly. The addition of potassium nitrate to the system resulted in a slight increase in the redox. Nitrogen was sparged once again which together with the nitrates resulted in a sharp drop in redox potential. The redox potential then stabilized at about -150 mV.

Figure II-9 shows a redox potential curve from the start of the denitrification batch test. Initially there was a sharp drop in the redox potential which was then followed by a period of stabilization. However, when the nitrates and nitrites were exhausted there was another sharp decline in redox potential which is often referred to as the ‘nitrate-knee’. The addition of more nitrates (15 mgN/l) to the system resulted in a sharp increase in the redox potential. After an overshoot the redox potential stabilized indicating that nitrate is the controlling species.

Figure II-10 highlights the importance of maintaining oxygen free conditions during denitrification. In this experiment there was a problem with the gas sparging line and thus there was no initial sharp decline in the redox values (Figure II-10). This stable redox potential was then followed by an increase in redox potential which indicates the introduction of oxygen during sampling. Nitrate-time profiles showed that

this increase in redox potential (*i.e.* an increase in oxygen) resulted in a concomitant decrease and finally a cessation of nitrate utilization (Figure II-10). Therefore, redox potential can be considered an important tool to monitor denitrification as it highlights the presence or absence of oxygen and / or nitrates in the reactor.



*Figure II-8: Typical redox curve under batch experimental conditions.*



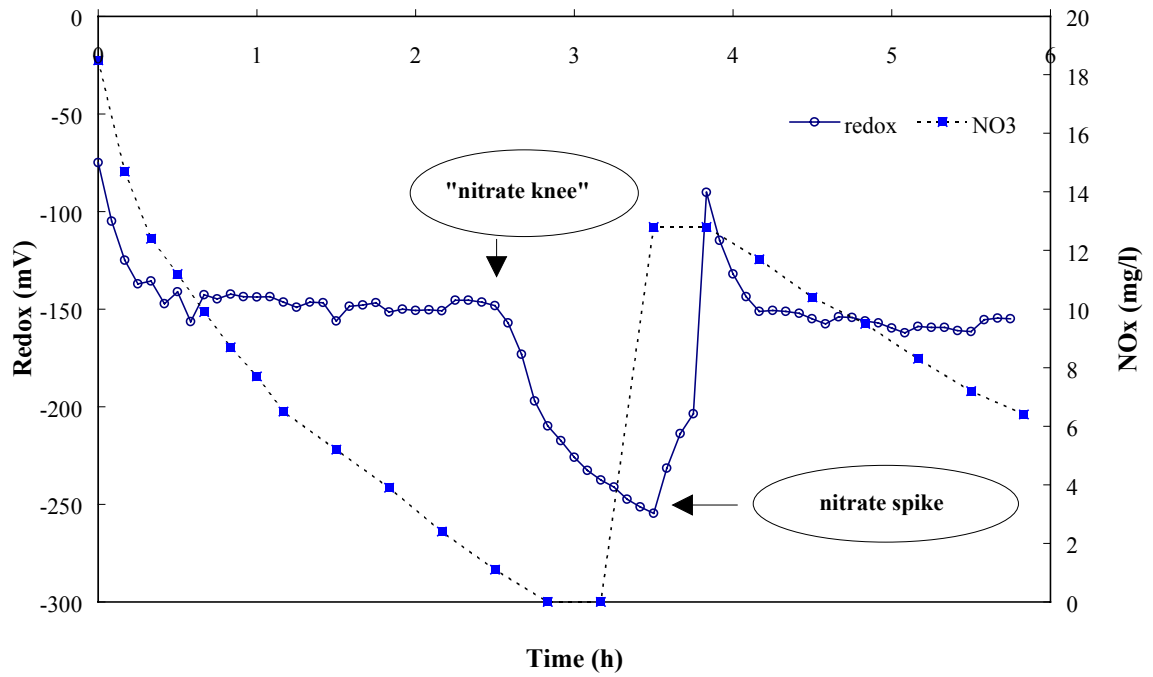


Figure II-9: The change in redox in the presence and absence of nitrates.

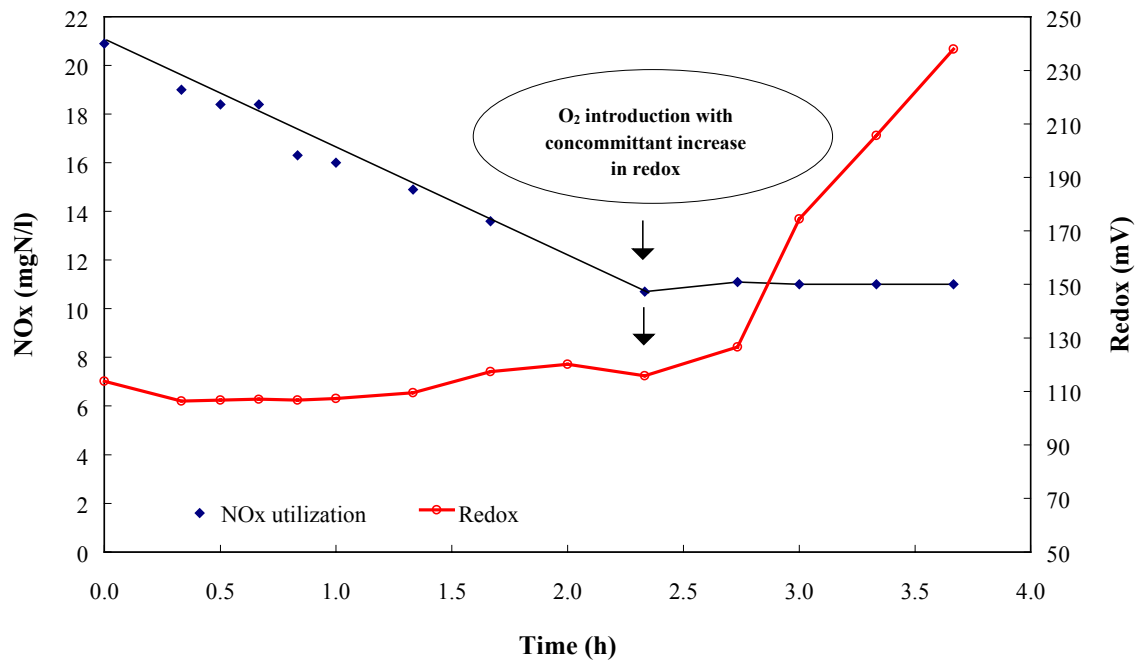


Figure II-10: Comparison of nitrate-N utilization and redox potential measurements under non-optimum anoxic conditions.

### ***II.3.2 The choice of dilutant***

The aim of this study was to assess and compare the influence of two dilutants : water and treated effluent on denitrification kinetics and the accumulation of nitrites, in particular. Initial denitrification tests showed that acetate-fed reactors produced higher concentrations of nitrites (5 to 7 mgN/l) than the other substrates (raw wastewater, raw wastewater particulates, and endogenous products) tested (Figure II-11). For these experiments water was used as a dilutant to adjust the volume whenever necessary to make up a total volume of 1.6 l. Acetate-fed reactors always contained 0.5 l of dilutant which is approximately one-third of the total working volume. One of the questions posed was whether acetate-fed reactors produced higher concentrations of nitrite and higher pH increases due to a lower buffering capacity of the dilutant, water as compared to raw wastewater.

For these tests, all conditions within the reactors were similar except for the dilutant used. Two dilutants, water and treated effluent from the WTP being tested were tested (Table II-6). Acetate was used as the organic carbon source. The COD/N ratio was  $3.10 \pm 0.20$  and the S/X ratio in the reactors varied between 0.05 and 0.06 (Table II-7).

Reactors with the dilutants water and treated effluent produced similar denitrification rates of  $2.20 \pm 0.10$  and  $2.30 \pm 0.06$  (mgN/gVSS.h), respectively. The same trends were observed for nitrate utilization (Table II-7).

Nitrite accumulation rates were found to be slightly higher for water than for treated effluent. (Figure II-12). Both reactors showed a similar change in pH of about 0.8 pH units (from pH 7.6 to 8.4) which means that the choice of dilutant does not influence the magnitude of the pH change. These results suggest that it was possible to use either water or treated effluent without significant changes of denitrification rates.

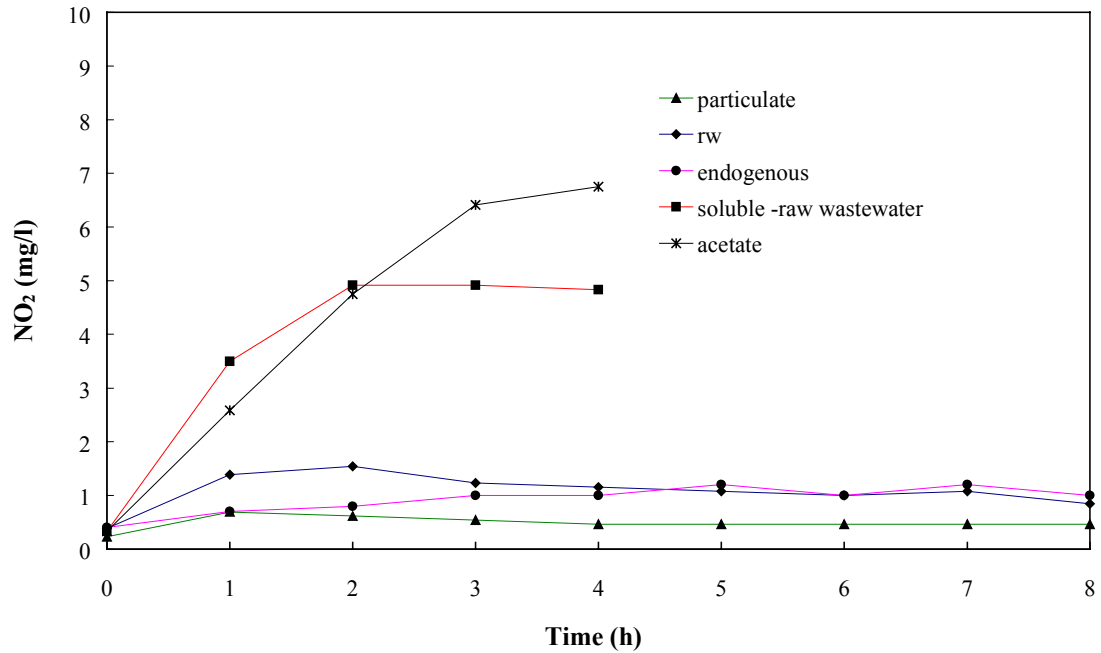


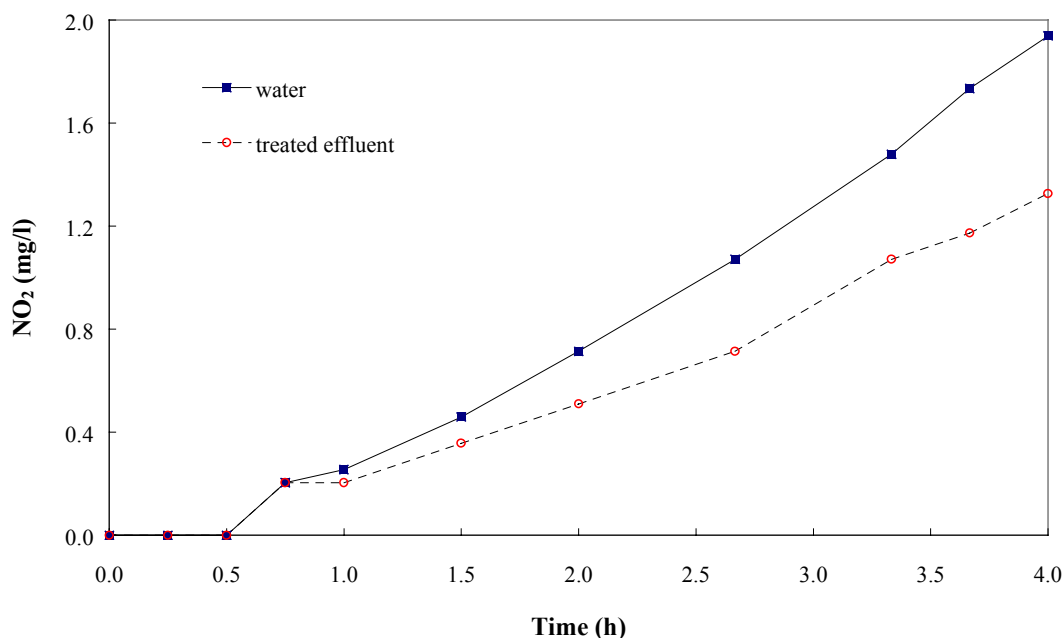
Figure II-11: Comparison of nitrite-N accumulation for different substrates (31 May 1996)(rw - raw wastewater).

Table II-5 : Raw NUR data for tests with water and treated effluent

Water (VSS = 1.40 g/l)			Treated effluent (VSS = 1.36 g/l)		
Time (h)	Nitrates-N	Nitrites-N	Time (h)	Nitrates-N	Nitrites-N
0.0	30.6	0.0	0.0	34.4	0.0
0.3	29.3	0.0	0.3	33.7	0.0
0.5	29.7	0.0	0.5	33.0	0.0
0.8	28.6	0.3	0.8	31.8	0.3
1.0	28.0	0.4	1.0	31.5	0.3
1.5	24.1	0.6	1.5	28.3	0.5
2.0	23.3	1.0	2.0	27.5	0.7
2.7	20.9	1.5	2.7	24.8	1.0
3.3	17.5	2.1	3.3	21.6	1.5
3.7	15.8	2.4	3.7	20.3	1.6
4.0	14.4	2.7	4.0	18.9	1.9

Table II-6: Summary of denitrification rates for different dilutants (mgN/gVSS.h at 20°C).

	COD/N	S/X	$k_{NO_x}$	$k_{NO_3-N}$	$k_{NO_2-N}$
<b>Water</b>	3.30	0.06	$2.20 \pm 0.10$	$2.90 \pm 0.11$	$0.60 \pm 0.02$
<b>Treated effluent</b>	2.90	0.06	$2.30 \pm 0.06$	$2.80 \pm 0.07$	$0.40 \pm 0.02$



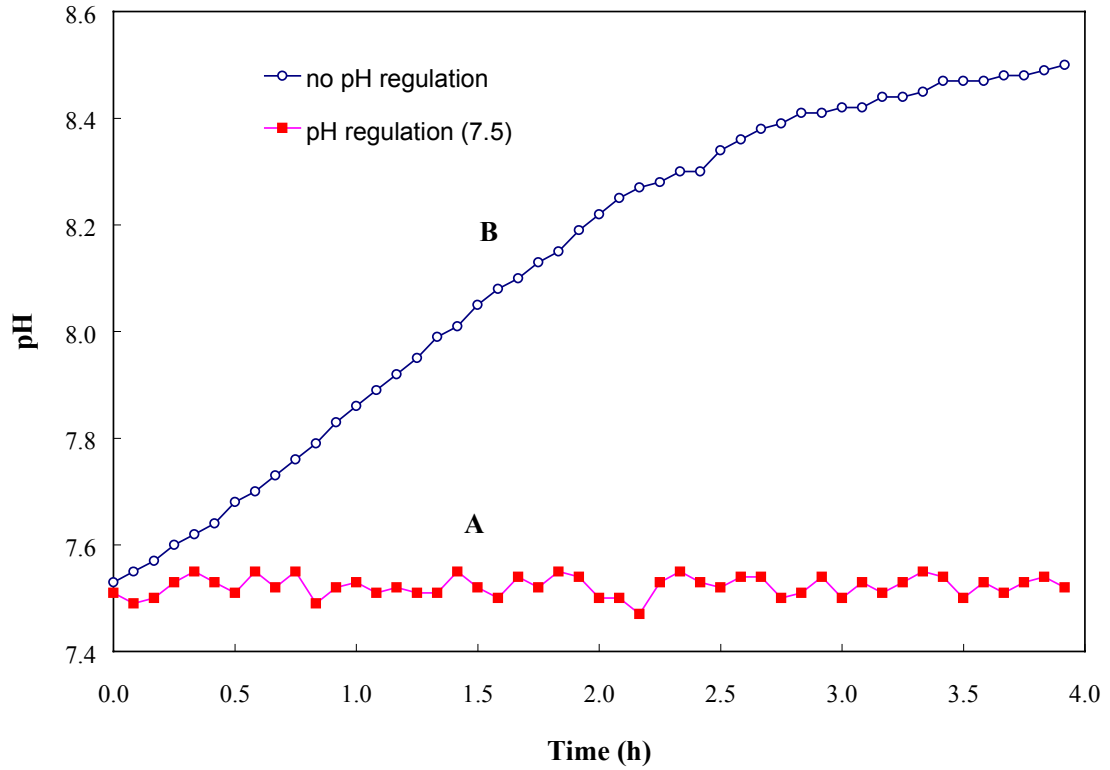
**Figure II-12: The influence of different dilutants on nitrite accumulation (acetate-fed reactor).**

### II.3.3 pH regulation

Several of the earlier denitrification tests resulted in pH increases of about 1 unit (Figure II-13 ; (B)). Initial experiments which were not pH-regulated also showed high nitrite concentrations, up to 5 mg/l, especially in the reactors containing readily biodegradable COD (*see* Figure II-11). Therefore, two reactors were set up : with pH regulation at 7.5 and without pH regulation (Figure II-13). The pH was regulated with 1M HCl. Acetate was chosen as the readily biodegradable substrate. The results from two separate NUR tests are presented (Table II-8).

The same trends were observed in both tests under similar NUR batch experimental conditions (Table II-9). The pH regulated reactors produced slightly higher denitrification rates than the non-regulated reactors (an increase in rate of ca. 8 %). An opposite trend was observed for nitrate-utilization : *i.e.* reactors without pH regulation produced higher nitrate utilization rates which indicated that pH increase did not inhibit nitrate utilization and might in fact be advantageous to the nitrate-utilizers. In addition the pH regulated reactors produced little or no nitrite accumulation (< 1 mg/l) while nitrites accumulated in the reactors without pH regulation (> 1 mg/l) (Figure II-13). Furthermore, nitrites accumulated at a fairly

steady linear rate for the non-pH-regulated reactors, while pH regulated reactors showed an initial rapid increase in nitrite concentration within the first 30 min which persisted before decreasing rapidly.



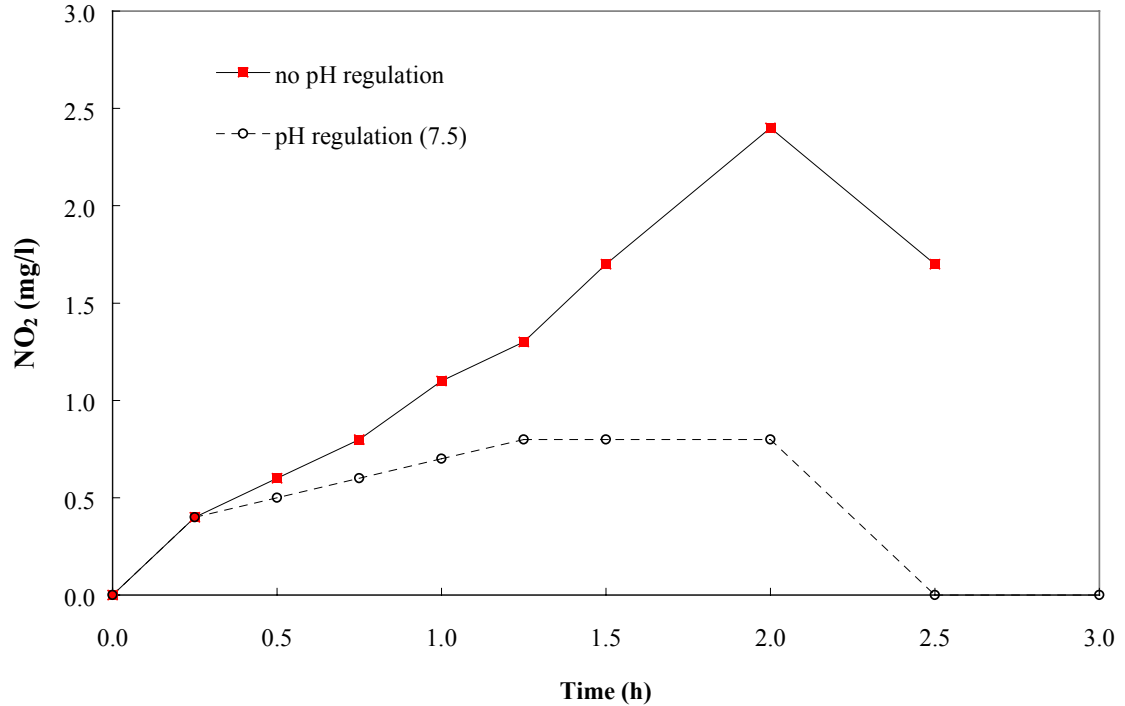
*Figure II-13 : Typical pH profiles from NUR batch tests with (A) and without (B) pH control.*

**Table II-7 : Raw data from NUR batch tests with and without pH regulation.**

<b>Test 1 : 30 October 1996</b>					
<b>No pH regulation</b>			<b>pH regulation</b>		
<b>Time (h)</b>	<b>NO<sub>3</sub>-N</b>	<b>NO<sub>2</sub>-N</b>	<b>Time (h)</b>	<b>NO<sub>3</sub>-N</b>	<b>NO<sub>2</sub>-N</b>
0.0	19.9	0.0	0.0	20.4	0.0
0.3	18.5	0.0	0.3	19.4	0.0
0.7	16.9	0.0	0.7	17.9	0.0
1.0	15.3	0.4	1.0	16.8	0.0
1.3	15.2	0.0	1.3	14.6	0.5
1.7	12.9	0.6	1.7	14.2	0.0
2.0	11.4	0.7	2.0	12.7	0.0
2.3	10.1	1.0	2.3	11.3	0.0
3.0	7.0	1.5	3.0	8.0	0.3
3.7	4.3	2.0	3.7	5.6	0.0
4.0	3.0	2.1	4.0	5.0	0.0
<b>Test 2 : 15 November 1996</b>					
<b>Time (h)</b>	<b>NO<sub>3</sub>-N</b>	<b>NO<sub>2</sub>-N</b>	<b>Time (h)</b>	<b>NO<sub>3</sub>-N</b>	<b>NO<sub>2</sub>-N</b>
0.0	16.3	0.0	0.0	16.3	0.0
0.3	14.4	0.4	0.3	14.0	0.4
0.5	12.3	0.6	0.5	12.2	0.5
0.8	11.0	0.8	0.8	11.2	0.6
1.0	9.2	1.1	1.0	9.1	0.7
1.3	7.5	1.3	1.3	7.8	0.8
1.5	5.7	1.7	1.5	6.1	0.8
2.0	2.2	2.4	2.0	2.7	0.8
2.5	0.0	1.7	2.5	0.0	0.0
3.0	0.0	0.0	3.0	0.0	0.0

**Table II-8 : Results from test 1 and 2 at 20°C, with or without pH regulation (denitrification rates are in mgN/gVSS.h).**

		<b>COD/N</b>	<b>S/X</b>	<b>k<sub>NOx-N</sub></b>	<b>k<sub>NO3</sub></b>
<b>Test 1</b>	<b>non-regulated</b>	3.8	0.05	3.30 ± 0.05	3.90 ± 0.08
	<b>regulated</b>	3.7	0.05	3.60 ± 0.05	3.60 ± 0.08
<b>Test 2</b>	<b>non-regulated</b>	4.6	0.04	3.90 ± 0.04	4.60 ± 0.06
	<b>regulated</b>	4.6	0.04	4.20 ± 0.10	4.40 ± 0.11



**Figure II-14 : Nitrite accumulation profiles from test 2.**

These results suggest that the nitrite-utilizers function more actively at pH 7.5, while the nitrate-utilizers seem to function better with increasing pH. However, maintaining a constant pH at 7.5 has a net positive effect on the overall denitrification rate because it reduces nitrite accumulation.

### ***II.3.4 Influence of different S/X ratios on denitrification kinetics***

The ratio between substrate and biomass is important in batch kinetics. When the S/X ratio is too high, substantial cell multiplication occurs and therefore, specific rates cannot be calculated directly from the kinetic. In addition, the S/X ratio might also influence the shape of the curve, allowing or not to determine the breaks related to the use of different substrates and thus, the reliability of the RBCOD and SBCOD calculated.

#### ***II.3.4.1 Acetate as a substrate***

This study was conducted to determine the effect of the S/X ratios in denitrification tests, with particular interest in the different ratios of biomass to readily biodegradable COD. Four ratios were tested : 0.02; 0.05; 0.09; and 0.20 gO<sub>2</sub>/gO<sub>2</sub>, with acetate as the substrate (Table II-10). The same concentration of biomass was added to each reactor, but the substrate concentration was increased from 40 to 400 mgO<sub>2</sub>/l to provide a 10-fold increase in the S/X ratio. The pH was controlled at 7.5 in the four reactors.

A slight decrease in rate was observed as the S/X ratio increased (Table II-11). However, consideration of the standard deviations for the different rates obtained and the coefficient of variation of 8 % derived from the reproducibility experiment, would suggest that there is no significant change in the rates. Tests conducted at the lowest S/X ratio allowed the observation of two rates, an initial rapid rate associated with the use of acetate and a second slower rate which was due to the use of endogenous carbon (Figure II-15). Operation of the batch reactors at S/X ratios  $\geq 0.05$  revealed only a single phase in the 4 h test. Nitrite accumulation was limited ( $< 1$  mg/l) due to the control of the pH at 7.5. Thus, changes in the S/X ratio between 0.02 and 0.20 did not significantly influence denitrification in batch conditions.

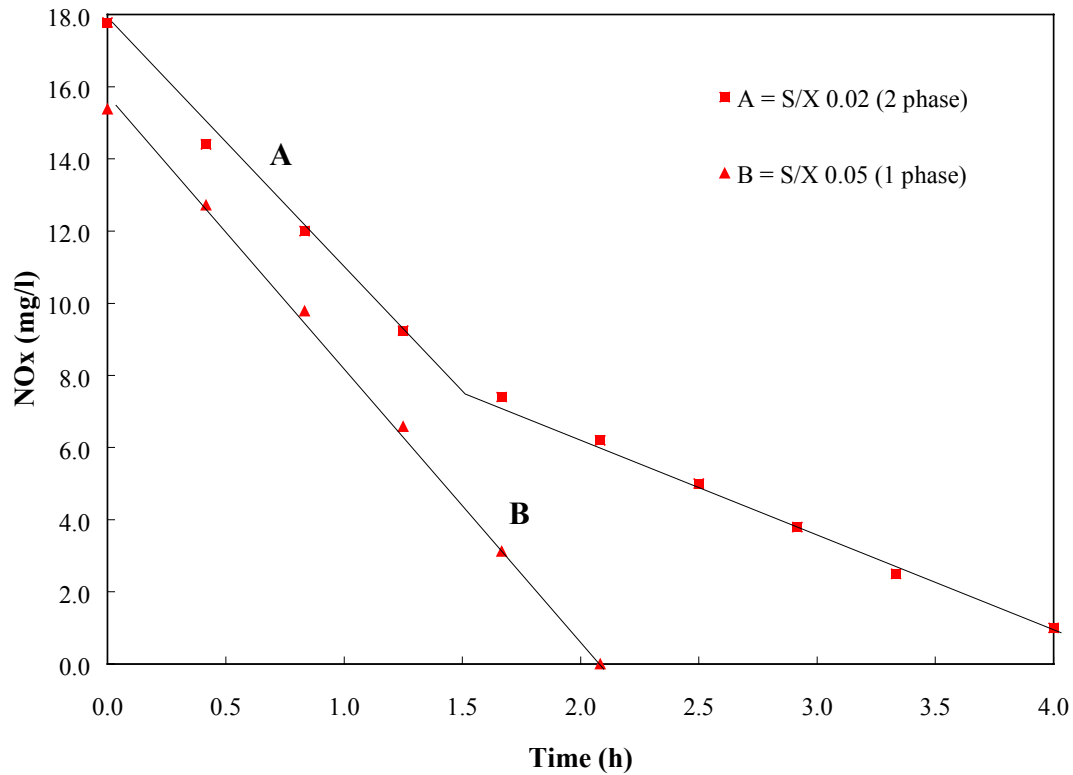
**Table II-9: Raw data from NUR batch tests (acetate-fed) operated at different S/X ratios**

Time(h)	S/X = 0.02		S/X = 0.05		S/X = 0.10		S/X = 0.20	
	NO3-N	NO2-N	NO3-N	NO2-N	NO3-N	NO2-N	NO3-N	NO2-N
0.0	17.6	0.3	15.2	0.3	14.8	0.4	13.0	0.4
0.4	14.1	0.5	12.3	0.7	12.5	0.6	12.2	0.5
0.8	11.7	0.5	9.3	0.8	9.4	0.7	9.6	0.7
1.3	9.0	0.4	6.1	0.8	6.7	0.7	6.9	0.7
1.7	7.4	0	2.7	0.7	3.5	0.7	4.1	0.7
2.1	6.2	0	0	0	0.9	0.6	1.5	0.6
2.5	5.0	0	0	0	0	0	0	0
2.9	3.8	0	0	0	0	0	0	0
3.3	2.5	0	0	0	0	0	0	0
4.0	1.0	0	0	0	0	0	0	0

**Table II-10: Denitrification rates for acetate-fed NUR tests at different S/X ratios ( $k_1$  and  $k_2$  in mgN/gVSS.h, refer to the first and second rates).**

Reactor	COD (mg/l)	COD/N	S/X (mgO <sub>2</sub> /gO <sub>2</sub> )	$k_1$	$k_2$
1	40	2.20	0.02	$5.2 \pm 0.22$	$2.1 \pm 0.05$
2	100	6.50	0.05	$5.0 \pm 0.18$	-
4	200	13.2	0.09	$4.8 \pm 0.12$	-
3	400	29.9	0.20	$4.6 \pm 0.07$	-





**Figure II-15: Denitrification rates produced under the lower S/X ratios (0.02 and 0.05).**

#### ***II.3.4.2 The S/X ratio of the particulate fraction of raw wastewater***

Initial experiments with the particulate component of raw wastewater at an S/X ratio of 0.05 showed a single linear phase (Figure II-16). Thus, the aim of this experiment was to determine if an increase in the S/X ratio would result in a change in the NUR profile *i.e.* number of phases and rates. Thus, two different S/X ratios were tested with only exogenous particulate organic carbon as a substrate. The particulate component of raw wastewater was separated by settling for 2 h in an Imhoff cone.

Tests done at higher S/X ratios, 0.63, and 1.12, clearly showed 2 phases of NO<sub>x</sub> utilization. The initial rates of utilization were 3.6 and 3.4 mgN/gVSS.h for S/X ratios 0.63 and 1.12, respectively (Figure II-17). This initial rate was more than two times that obtained for tests done at a S/X ratio of 0.05. The k<sub>2</sub> values of the tests done at S/X ratios of 0.63 and 1.12 were found to be 1.2 and 1.5 mgN/gVSS.h, respectively (Figure II-17). These values were comparable to the single rate of 1.5 mgN/gVSS.h observed at a S/X ratio of 0.05 (Figure II-16).

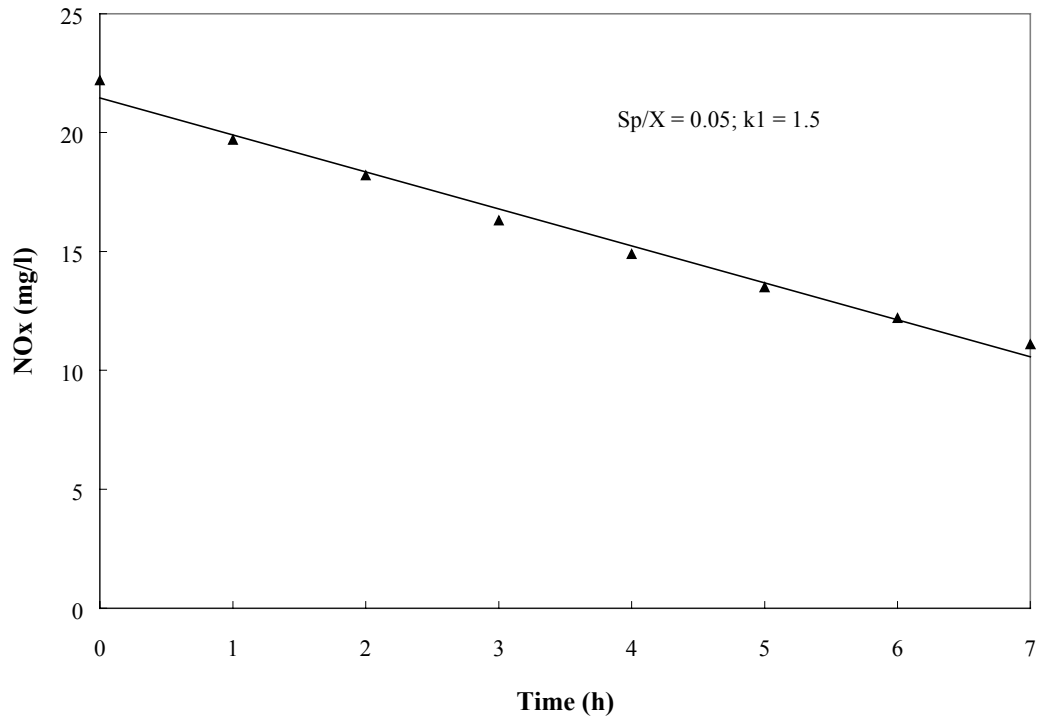


Figure II-16: Denitrification profile with particulate component of raw wastewater for a  $S/X$  ratio of 0.05 (Boran - 15/05/96).

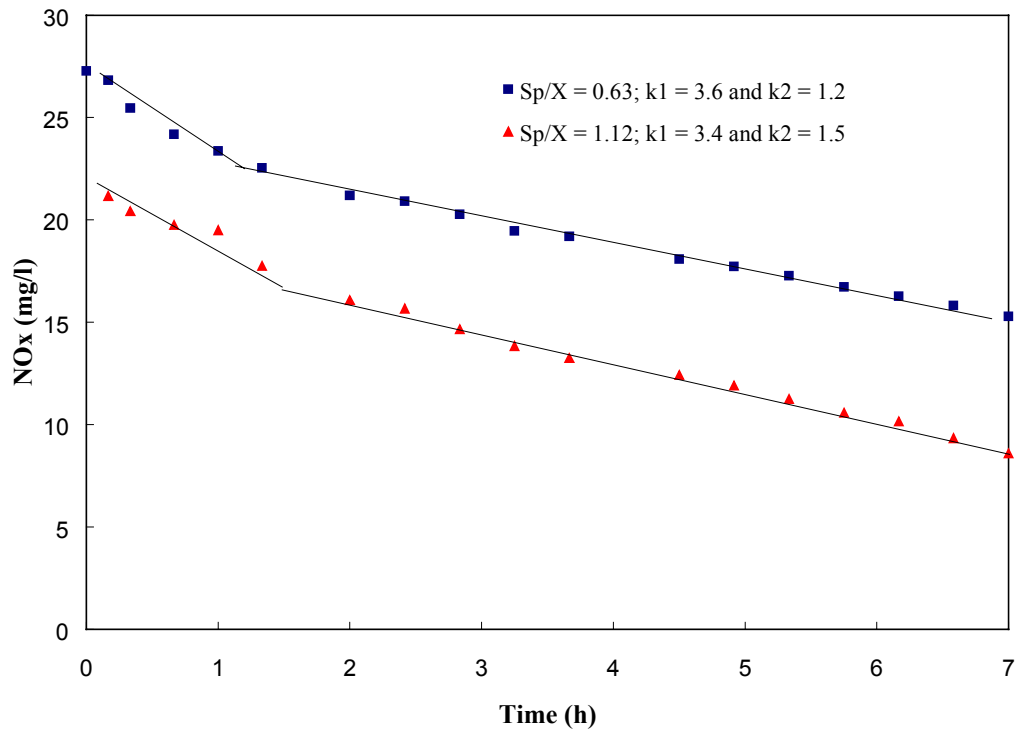


Figure II-17: Denitrification profiles with particulate component of raw wastewater at  $S/X$  ratios of 0.63 and 1.12. (Artemps-Seraucourt - 14/08/97)

### ***II.3.5 NUR test procedure***

The NUR batch test procedure used for these investigations are outlined below. The tests were carried out in 2 l reactors with a working volume of 1.4 or 1.6 l.

- Switch on the waterbath and ensure that the temperature is set at 20°C (or the temperature that is required).
- Add 1l activated sludge. Tests with sludges from 20 different plants have shown that the activated sludge COD concentration is generally greater than 2.0 gO<sub>2</sub>/l. If the sludge concentration is considered to be too low then the sludge can be concentrated by settling. Higher sludge concentrations are advantageous since they shorten the test time by increasing the NO<sub>x</sub> removal rate. However, sludge that is too concentrated *i.e.* COD values greater than 4 gO<sub>2</sub>/l of total suspended solids may increase the rate to an extent that jeopardizes the correct observation and calculation of the first rate which is generally fast and of too short duration.
- Calibrate the pH electrode and redox electrode (if used) and insert into reactor.
- Sparge nitrogen through the sludge to remove oxygen from solution (1 min).
- Add 0.3 to 0.4 l of the raw wastewater sample to the reactor. By using equation (4-3) it is possible to estimate the correct volume of raw wastewater required. This should give filtered COD concentration > 50 mgO<sub>2</sub>/l in the batch reactor. This concentration is sufficient to allow one to observe a first rate which lasts for about 1 hour and thus, provides time for sufficient samples to be taken to obtain sufficient data to determine an acceptable first rate. If the S-f<sub>0.45</sub> COD concentration of the wastewater is less than 250 mgO<sub>2</sub>/l then the volumetric addition has to be increased (*i.e.* > 400 ml). In this case the sludge has to be allowed to settle (or centrifuged) to remove the necessary volume in order to maintain the total volume of 1.4 l.
- Add potassium nitrate (20 to 25 mgN/l was used in this study) and close reactor. It is important to ensure that all the ports except the gas outlet (which passes through a water trap) is gas tight.
- Sparge nitrogen through liquid for 30 sec to remove oxygen.
- Remove first sample (25 ml at time = 0) with a syringe. Note the volume removed will depend on the type and number of analyses to be conducted. However, if the sample volume is too large (> 50 ml) it will increase the time required for filtration.
- Samples are pre-filtered through paper filters and then through 0.45 µm membrane filters. The liquid samples are then stored at 4°C until analysis. Samples which cannot be analyzed within the first 24 h were frozen.

- The pH is checked continually and regulated at 7.5 throughout the test.
- Once the first sample has been taken the gas channel is switched from nitrogen passing through the liquid to one passing nitrogen gas over the liquid to minimize foaming and pH increase. Note gas is passed over the liquid during each sampling step to prevent oxygen introduction.
- Steps 9 to 12 are repeated for the duration of the experiment. It is essential to sample at 10 min intervals for the first hour. Thereafter, the sample interval can be increased to every 20 to 25 min. The duration of the test should be a minimum of 6 h under the conditions outlined above in order to observe the three degradation phases. The test can be shortened by increasing the sludge concentration. In this case the correct substrate (soluble fraction) to biomass ratio ( $S-f/X$ ) needs to be determined by trial and error so that a suitable Nitrate-N as a function of time ( $\text{NO}_x\text{-N} = f(t)$ ) plot is obtained.
- At the end of the test a 100 ml sample is removed from the reactor for TSS and VSS analysis.

$$V_{ww} = \frac{C_R \times V_T}{C_M} \quad (\text{II-4})$$

$V_{ww}$  volume of wastewater that is required to avoid RBCOD limitation (l)

$C_R$  refers to the concentration of Ss required (*i.e.*  $> 50 \text{ mgO}_2/\text{l}$ )

$V_t$  total working volume of the reactor (l)

$C_M$  measured CODs concentration ( $\text{mgO}_2/\text{l}$ )

# ***APPENDIX III***

## ***RAW DATA FROM NUR TESTS WITH ACETATE***

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Appendix III contains data from tests where acetate was used as a synthetic substrate with different sludges. The tests are listed alphabetically and contains the raw data from the NUR tests, the experimental conditions within the batch reactor, and the kinetic data derived from the curves.

### ***Abbreviations***

<b>C/N</b>	the initial COD to nitrates as N ratio (within the reactor)
<b>S/X</b>	the initial substrate (acetate) to biomass ratio (within the reactor)
<b>k<sub>1</sub></b>	first rate observed
<b>k<sub>2</sub></b>	second rate observed
<b>k<sub>3</sub></b>	third rate observed
<b>N</b>	sum nitrates and nitrite concentration as defined in equation 4-3
<b>NO<sub>x</sub></b>	sum nitrates and nitrite concentration as defined in equation 4-4
<b>P</b>	ortho-phosphate as P
<b>Y1</b>	first Y intercept in NO <sub>x</sub> vs t curve
<b>Y2</b>	second Y intercept in NO <sub>x</sub> vs t curve
<b>Y3</b>	third Y intercept in NO <sub>x</sub> vs t curve
<b>Ace 1</b>	acetate recovery 1 based on $\Delta\text{NO}_x$ 1
<b>Ace 2</b>	acetate recovery 2 based on $\Delta\text{NO}_x$ 2
<b>Ace (%)</b>	$[\text{acetate recovered}] / [\text{acetate added}] \times 100$

**A**

Table III-A1: Batch data with samples from Asnieres-sur-oise WTP (11/09/97)

Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	37.5	0.8	38.3	38.0	2.0
10	0.2	37.0	1.0	38.0	37.6	-
20	0.3	36.0	1.2	37.2	36.7	1.0
30	0.5	35.5	1.4	36.9	36.3	-
40	0.7	34.5	1.6	36.1	35.5	-
50	0.8	33.5	1.6	35.1	34.5	2.0
80	1.3	32.0	1.9	33.9	33.1	-
100	1.7	31.5	1.9	33.4	32.6	5.0
120	2.0	30.5	2.0	32.5	31.7	-
145	2.4	30.5	2.0	32.5	31.7	-
170	2.8	30.5	2.0	32.5	31.7	-
195	3.3	29.5	2.0	31.5	30.7	-
220	3.7	29.0	2.0	31.0	30.2	-
245	4.1	28.0	1.9	29.9	29.1	-
270	4.5	28.0	1.9	29.9	29.1	-
295	4.9	28.5	1.8	30.3	29.6	-
320	5.3	27.5	1.7	29.2	28.5	-
345	5.8	27.0	1.7	28.7	28.0	-
360	6.0	27.0	1.7	28.7	28.0	2.0

Experimental conditions			
St	50	(mgO <sub>2</sub> /l)	
Sf	50	(mgO <sub>2</sub> /l)	
Xt	1405	(mgO <sub>2</sub> /l)	
Xf	38	(mgO <sub>2</sub> /l)	
V <sub>ww</sub>	-	-	
V <sub>x</sub>	1	(l)	
V <sub>d</sub>	0.4	(l)	
S/X	0.04	(mgO <sub>2</sub> /mgO <sub>2</sub> )	
C/N	1.32		

Kinetic data			
k <sub>1</sub>	-4.57	Y1	37.89
k <sub>2</sub>	-1.13	Y2	33.07
k <sub>3</sub>		NO <sub>x</sub> 1	4.83
		Ace 1	37
		Ace (%)	74

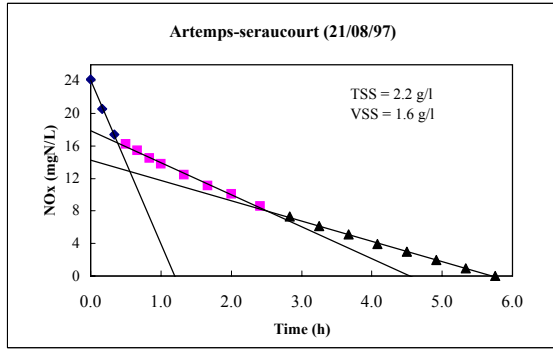
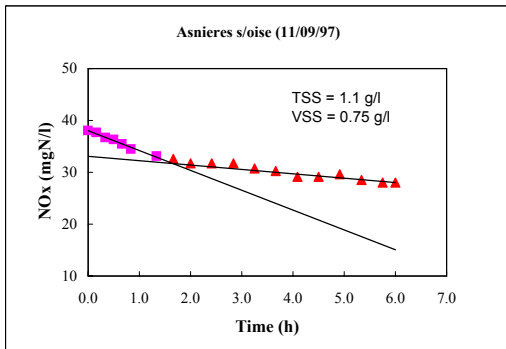


Table III-A2: Batch data with samples from Artemps-Seraucourt 1 (21/08/97)

Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	23.5	1.1	24.6	24.2	14.5
10	0.2	18.5	3.5	22.0	20.6	-
20	0.3	14.2	5.4	19.6	17.4	-
30	0.5	12.9	5.6	18.5	16.3	15.0
40	0.7	12.0	5.7	17.7	15.4	-
50	0.8	11.1	5.6	16.7	14.5	-
60	1.0	10.4	5.7	16.1	13.8	14.5
80	1.3	9.1	5.6	14.7	12.5	-
100	1.7	7.9	5.4	13.3	11.1	-
120	2.0	7.0	5.1	12.1	10.1	-
145	2.4	5.8	4.7	10.5	8.6	-
170	2.8	4.8	4.2	9.0	7.3	-
195	3.3	3.9	3.7	7.6	6.1	-
220	3.7	3.2	3.2	6.4	5.1	-
245	4.1	2.4	2.6	5.0	4.0	-
270	4.5	1.7	2.1	3.8	3.0	-
295	4.9	1.0	1.6	2.6	2.0	-
320	5.3	0.3	1.1	1.4	1.0	-
345	5.8	0.0	0.0	0.0	0.0	-
370	6.2	0.0	0.0	0.0	0.0	-
395	6.6	0.0	0.0	0.0	0.0	14.3
420	7.0	0	0.0	0.0	0.0	-

Experimental conditions			
St	50	(mgO <sub>2</sub> /l)	
Sf	50	(mgO <sub>2</sub> /l)	
Xt	1881	(mgO <sub>2</sub> /l)	
Xf	41	(mgO <sub>2</sub> /l)	
V <sub>ww</sub>	-	-	
V <sub>x</sub>	1	(l)	
V <sub>d</sub>	0.4	(l)	
S/X	0.03	(mgO <sub>2</sub> /mgO <sub>2</sub> )	
C/N	2.03		

Kinetic data			
k <sub>1</sub>	-12.5	Y1	24.09
k <sub>2</sub>	-2.3	Y2	17.47
k <sub>3</sub>	-1.5	Y3	14.28
		NO <sub>x</sub> 1	6.62
		NO <sub>x</sub> 2	3.19
		Ace 1 and 2	50 +24
		Ace (%) 1&2	100+24

**A**

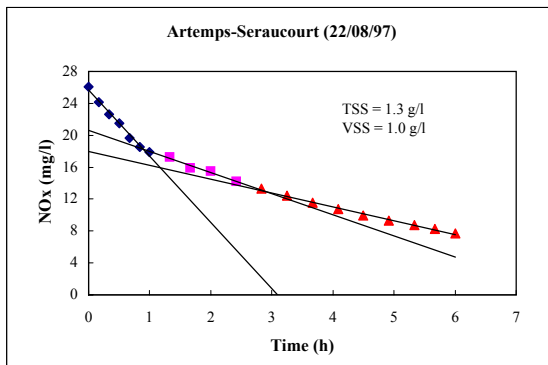
Table III-A3: Batch data with samples from Artemps-Seraucourt 2 WTP (22/08/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	25.6	0.8	26.4	26.1	10.3
10	0.2	23.0	1.9	24.9	24.1	—
20	0.3	20.9	2.9	23.8	22.6	—
30	0.5	19.2	3.8	23.0	21.5	10.9
40	0.7	16.7	4.9	21.6	19.6	—
50	0.8	15.4	5.2	20.6	18.5	—
60	1.0	14.8	5.2	20.0	17.9	11.1
80	1.3	14.1	5.2	19.3	17.2	—
100	1.7	12.8	5.1	17.9	15.9	—
120	2.0	12.5	5.0	17.5	15.5	—
145	2.4	11.3	4.8	16.1	14.2	—
170	2.8	10.5	4.7	15.2	13.3	—
195	3.3	9.8	4.4	14.2	12.4	—
220	3.7	9.0	4.2	13.2	11.5	—
245	4.1	8.5	3.7	12.2	10.7	—
270	4.5	7.9	3.4	11.3	9.9	—
295	4.9	7.5	3.0	10.5	9.3	—
320	5.3	7.1	2.7	9.8	8.7	—
340	5.7	6.8	2.5	9.3	8.3	—
360	6.0	6.4	2.2	8.6	7.7	9.4

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	1905	(mgO <sub>2</sub> /l)
Xf	36	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	—	—
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.03	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	1.92	

Kinetic data			
k <sub>1</sub>	-7.8	Y1	26.01
k <sub>2</sub>	-2.8	Y2	20.6
k <sub>3</sub>	-2.1	Y3	18.43
		NO <sub>x</sub> 1	5.41
		NO <sub>x</sub> 2	2.17
		Ace 1 and 2	42+17
		Ace (%) 1&2	83+33



**B**

Table III-B1 : Batch data with samples from Berwick (2/05/97)

Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	25.0	0.0	25.0	25.0	-
10	0.2	24.3	0.0	24.3	24.3	-
20	0.3	23.0	0.0	23.0	23.0	-
35	0.6	21.3	0.0	21.3	21.3	-
45	0.8	20.0	0.0	20.0	20.0	-
60	1.0	18.4	0.0	18.4	18.4	-
85	1.4	16.8	0.0	16.8	16.8	-
135	2.3	13.4	0.0	13.4	13.4	-
160	2.7	11.9	0.0	11.9	11.9	-
185	3.1	10.3	0.0	10.3	10.3	-
210	3.5	9.4	0.0	9.4	9.4	-
235	3.9	8.2	0.0	8.2	8.2	-
255	4.3	7.4	0.0	7.4	7.4	-
270	4.5	6.5	0.0	6.5	6.5	-

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	2671	(mgO <sub>2</sub> /l)
Xf	82	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.46	(l)
S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	2.00	

Kinetic data			
k <sub>1</sub>	-4.53	Y1	25.21
k <sub>2</sub>	-1.8	Y2	19.25
k <sub>3</sub>	-	NO <sub>x</sub> 1	5.97
		Ace 1	34
		Ace (%) 1	68

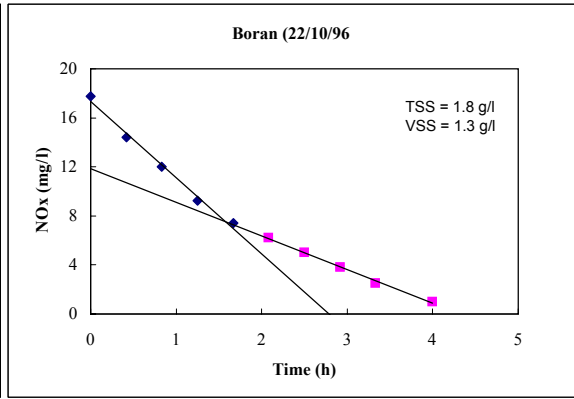
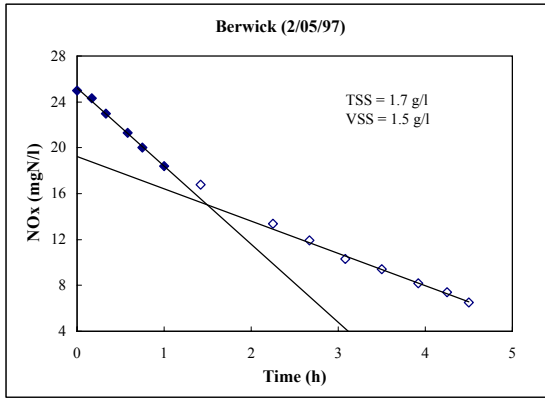


Table III-B2 : Batch data with samples from Boran 1 WTP (22/10/96)

Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0.0	0.0	17.6	0.3	17.9	18.2	-
25.0	0.4	14.1	0.5	14.6	15.1	-
50.0	0.8	11.7	0.5	12.2	12.7	-
75.0	1.3	9.0	0.4	9.4	9.8	-
100.0	1.7	7.4	0.0	7.4	7.4	-
125.0	2.1	6.2	0.0	6.2	6.2	-
150.0	2.5	5.0	0.0	5.0	5.0	-
175.0	2.9	3.8	0.0	3.8	3.8	-
200.0	3.3	2.5	0.0	2.5	2.5	-
240.0	4.0	1.0	0.0	1.0	1.0	-

Experimental conditions		
St	40	(mgO <sub>2</sub> /l)
Sf	40	(mgO <sub>2</sub> /l)
Xt	3289	(mgO <sub>2</sub> /l)
Xf	19	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0.5	(l)
S/X	0.01	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	2.20	

Kinetic data			
k <sub>1</sub>	-4.8	Y1	17.94
k <sub>2</sub>	-2.1	Y2	11.85
k <sub>3</sub>		NO <sub>x</sub> 1	6.05
		Ace 1	46
		Ace (%) 1	115



**B**

Table III-B3 : Raw data for samples taken from Boran 2 WTP (25/02/97)						
Raw data						Experimental conditions
Time(min)	Time (h)	NO <sub>2</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	23.2	0.6	23.8	23.6	-
10	0.2	22.1	0.8	22.9	22.6	-
20	0.3	20.9	1.0	21.9	21.5	-
30	0.5	19.9	1.1	21.0	20.6	-
40	0.7	18.7	1.3	20.0	19.5	-
50	0.8	17.6	1.4	19.0	18.4	-
60	1.0	16.1	1.5	17.6	17.0	-
80	1.3	14.6	1.7	16.3	15.6	-
100	1.7	12.3	1.9	14.2	13.4	-
120	2.0	10.4	2.1	12.5	11.7	-
140	2.3	7.8	2.4	10.2	9.2	-
160	2.7	6.7	2.3	9.0	8.1	-
180	3.0	6.1	2.2	8.3	7.4	-
200	3.3	5.3	2.0	7.3	6.5	-
220	3.7	4.6	1.8	6.4	5.7	-
240	4.0	4.0	1.7	5.7	5.0	-

Kinetic data			
k <sub>1</sub>	-4.6	Y1	23.48
k <sub>2</sub>	-1.8	Y2	14.4
k <sub>3</sub>	-	Y3	-
		NO <sub>x</sub> 1	8.82
		Ace 1	50
		Ace (%) 1	72

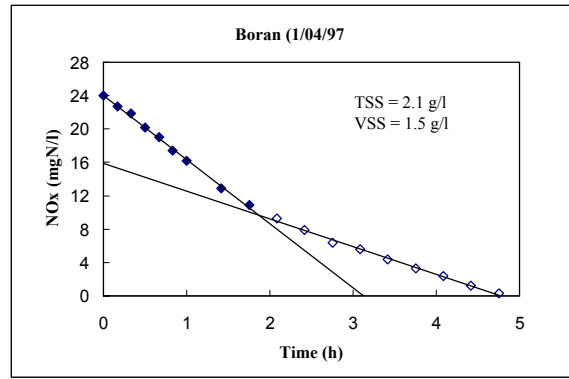
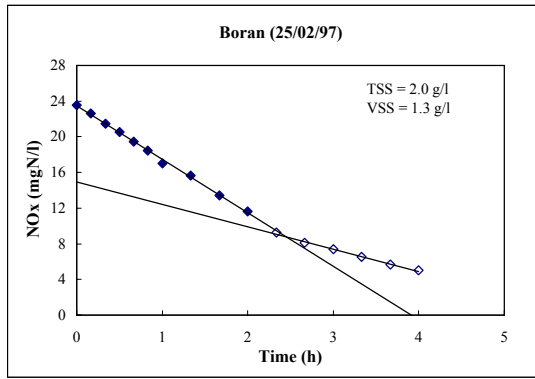


Table III-B4 : Raw data for samples taken from Boran 3 WTP (1/04/97)						
Raw data						Experimental conditions
Time(min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	23.7	0.5	24.2	24.0	-
10	0.2	22.2	0.8	23.0	22.7	-
20	0.3	21.4	0.8	22.2	21.9	-
30	0.5	19.6	0.9	20.5	20.1	-
40	0.7	18.4	1.0	19.4	19.0	-
50	0.8	16.8	1.0	17.8	17.4	-
60	1.0	15.6	1.0	16.6	16.2	-
85	1.4	12.3	1.0	13.3	12.9	-
105	1.8	10.3	1.0	11.3	10.9	-
125	2.1	8.8	0.8	9.6	9.3	-
145	2.4	7.6	0.5	8.1	7.9	-
165	2.8	6.4	0.0	6.4	6.4	-
185	3.1	5.4	0.3	5.7	5.6	-
205	3.4	4.2	0.3	4.5	4.4	-
225	3.8	3.1	0.3	3.4	3.3	-
245	4.1	2.2	0.3	2.5	2.4	-
265	4.4	1.2	0.0	1.2	1.2	-
285	4.8	0.3	0.0	0.3	0.3	-

Kinetic data			
k <sub>1</sub>	-5.1	Y1	24.04
k <sub>2</sub>	-2.3	Y2	15.86
k <sub>3</sub>	-	Y3	-
		NO <sub>x</sub> 1	8.18
		Ace 1	63
		Ace (%) 1	105

**B**

Table III-B5 : Batch data with samples from Boran 4 WTP (2/04/97)						
Raw data						
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	44.0	0.7	44.7	45.4	-
10	0.2	40.5	1.0	41.5	42.5	-
20	0.3	40.5	1.2	41.7	42.9	-
30	0.5	38.5	1.3	39.8	41.1	-
40	0.7	36.0	1.4	37.4	38.8	-
50	0.8	36.0	1.4	37.4	38.8	-
60	1.0	34.5	1.6	36.1	37.7	-
80	1.3	27.5	1.6	29.1	30.7	-
100	1.7	26.5	1.4	27.9	29.3	-
120	2.0	26.5	1.2	27.7	28.9	-
140	2.3	24.5	0.9	25.4	26.3	-
160	2.7	23.5	0.7	24.2	24.9	-
180	3.0	22.0	0.6	22.6	23.2	-
200	3.3	19.5	0.7	20.2	20.9	-
220	3.7	19.0	0.6	19.6	20.2	-
240	4.0	18.0	0.5	18.5	19.0	-
260	4.3	16.5	0.5	17.0	17.5	-
280	4.7	14.0	0.4	14.4	14.8	-
300	5.0	13.0	0.4	13.4	13.8	-
320	5.3	12.0	0.4	12.4	12.8	-
340	5.7	12.5	0.4	12.9	13.3	-
360	6.0	10.5	0.4	10.9	11.3	-

Experimental conditions		
St	70	(mgO <sub>2</sub> /l)
Sf	70	(mgO <sub>2</sub> /l)
Xt	2544	(mgO <sub>2</sub> /l)
Xf	37	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0.5	(l)
S/X	0.03	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	1.54	

Kinetic data			
k <sub>1</sub>	-5.7	Y1	43.65
k <sub>2</sub>	-2.5	Y2	33.97
k <sub>3</sub>	-	NO <sub>x</sub> 1	9.67
		Ace 1	74
		Ace (%) 1	106

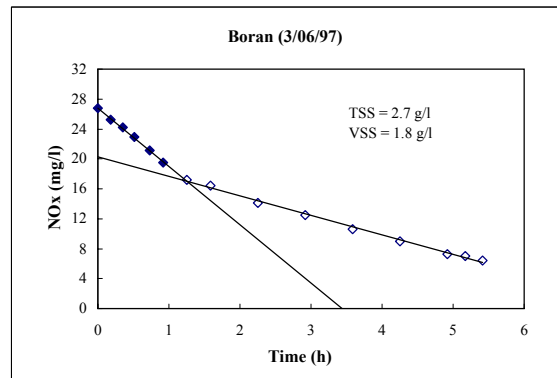
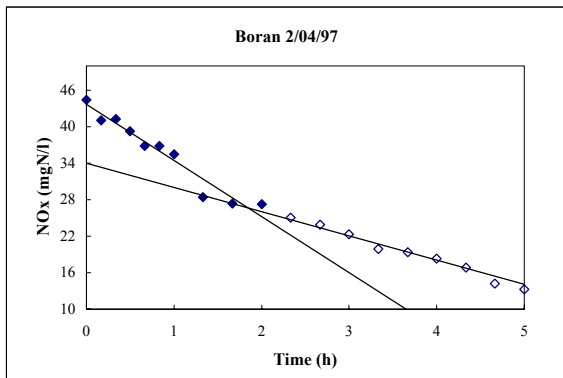


Table III-B6 : Raw data for samples taken from Boran 5 WTP (03/06/97)						
Raw data						
Time(min)	Time (h)	NO <sub>2</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	26.5	0.4	26.9	26.7	10.0
11	0.2	25.0	0.4	25.4	25.2	-
21	0.4	23.9	0.5	24.4	24.2	-
31	0.5	22.7	0.4	23.1	22.9	-
44	0.7	20.9	0.4	21.3	21.1	-
55	0.9	19.5	0.0	19.5	19.5	10.0
75	1.3	17.2	0.0	17.2	17.2	-
95	1.6	16.4	0.0	16.4	16.4	10.0
135	2.3	14.1	0.0	14.1	14.1	-
175	2.9	12.3	0.3	12.6	12.5	-
215	3.6	10.6	0.0	10.6	10.6	-
255	4.3	9.0	0.0	9.0	9.0	-
295	4.9	7.3	0.0	7.3	7.3	-
310	5.2	7.0	0.0	7.0	7.0	-
325	5.4	6.4	0.0	6.4	6.4	11.0

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	3191	(mgO <sub>2</sub> /l)
Xf	13	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	1.86	

Kinetic data			
k <sub>1</sub>	-4.3	Y1	26.8
k <sub>2</sub>	-1.4	Y2	20.07
k <sub>3</sub>	-	Y3	-
		NO <sub>x</sub> 1	6.73
		Ace 1	52
		Ace (%) 1	104

**B**

Table III-B7 : Batch data with samples from Boran 6 WTP (09/06/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	28.5	0.0	28.5	28.5	10.5
10	0.2	26.5	0.0	26.5	26.5	-
20	0.3	25.4	0.0	25.4	25.4	-
30	0.5	22.6	0.0	22.6	22.6	-
40	0.7	22.2	0.0	22.2	22.2	-
50	0.8	20.9	0.0	20.9	20.9	10.4
65	1.1	20.4	0.0	20.4	20.4	-
90	1.5	18.6	0.0	18.6	18.6	-
115	1.9	18.6	0.0	18.6	18.6	9.0
140	2.3	16.3	0.0	16.3	16.3	-
190	3.2	14.1	0.0	14.1	14.1	-
215	3.6	13.3	0.0	13.3	13.3	-
240	4.0	12.1	0.0	12.1	12.1	-
265	4.4	11.2	0.0	11.2	11.2	-
285	4.8	10.4	0.0	10.4	10.4	-
300	5.0	10.0	0.0	10.0	10.0	11.0

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	4206	(mgO <sub>2</sub> /l)
Xf	34	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.01	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	1.75	

Kinetic data			
k <sub>1</sub>	-4.2	Y1	28.19
k <sub>2</sub>	-1.1	Y2	21.76
k <sub>3</sub>	-	Y3	
		NO <sub>x</sub> 1	6.43
		Ace 1	50
		Ace (%) 1	100

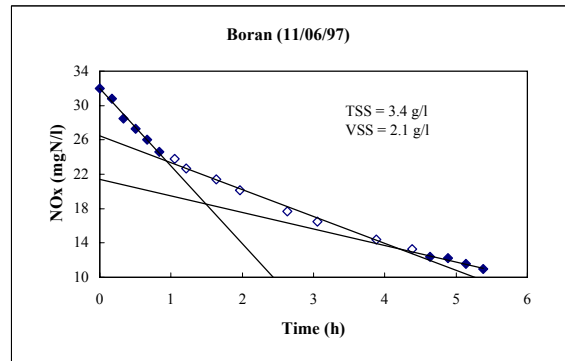
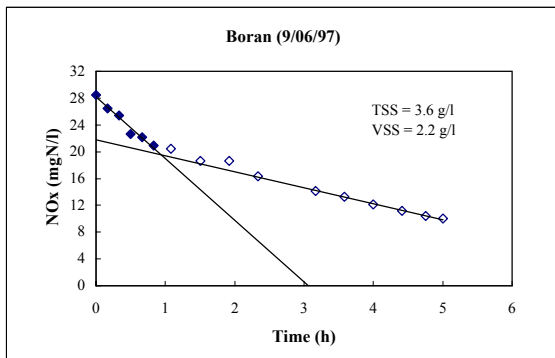


Table III-B8 : Raw data for samples taken from Boran 7 WTP (11/06/97)						
Raw data						
Time(min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	32.0	0.0	32.0	32.0	8.5
10	0.2	30.8	0.0	30.8	30.8	-
20	0.3	28.5	0.0	28.5	28.5	-
30	0.5	27.3	0.0	27.3	27.3	7.0
40	0.7	26.0	0.0	26.0	26.0	-
50	0.8	24.6	0.0	24.6	24.6	-
63	1.1	23.8	0.0	23.8	23.8	7.5
73	1.2	22.7	0.0	22.7	22.7	-
98	1.6	21.4	0.0	21.4	21.4	8.5
118	2.0	20.1	0.0	20.1	20.1	-
158	2.6	17.7	0.0	17.7	17.7	6.5
183	3.1	16.5	0.0	16.5	16.5	-
233	3.9	14.4	0.0	14.4	14.4	6.0
263	4.4	13.3	0.0	13.3	13.3	-
278	4.6	12.4	0.0	12.4	12.4	6.5
293	4.9	12.2	0.0	12.2	12.2	-
308	5.1	11.6	0.0	11.6	11.6	-
323	5.4	11.0	0.0	11.0	11.0	8.0

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	4016	(mgO <sub>2</sub> /l)
Xf	49	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.01	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	1.56	

Kinetic data			
k <sub>1</sub>	-4.3	Y1	31.96
k <sub>2</sub>	-1.4	Y2	26.09
k <sub>3</sub>	-0.9	Y3	21.42
		NO <sub>x</sub> 1	5.86
		NO <sub>x</sub> 2	4.68
		Ace 1 & 2	45+36
		Ace (%) 1&2	90+72

**B**

Table III-B9 : Raw data for samples taken from Boran 8 WTP (17/07/97)						
Raw data						Experimental conditions
Time(min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	14.6	0.0	14.6	14.6	8.7
10	0.2	14.7	0.0	14.7	14.7	-
20	0.3	12.6	0.0	12.6	12.6	-
30	0.5	11.3	0.0	11.3	11.3	10.0
40	0.7	10.0	0.0	10.0	10.0	-
50	0.8	8.8	0.0	8.8	8.8	-
60	1.0	8.2	0.0	8.2	8.2	11.5
80	1.3	7.4	0.0	7.4	7.4	-
100	1.7	6.5	0.0	6.5	6.5	-
120	2.0	5.6	0.0	5.6	5.6	-
145	2.4	4.7	0.0	4.7	4.7	-
170	2.8	3.8	0.0	3.8	3.8	-
195	3.3	2.8	0.0	2.8	2.8	-
220	3.7	2.0	0.0	2.0	2.0	-
245	4.1	1.1	0.0	1.1	1.1	-
270	4.5	0.4	0.0	0.4	0.4	-
290	4.8	0.0	0.0	0.0	0.0	-
310	5.2	0.0	0.0	0.0	0.0	-
330	5.5	0.0	0.0	0.0	0.0	-
345	5.8	0.0	0.0	0.0	0.0	-
360	6.0	0.0	0.0	0.0	0.0	9.7

Experimental conditions			
St	50	(mgO <sub>2</sub> /l)	
Sf	50	(mgO <sub>2</sub> /l)	
Xt	3817	(mgO <sub>2</sub> /l)	
Xf	28	(mgO <sub>2</sub> /l)	
V <sub>ww</sub>	-	(l)	
V <sub>x</sub>	1	(l)	
V <sub>d</sub>	0.4	(l)	
S/X	0.01	(mgO <sub>2</sub> /mgO <sub>2</sub> )	
C/N	3.42		

Kinetic data			
k <sub>1</sub>	-3	Y1	16
k <sub>2</sub>	-0.9	Y2	10.85
k <sub>3</sub>	-0.6	Y3	9.11
		NOx1	5.15
		NOx2	1.74
		Ace 1&2	40+13
		Ace (%) 1&2	79+27

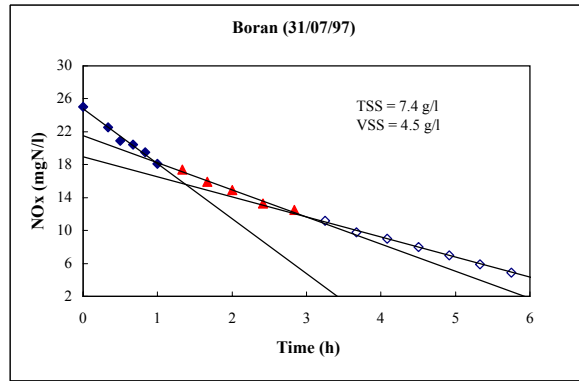
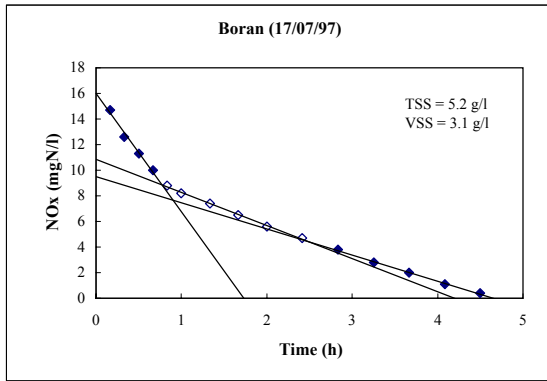


Table III-B10 : Batch data with samples from Boran 9 WTP (31/07/97) -						
Raw data						Experimental conditions
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	25.0	0.0	25.0	25.0	19.5
10	0.2	22.5	0.0	22.5	22.5	23.0
20	0.3	22.5	0.0	22.5	22.5	28.0
30	0.5	20.9	0.0	20.9	20.9	29.0
40	0.7	20.4	0.0	20.4	20.4	28.0
50	0.8	19.5	0.0	19.5	19.5	27.0
60	1.0	18.1	0.0	18.1	18.1	27.0
80	1.3	17.4	0.0	17.4	17.4	27.0
100	1.7	15.9	0.0	15.9	15.9	25.5
120	2.0	14.9	0.0	14.9	14.9	25.0
145	2.4	13.3	0.0	13.3	13.3	24.0
170	2.8	12.5	0.0	12.5	12.5	24.0
195	3.3	11.2	0.0	11.2	11.2	23.5
220	3.7	9.8	0.0	9.8	9.8	23.0
245	4.1	9.0	0.0	9.0	9.0	22.5
270	4.5	8.0	0.0	8.0	8.0	21.5
295	4.9	7.0	0.0	7.0	7.0	21.0
320	5.3	5.9	0.0	5.9	5.9	20.5
345	5.8	4.9	0.0	4.9	4.9	20.0
370	6.2	4.0	0.0	4.0	4.0	20.0

Experimental conditions			
St	50	(mgO <sub>2</sub> /l)	
Sf	50	(mgO <sub>2</sub> /l)	
Xt	7476	(mgO <sub>2</sub> /l)	
Xf	34	(mgO <sub>2</sub> /l)	
V <sub>ww</sub>	-	(l)	
V <sub>x</sub>	1.0	(l)	
V <sub>d</sub>	0.4	(l)	
S/X	0.01	(mgO <sub>2</sub> /mgO <sub>2</sub> )	
C/N	2.00		

Kinetic data			
k <sub>1</sub>	-2.4	Y1	25.7
k <sub>2</sub>	-0.8	Y2	21.54
k <sub>3</sub>	-0.6	Y3	18.94
		NOx1	3.46
		NOx2	2.61
		Ace 1&2	27+20
		Ace (%) 1&2	53+40

**B**

Table III-B11 : Raw data for samples taken from Boran 10 WTP (22/08/97)						
Raw data						Experimental conditions
Time(min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	27.3	0.0	27.3	27.3	7.2
10	0.2	26.3	0.0	26.3	26.3	-
20	0.3	25.9	0.0	25.9	25.9	-
30	0.5	24.1	0.0	24.1	24.1	8.8
40	0.7	24.5	0.0	24.5	24.5	-
50	0.8	24	0.0	24.0	24.0	-
60	1.0	23.5	0.0	23.5	23.5	9.8
80	1.3	21.9	0.0	21.9	21.9	-
100	1.7	20.6	0.0	20.6	20.6	-
120	2.0	19.8	0.0	19.8	19.8	10.0
145	2.4	19.2	0.0	19.2	19.2	-
170	2.8	18.4	0.0	18.4	18.4	-
195	3.3	17.5	0.0	17.5	17.5	-
220	3.7	16.9	0.0	16.9	16.9	-
245	4.1	16.8	0.0	16.8	16.8	-
270	4.5	15.8	0.0	15.8	15.8	-
295	4.9	14.9	0.0	14.9	14.9	-
320	5.3	14.4	0.0	14.4	14.4	-
340	5.7	14.3	0.0	14.3	14.3	-
360	6.0	13.7	0.0	13.7	13.7	7.6

Experimental conditions			
St	50	(mgO <sub>2</sub> /l)	
Sf	50	(mgO <sub>2</sub> /l)	
Xt	3079	(mgO <sub>2</sub> /l)	
Xf	23	(mgO <sub>2</sub> /l)	
V <sub>ww</sub>	-	(l)	
V <sub>x</sub>	1	(l)	
V <sub>d</sub>	0.4	(l)	
S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )	
C/N	1.83		

Kinetic data			
k <sub>1</sub>	-3.7	Y1	26.95
k <sub>2</sub>	-1.6	Y2	23.32
k <sub>3</sub>		Y3	-
		NO <sub>x</sub> 1	3.98
		Ace 1	31
		Ace (%)	61

\* data was used in origin of sludge experiments conducted on 22/08/97

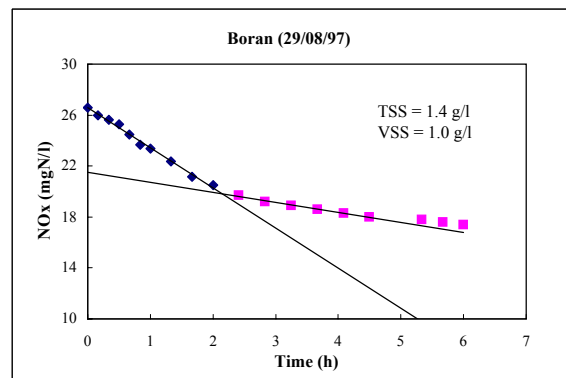
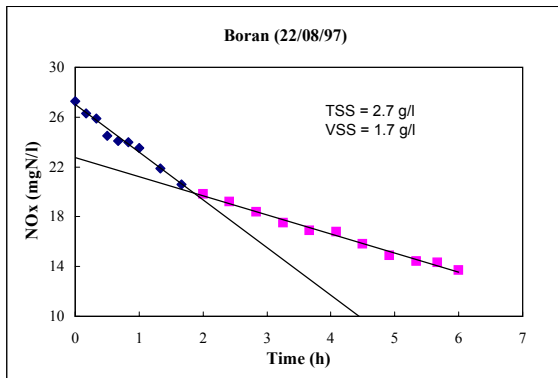


Table III-B12 : Batch data with samples from Boran 11 WTP (29/08/97)						
Raw data						Experimental conditions
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	26.6	0	26.6	26.6	4.5
10	0.2	25.8	0.3	26.1	26.4	-
20	0.3	25.4	0.4	25.8	26.2	6.0
30	0.5	25.1	0.3	25.4	25.7	-
40	0.7	24.3	0.3	24.6	24.9	7.0
50	0.8	23.5	0.3	23.8	24.1	-
60	1.0	23.2	0.3	23.5	23.8	8.0
80	1.3	22.2	0.3	22.5	22.8	-
100	1.7	21.0	0.3	21.3	21.6	-
120	2.0	20.3	0.3	20.6	20.9	-
145	2.4	19.7	0	19.7	19.7	-
170	2.8	19.2	0	19.2	19.2	-
195	3.3	18.9	0	18.9	18.9	-
220	3.7	18.6	0	18.6	18.6	-
245	4.1	18.3	0	18.3	18.3	-
270	4.5	18.0	0	18.0	18.0	-
295	4.9	18.0	0	18.0	18.0	-
320	5.3	17.8	0	17.8	17.8	-
340	5.7	17.6	0	17.6	17.6	-
360	6.0	17.4	0	17.4	17.4	4.0

Experimental conditions			
St	50	(mgO <sub>2</sub> /l)	
Sf	50	(mgO <sub>2</sub> /l)	
Xt	1833	(mgO <sub>2</sub> /l)	
Xf	16	(mgO <sub>2</sub> /l)	
V <sub>ww</sub>	-	(l)	
V <sub>x</sub>	1.0	(l)	
V <sub>d</sub>	0.4	(l)	
S/X	0.03	(mgO <sub>2</sub> /mgO <sub>2</sub> )	
C/N	1.88		

Kinetic data			
k <sub>1</sub>	-3.2	Y1	26.59
k <sub>2</sub>	-0.8	Y2	21.51
k <sub>3</sub>		NO <sub>x</sub> 1	5.08
		Ace 1	39
		Ace (%) 1	78

**B**

Table III-B13 : Raw data for samples taken from Brno WTP (1/06/97)							
Raw data							Experimental conditions
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P	
0	0.0	27.3	1.2	28.5	28.0	-	St 50 (mgO <sub>2</sub> /l)
16	0.3	23.2	2.5	25.7	24.7	-	Sf 50 (mgO <sub>2</sub> /l)
27	0.5	19.8	3.2	23.0	21.7	-	Xt 1416 (mgO <sub>2</sub> /l)
37	0.6	18.3	3.4	21.7	20.3	-	Xf 47 (mgO <sub>2</sub> /l)
47	0.8	17.7	3.3	21.0	19.7	-	Vww - (l)
57	1.0	16.7	3.2	19.9	18.6	-	Vx 1 (l)
72	1.2	16.0	2.9	18.9	17.7	-	Vd 0.46 (l)
97	1.6	14.7	2.3	17.0	16.1	-	S/X 0.04 (mgO <sub>2</sub> /mgO <sub>2</sub> )
122	2.0	13.3	1.9	15.2	14.4	-	C/N 1.75
147	2.5	12.3	1.5	13.8	13.2	-	
172	2.9	11.1	1.2	12.3	11.8	-	
197	3.3	10.4	0.9	11.3	10.9	-	
222	3.7	9.5	0.7	10.2	9.9	-	
247	4.1	8.8	0.6	9.4	9.2	-	
272	4.5	7.9	0.5	8.4	8.2	-	
292	4.9	7.3	0.4	7.7	7.5	-	
312	5.2	6.7	0.4	7.1	6.9	-	
332	5.5	6.2	0.3	6.5	6.4	-	
352	5.9	5.4	0.3	5.7	5.6	-	

Kinetic data			
k <sub>1</sub>	-16.4	Y1	27.97
k <sub>2</sub>	-4.5	Y2	21.84
k <sub>3</sub>	-2.6	Y3	17.5
		NOx1	6.14
		NOx2	4.34
		Ace 1&2	47 + 33
		Ace (%) 1&2	94 + 67

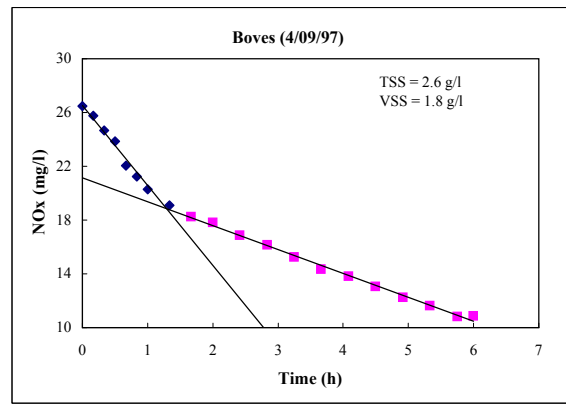
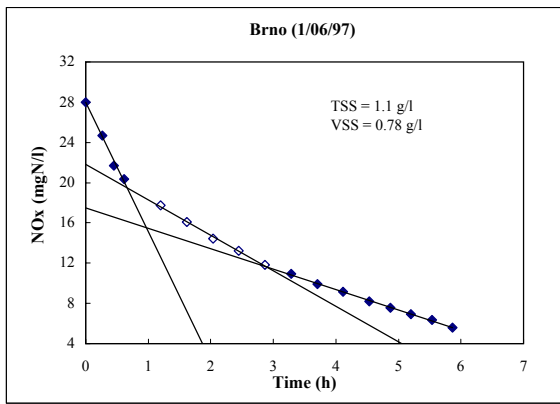


Table III-B14 : Batch data with samples from Boves (04/09/97)							
Raw data							Experimental conditions
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P	
0	0.0	26.5	0.0	26.5	26.5	11.5	St 50 (mgO <sub>2</sub> /l)
10	0.2	25.4	0.6	26.0	25.8	-	Sf 50 (mgO <sub>2</sub> /l)
20	0.3	24.0	1.1	25.1	24.7	12.5	Xt 2714 (mgO <sub>2</sub> /l)
30	0.5	22.9	1.6	24.5	23.9	-	Xf 33 (mgO <sub>2</sub> /l)
40	0.7	20.9	1.9	22.8	22.0	14.5	Vww - (l)
50	0.8	19.7	2.6	22.3	21.3	-	Vx 1.0 (l)
60	1.0	18.5	3.0	21.5	20.3	14.0	Vd 0.4 (l)
80	1.3	17.3	3.0	20.3	19.1	-	S/X 0.02 (mgO <sub>2</sub> /mgO <sub>2</sub> )
100	1.7	16.5	2.9	19.4	18.2	-	C/N 1.89
120	2.0	16.2	2.7	18.9	17.8	-	
145	2.4	15.4	2.4	17.8	16.8	-	
170	2.8	14.8	2.2	17.0	16.1	-	
195	3.3	14.1	1.9	16.0	15.2	-	
220	3.7	13.3	1.7	15.0	14.3	-	
245	4.1	12.9	1.5	14.4	13.8	-	
270	4.5	12.2	1.4	13.6	13.0	-	
295	4.9	11.6	1.1	12.7	12.3	-	
320	5.3	11.1	0.9	12.0	11.6	-	
345	5.8	10.4	0.7	11.1	10.8	-	
360	6.0	10.5	0.6	11.1	10.9	11.0	

Kinetic data			
k <sub>1</sub>	-3.4	Y1	26.53
k <sub>2</sub>	-1.0	Y2	21.09
k <sub>3</sub>	-	NOx1	5.43
		Ace 1	42
		Ace (%) 1	84

C

Table III-C1 : Batch data with samples from Crespières 1(24/02/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	18.4	0.8	30.5	30.2	-
10	0.2	16.2	1.2	28.7	28.2	-
20	0.3	14.2	1.5	27.0	26.4	-
30	0.5	12.1	1.9	25.3	24.5	-
40	0.7	10.4	2.2	23.9	23.0	-
50	0.8	8.6	2.5	22.4	21.4	-
60	1.0	6.6	2.9	20.8	19.6	-
80	1.3	3.9	3.4	18.6	17.2	-
100	1.7	0.5	3.7	15.5	14.0	-
120	2.0	0.0	2.4	13.7	12.7	-
140	2.3	0.0	0.7	12.0	11.7	-
164	2.7	0.9	0.3	12.5	12.4	-
180	3.0	11.3	0.4	23.0	22.8	-
200	3.3	9.7	0.6	21.6	21.4	-
220	3.7	8.5	0.8	20.6	20.3	-
255	4.3	6.6	0.9	18.8	18.4	-
290	4.8	5.0	1.0	17.3	16.9	-

Experimental conditions		
St	70	(mgO <sub>2</sub> /l)
Sf	70	(mgO <sub>2</sub> /l)
Xt	3017	(mgO <sub>2</sub> /l)
Xf	47	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0.5	(l)
S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	2.32	

Kinetic data			
k <sub>1</sub>	-5.2	Y1	29.96
k <sub>2</sub>	-1.7	Y2	19.7
k <sub>3</sub>	-	NOx1	10.25
		Ace 1	59
		Ace (%) 1	84

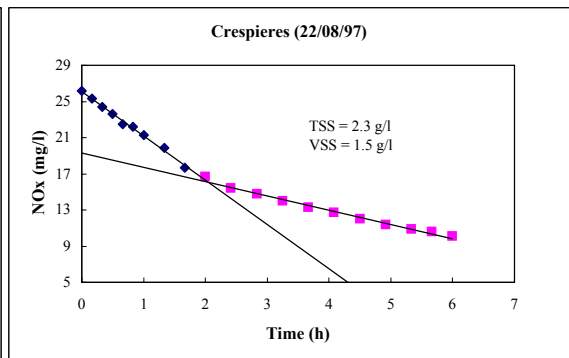
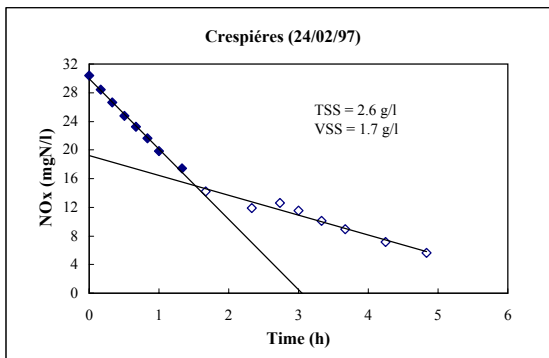


Table III-C2 : Raw data for samples taken from Crespières 2 WTP (22/08/97)						
Raw data						
Time(min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	25.9	0.5	26.4	26.2	8.8
10	0.2	25.0	0.3	25.3	25.2	-
20	0.3	24.4	0.0	24.4	24.4	-
30	0.5	23.6	0.0	23.6	23.6	10.5
40	0.7	22.5	0.0	22.5	22.5	-
50	0.8	22.2	0.0	22.2	22.2	-
60	1.0	21.3	0.0	21.3	21.3	10.7
80	1.3	19.9	0.0	19.9	19.9	-
100	1.7	17.7	0.0	17.7	17.7	-
120	2.0	16.7	0.0	16.7	16.7	10.7
145	2.4	15.4	0.0	15.4	15.4	-
170	2.8	14.8	0.0	14.8	14.8	-
195	3.3	14.0	0.0	14.0	14.0	-
220	3.7	13.3	0.0	13.3	13.3	-
245	4.1	12.7	0.0	12.7	12.7	-
270	4.5	12.0	0.0	12.0	12.0	-
295	4.9	11.4	0.0	11.4	11.4	-
320	5.3	10.9	0.0	10.9	10.9	-
340	5.7	10.6	0.0	10.6	10.6	-
360	6.0	10.1	0.0	10.1	10.1	9.3

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	2857	(mgO <sub>2</sub> /l)
Xf	22	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	1.89	

Kinetic data			
k <sub>1</sub>	-3.3	Y1	26.09
k <sub>2</sub>	-1.2	Y2	20.64
k <sub>3</sub>	-	Y3	-
		NOx1	5.45
		NOx2	-
		Ace 1	42
		Ace (%) 1	84

C

Table III-C3 : Raw data for samples taken from Compiègne 1 WTP (3/06/97)						
Raw data						
Time(min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	28.9	0.0	28.9	28.9	3.0
11	0.2	28.2	0.0	28.2	28.2	-
21	0.4	27.4	0.0	27.4	27.4	-
31	0.5	26.7	0.0	26.7	26.7	-
44	0.7	25.8	0.0	25.8	25.8	-
55	0.9	25.0	0.3	25.3	25.2	10.0
75	1.3	23.5	0.0	23.5	23.5	-
95	1.6	22.5	0.0	22.5	22.5	10.0
135	2.3	21.0	0.0	21.0	21.0	-
175	2.9	19.4	0.0	19.4	19.4	9.0
215	3.6	18.1	0.0	18.1	18.1	-
255	4.3	16.8	0.0	16.8	16.8	7.0
295	4.9	15.4	0.0	15.4	15.4	-
310	5.2	15.1	0.0	15.1	15.1	-
325	5.4	14.8	0.0	14.8	14.8	6.5

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	1237	(mgO <sub>2</sub> /l)
Xf	11	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.04	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	1.73	

Kinetic data			
k <sub>1</sub>	-3.4	Y1	28.94
k <sub>2</sub>	-1.6	Y2	25.51
k <sub>3</sub>	-	NO <sub>x</sub> 1	3.43
		Ace 1	26
		Ace (%)	54

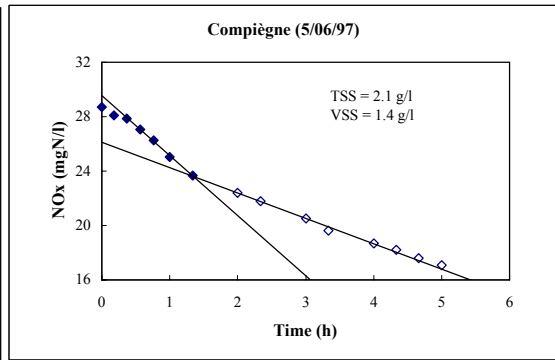
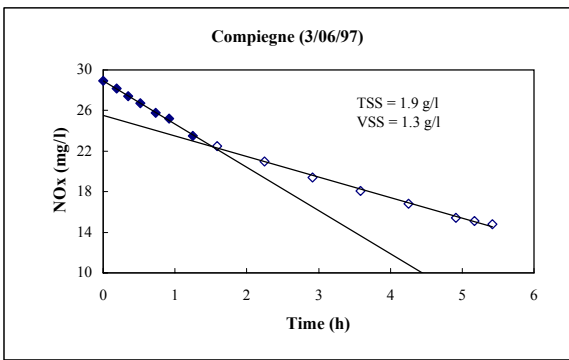


Table III-C4 : Batch data with samples from Compiègne 2 WTP (5/06/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	28.7	0.0	28.7	28.7	-
11	0.2	28.1	0.0	28.1	28.1	1.5
22	0.4	27.7	0.3	28.0	27.9	-
34	0.6	26.9	0.3	27.2	27.1	-
46	0.8	26.0	0.4	26.4	26.2	7.5
60	1.0	24.8	0.4	25.2	25.0	-
80	1.3	23.5	0.3	23.8	23.7	-
120	2.0	22.4	0.0	22.4	22.4	8.0
140	2.3	21.8	0.0	21.8	21.8	-
180	3.0	20.5	0.0	20.5	20.5	5.5
200	3.3	19.6	0.0	19.6	19.6	-
240	4.0	18.7	0.0	18.7	18.7	4.0
260	4.3	18.2	0.0	18.2	18.2	-
280	4.7	17.6	0.0	17.6	17.6	-
300	5.0	17.1	0.0	17.1	17.1	-
330	5.5	15.4	0.0	15.4	15.4	3.0

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	2222	(mgO <sub>2</sub> /l)
Xf	13	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	1.74	

Kinetic data			
k <sub>1</sub>	-3.2	Y1	29.54
k <sub>2</sub>	-1.3	Y2	26.14
k <sub>3</sub>	-	NO <sub>x</sub> 1	3.41
		Ace 1	26
		Ace (%)	52



C

Table III-C5 : Raw data for samples taken from Compiègne 3 WTP (09/06/97)						
Raw data						Experimental conditions
Time(min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	31.3	0.0	31.3	31.3	3.0
10	0.2	30.3	0.0	30.3	30.3	-
20	0.3	29.7	0.0	29.7	29.7	-
30	0.5	28.9	0.3	29.2	29.1	-
40	0.7	27.9	0.3	28.2	28.1	9.0
50	0.8	27.2	0.3	27.5	27.4	-
65	1.1	26.0	0.4	26.4	26.2	9.0
90	1.5	24.0	0.3	24.3	24.2	-
115	1.9	23.0	0.0	23.0	23.0	-
140	2.3	22.3	0.0	22.3	22.3	9.0
190	3.2	20.8	0.0	20.8	20.8	-
215	3.6	19.8	0.0	19.8	19.8	9.0
240	4.0	19.2	0.0	19.2	19.2	-
265	4.4	18.4	0.0	18.4	18.4	-
285	4.8	17.7	0.0	17.7	17.7	-
300	5.0	17.5	0.0	17.5	17.5	8.0

Kinetic data			
k <sub>1</sub>	-3.4	Y1	31.25
k <sub>2</sub>	-1.3	Y2	26.54
k <sub>3</sub>	-	Y3	-
		NO <sub>x</sub> 1	4.72
		Ace 1	36
		Ace (%)	73

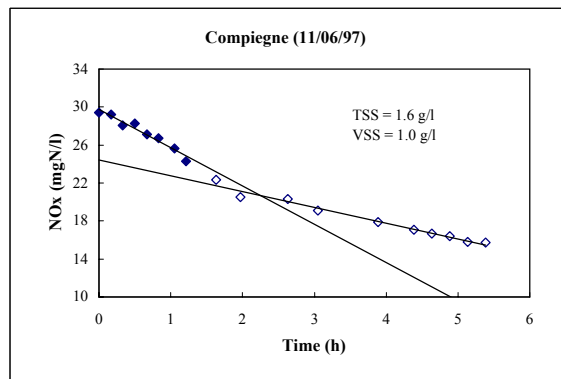
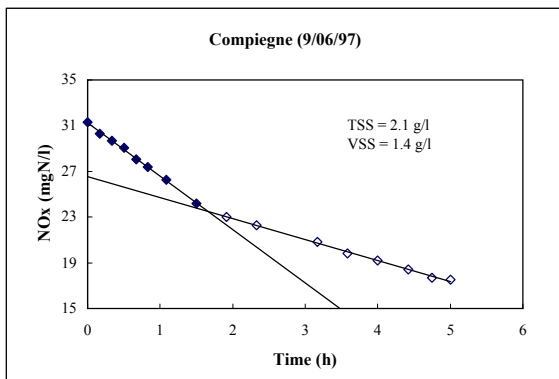


Table III-C6 : Batch data with samples from Compiègne 4 WTP (11/06/97)						
Raw data						Experimental conditions
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	29.4	0.0	29.4	29.4	3.5
10	0.2	29.2	0.0	29.2	29.2	-
20	0.3	28.1	0.0	28.1	28.1	-
30	0.5	28.1	0.3	28.4	28.3	7.0
40	0.7	26.9	0.4	27.3	27.1	-
50	0.8	26.5	0.4	26.9	26.7	-
63	1.1	25.4	0.4	25.8	25.6	8.6
73	1.2	24.0	0.5	24.5	24.3	-
98	1.6	22.0	0.6	22.6	22.4	10.5
118	2.0	20.5	0	20.5	20.5	-
158	2.6	20.3	0.0	20.3	20.3	8.8
183	3.1	19.1	0.0	19.1	19.1	-
233	3.9	17.9	0.0	17.9	17.9	9.3
263	4.4	17.1	0.0	17.1	17.1	-
278	4.6	16.7	0.0	16.7	16.7	10.2
293	4.9	16.4	0.0	16.4	16.4	-
308	5.1	15.8	0.0	15.8	15.8	-
323	5.4	15.7	0.0	15.7	15.7	7.0

Kinetic data			
k <sub>1</sub>	-3.9	Y1	30
k <sub>2</sub>	-1.5	Y2	24.44
k <sub>3</sub>	-	NO <sub>x</sub> 1	5.56
		Ace 1	43
		Ace (%)	86

C

Table III-C7 : Raw data for samples taken from Compiègne 5 WTP (28/08/97)						
Raw data						
Time(min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	26.2	0.0	26.2	26.2	6.0
10	0.2	26.2	0.0	26.2	26.2	-
20	0.3	26.5	0.0	26.5	26.5	6.5
30	0.5	25.3	0.0	25.3	25.3	-
40	0.7	24.4	0.6	25.0	24.8	7.5
50	0.8	23.2	0.8	24.0	23.7	-
60	1.0	22.1	0.9	23.0	22.6	-
80	1.3	20.9	1.1	22.0	21.6	8.5
100	1.7	19.4	1.3	20.7	20.2	-
120	2.0	18.5	1.5	20.0	19.4	-
170	2.8	16.3	1.6	17.9	17.3	-
195	3.3	15.1	1.7	16.8	16.1	-
220	3.7	14.2	1.7	15.9	15.2	-
270	4.5	12.4	1.9	14.3	13.5	-
295	4.9	11.6	1.9	13.5	12.7	-
320	5.3	10.8	1.9	12.7	11.9	-
345	5.8	10.0	1.9	11.9	11.1	-
360	6.0	9.7	1.9	11.6	10.8	4.5

Experimental conditions			
St	50	(mgO <sub>2</sub> /l)	
Sf	50	(mgO <sub>2</sub> /l)	
Xt	1730	(mgO <sub>2</sub> /l)	
Xf	35	(mgO <sub>2</sub> /l)	
V <sub>ww</sub>	-	(l)	
V <sub>x</sub>	1	(l)	
V <sub>d</sub>	0.4	(l)	
S/X	0.03	(mgO <sub>2</sub> /mgO <sub>2</sub> )	
C/N	1.91		

Kinetic data			
k <sub>1</sub>	-3.9	Y1	27.48
k <sub>2</sub>	-1.7	Y2	-22.73
k <sub>3</sub>	-	Y3	-
		NO <sub>x</sub> 1	4.75
		Ace 1	37
		Ace (%)	73

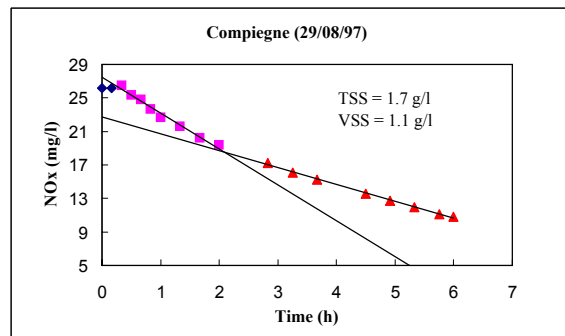
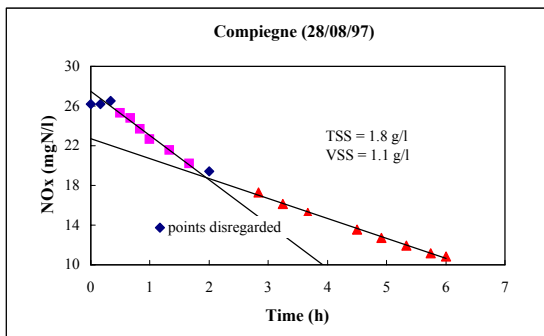


Table III-C8 : Batch data with samples from Compiègne 6 WTP (29/08/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	26.2	0.0	26.2	26.2	6.0
10	0.2	26.2	0.0	26.2	26.2	-
20	0.3	26.5	0.0	26.5	26.5	7.5
30	0.5	25.3	0.0	25.3	25.3	-
40	0.7	24.4	0.6	25.0	24.8	7.5
50	0.8	23.2	0.8	24.0	23.7	-
60	1.0	22.1	0.9	23.0	22.6	8.5
80	1.3	20.9	1.1	22.0	21.6	-
100	1.7	19.4	1.3	20.7	20.2	-
120	2.0	18.5	1.5	20.0	19.4	-
170	2.8	16.3	1.6	17.9	17.3	-
195	3.3	15.1	1.7	16.8	16.1	-
220	3.7	14.2	1.7	15.9	15.2	-
270	4.5	12.4	1.9	14.3	13.5	-
295	4.9	11.6	1.9	13.5	12.7	-
320	5.3	10.8	1.9	12.7	11.9	-
345	5.8	10.0	1.9	11.9	11.1	-
360	6.0	9.7	1.9	11.6	10.8	4.5

Experimental conditions			
St	50	(mgO <sub>2</sub> /l)	
Sf	50	(mgO <sub>2</sub> /l)	
Xt	1730	(mgO <sub>2</sub> /l)	
Xf	35	(mgO <sub>2</sub> /l)	
V <sub>ww</sub>	-	(l)	
V <sub>x</sub>	1.0	(l)	
V <sub>d</sub>	0.4	(l)	
S/X	0.03	(mgO <sub>2</sub> /mgO <sub>2</sub> )	
C/N	1.91		

Kinetic data			
k <sub>1</sub>	-3.6	Y1	27.45
k <sub>2</sub>	-1.7	Y2	22.73
k <sub>3</sub>	-	NO <sub>x</sub> 1	4.72
		RBCOD	36
		%RBCOD	73

C

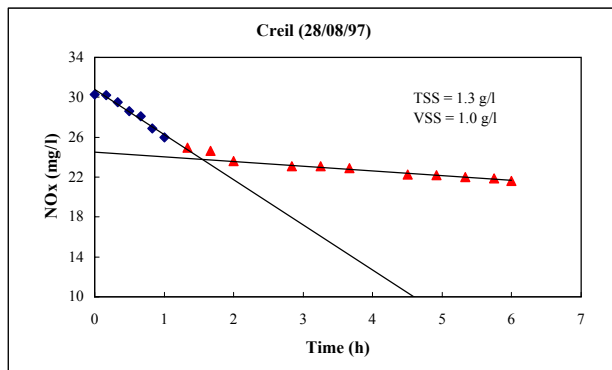
Table III-C9 : Batch data with samples from Creil (28/08/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	30.3	0.0	30.3	30.3	-
10	0.2	30.2	0.0	30.2	30.2	-
20	0.3	29.0	0.9	29.9	29.5	-
30	0.5	27.8	1.4	29.2	28.6	-
40	0.7	27.0	1.8	28.8	28.1	-
50	0.8	25.5	2.3	27.8	26.9	-
60	1.0	24.1	3.1	27.2	26.0	-
80	1.3	22.6	3.9	26.5	24.9	-
100	1.7	22.2	4.0	26.2	24.6	-
120	2.0	21.2	4.0	25.2	23.6	-
170	2.8	20.6	4.1	24.7	23.1	-
195	3.3	20.5	4.3	24.8	23.1	-
220	3.7	20.3	4.3	24.6	22.9	-
270	4.5	19.6	4.4	24.0	22.2	-
295	4.9	19.6	4.3	23.9	22.2	-
320	5.3	19.4	4.3	23.7	22.0	-
345	5.8	19.4	4.1	23.5	21.9	-
360	6.0	19.4	3.7	23.1	21.6	-

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	2690	(mgO <sub>2</sub> /l)
Xf	30	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	1.65	

Kinetic data			
k <sub>1</sub>	-4.6	Y1	30.8
k <sub>2</sub>	-0.5	Y2	24.5
k <sub>3</sub>	-	NOx1	6.3
		Ace 1	48
		Ace (%)	96



G

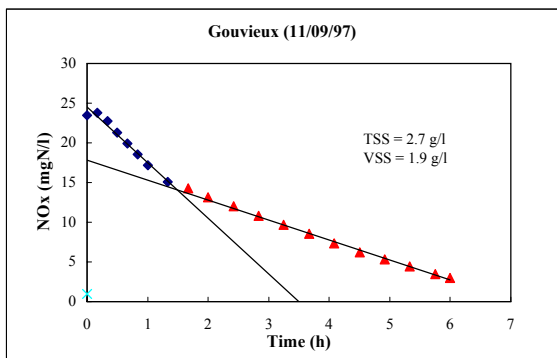
Table III-G1: Batch data with samples from Gouvioux (11/09/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	23.2	0.5	23.7	23.5	4.0
10	0.2	23.3	0.8	24.1	23.8	-
20	0.3	22.1	1.1	23.2	22.8	2.0
30	0.5	20.5	1.3	21.8	21.3	-
40	0.7	19.0	1.5	20.5	19.9	2.0
50	0.8	17.5	1.7	19.2	18.5	-
60	1.0	16.1	1.8	17.9	17.2	3.0
80	1.3	14.0	1.8	15.8	15.1	-
100	1.7	13.3	1.6	14.9	14.3	-
120	2.0	12.3	1.4	13.7	13.1	-
145	2.4	11.4	1.0	12.4	12.0	-
170	2.8	10.3	0.8	11.1	10.8	-
195	3.3	9.4	0.5	9.9	9.7	-
220	3.7	8.4	0.3	8.7	8.6	-
245	4.1	7.3	0.0	7.3	7.3	-
270	4.5	6.2	0.0	6.2	6.2	-
295	4.9	5.3	0.0	5.3	5.3	-
320	5.3	4.4	0.0	4.4	4.4	-
345	5.8	3.5	0.0	3.5	3.5	-
360	6.0	3.0	0.0	3.0	3.0	2.0

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	3658	(mgO <sub>2</sub> /l)
Xf	28	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.01	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	2.13	

Kinetic data			
k <sub>1</sub>	-3.7	Y1	24.48
k <sub>2</sub>	-1.3	Y2	17.86
k <sub>3</sub>	-	NOx1	6.62
		Ace 1	51
		Ace (%)	102



**L**

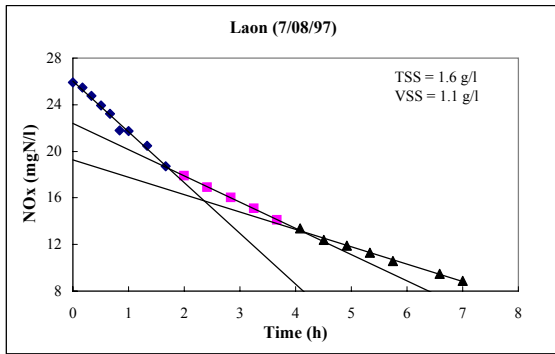
Table III-L-1: Batch data with samples from Laon (11/09/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	25.9	0.0	25.9	25.9	7.8
10	0.2	25.3	0.3	25.6	25.5	-
20	0.3	24.5	0.4	24.9	24.7	-
30	0.5	23.7	0.4	24.1	23.9	9.7
40	0.7	23.0	0.4	23.4	23.2	-
50	0.8	21.5	0.5	22.0	21.8	-
60	1.0	21.5	0.4	21.9	21.7	11.6
80	1.3	20.2	0.5	20.7	20.5	-
100	1.7	18.5	0.4	18.9	18.7	-
120	2.0	17.9	0.0	17.9	17.9	-
145	2.4	16.9	0.0	16.9	16.9	-
170	2.8	16.0	0.0	16.0	16.0	-
195	3.3	15.1	0.0	15.1	15.1	-
220	3.7	14.1	0.0	14.1	14.1	-
245	4.1	13.4	0.0	13.4	13.4	-
270	4.5	12.4	0.0	12.4	12.4	-
295	4.9	11.9	0.0	11.9	11.9	-
320	5.3	11.3	0.0	11.3	11.3	-
345	5.8	10.6	0.0	10.6	10.6	-
395	6.6	9.5	0.0	9.5	9.5	6.8
420	7.0	8.9	0.0	8.9	8.9	6.8

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	2273	(mgO <sub>2</sub> /l)
Xf	15	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	1.93	

Kinetic data			
k <sub>1</sub>	-4.1	Y1	26.04
k <sub>2</sub>	-2.2	Y2	22.39
k <sub>3</sub>	-1.4	Y3	19.27
		NOx1	3.65
		NOx2	3.12
		Acc 1&2	28+24
		Acc (%) 1&2	56+48



# M

Table III-M1: Batch data with samples from Morainvilliers (26/02/97)

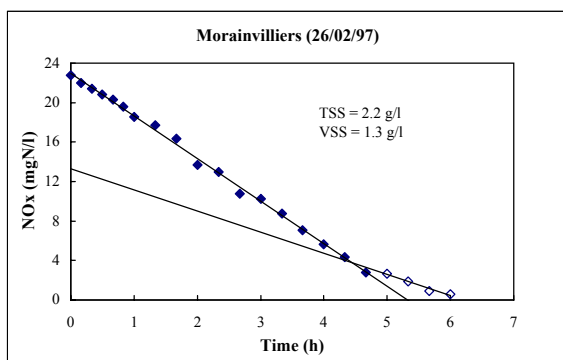
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	22.5	0.4	22.9	22.7	-
10	0.2	21.6	0.6	22.2	22.0	-
20	0.3	21.0	0.7	21.7	21.4	-
30	0.5	20.2	1.0	21.2	20.8	-
40	0.7	19.7	1.0	20.7	20.3	-
50	0.8	19.0	1.0	20.0	19.6	-
60	1.0	17.9	1.1	19.0	18.6	-
80	1.3	16.9	1.3	18.2	17.7	-
100	1.7	15.5	1.4	16.9	16.3	-
120	2.0	12.7	1.6	14.3	13.7	-
140	2.3	11.9	1.8	13.7	13.0	-
160	2.7	9.6	2.0	11.6	10.8	-
180	3.0	9.0	2.1	11.1	10.3	-
200	3.3	7.4	2.3	9.7	8.8	-
220	3.7	5.7	2.3	8.0	7.1	-
240	4.0	4.2	2.4	6.6	5.6	-
260	4.3	2.9	2.4	5.3	4.3	-
280	4.7	2.2	1.0	3.2	2.8	-
300	5.0	1.4	2.1	3.5	2.7	-
320	5.3	0.8	1.8	2.6	1.9	-
340	5.7	0.0	1.5	1.5	0.9	-
360	6.0	0.0	1.0	1.0	0.6	-

Experimental conditions		
St	70	(mgO <sub>2</sub> /l)
Sf	70	(mgO <sub>2</sub> /l)
Xt	1879	(mgO <sub>2</sub> /l)
Xf	17	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0.5	(l)
S/X	0.04	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	3.08	

Kinetic data			
k <sub>1</sub>	-3.3	Y1	22.95
k <sub>2</sub>	-1.6	Y2	13.32
k <sub>3</sub>	-	Y3	-
		NO <sub>x</sub> 1	11.2
		NO <sub>x</sub> 1	-
		Ace 1	64
		Ace (%)	92



O

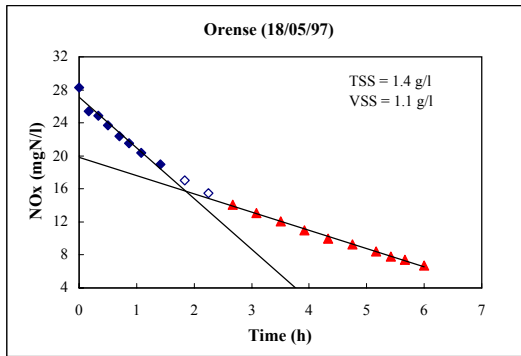
Table III-O1 : Batch data with samples from Orense (18/05/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	28.3	0.0	28.3	28.3	-
10	0.2	24.9	0.0	24.9	24.9	-
20	0.3	25.4	0.0	25.4	25.4	-
30	0.5	23.7	0.0	23.7	23.7	-
42	0.7	22.4	0.0	22.4	22.4	-
52	0.9	21.5	0.0	21.5	21.5	-
65	1.1	20.4	0.0	20.4	20.4	-
85	1.4	19.0	0.0	19.0	19.0	-
110	1.8	17.0	0.0	17.0	17.0	-
135	2.3	15.5	0.0	15.5	15.5	-
160	2.7	14.1	0.0	14.1	14.1	-
185	3.1	13.1	0.0	13.1	13.1	-
210	3.5	12.1	0.0	12.1	12.1	-
235	3.9	11.0	0.0	11.0	11.0	-
260	4.3	10.0	0.0	10.0	10.0	-
285	4.8	9.3	0.0	9.3	9.3	-
310	5.2	8.4	0.0	8.4	8.4	-
325	5.4	7.8	0.0	7.8	7.8	-
340	5.7	7.4	0.0	7.4	7.4	-
360	6.0	6.7	0.0	6.7	6.7	-

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	2733	(mgO <sub>2</sub> /l)
Xf	24	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	1.77	

Kinetic data			
k <sub>1</sub>	-5.2	Y1	26.89
k <sub>2</sub>	-2.0	Y2	19.84
k <sub>3</sub>	-	Y3	-
		NOx1	7
		NOx2	-
		Ace 1	54
		Ace (%)	108



# R

Table III-R1: Batch data with samples from Rostock (15/03/97)

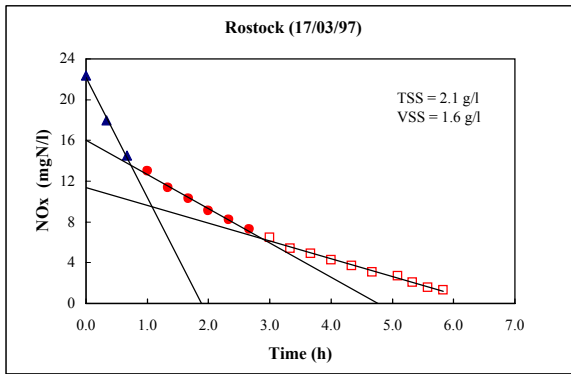
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	22.1	0.4	22.5	22.3	-
20	0.3	17.6	0.6	18.2	18.0	-
40	0.7	14.2	0.5	14.7	14.5	-
60	1.0	12.8	0.3	13.1	13.0	-
80	1.3	11.4	0.0	11.4	11.4	-
100	1.7	10.3	0.0	10.3	10.3	-
120	2.0	9.1	0.0	9.1	9.1	-
140	2.3	8.2	0.0	8.2	8.2	-
160	2.7	7.3	0.0	7.3	7.3	-
180	3.0	6.5	0.0	6.5	6.5	-
200	3.3	5.4	0.0	5.4	5.4	-
220	3.7	4.9	0.0	4.9	4.9	-
240	4.0	4.3	0.0	4.3	4.3	-
260	4.3	3.7	0.0	3.7	3.7	-
280	4.7	3.1	0.0	3.1	3.1	-
305	5.1	2.7	0.0	2.7	2.7	-
320	5.3	2.1	0.0	2.1	2.1	-
335	5.6	1.6	0.0	1.6	1.6	-
350	5.8	1.3	0.0	1.3	1.3	-

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	2444	(mgO <sub>2</sub> /l)
Xf	46	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0.5	(l)
S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	2.24	

Kinetic data			
k <sub>1</sub>	-7.3	Y1	22.2
k <sub>2</sub>	-1.9	Y2	15.4
k <sub>3</sub>	-1.1	Y3	11.5
		NO <sub>x</sub> 1	6.65
		NO <sub>x</sub> 1	3.97
		Ace 1&2	51+31
		Ace (%) 1&2	102+61





S

Table III-S1: Batch data with samples from Samaritaine 1 WTP (23/04/97)

Raw data							Experimental conditions		
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P	St	Sf	Xt
0	0.0	29.5	0.0	29.5	29.5	-	50	50	2450
35	0.6	26.0	0.8	26.8	27.6	-	(mgO <sub>2</sub> /l)	(mgO <sub>2</sub> /l)	(mgO <sub>2</sub> /l)
45	0.8	25.0	1.0	26.0	27.0	-	Xf	12	(mgO <sub>2</sub> /l)
60	1.0	23.5	0.9	24.4	25.3	-	V <sub>ww</sub>	-	(l)
85	1.4	20.0	0.6	20.6	21.2	-	V <sub>x</sub>	1.0	(l)
110	1.8	20.5	0.3	20.8	21.1	-	V <sub>d</sub>	0.4	(l)
135	2.3	20.5	0.0	20.5	20.5	-	S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
175	2.9	20.0	0.0	20.0	20.0	-	C/N	1.69	
195	3.3	19.3	0.0	19.3	19.3	-			
215	3.6	18.7	0.0	18.7	18.7	-			
235	3.9	17.9	0.0	17.9	17.9	-			
255	4.3	17.4	0.0	17.4	17.4	-			

Kinetic data			
k <sub>1</sub>	-5.1	Y1	29.56
k <sub>2</sub>	1.2	Y2	23.65
k <sub>3</sub>	-	Y3	-
		NO <sub>x</sub> 1	5.9
		NO <sub>x</sub> 2	-
		Ace 1	45
		Ace (%)	91

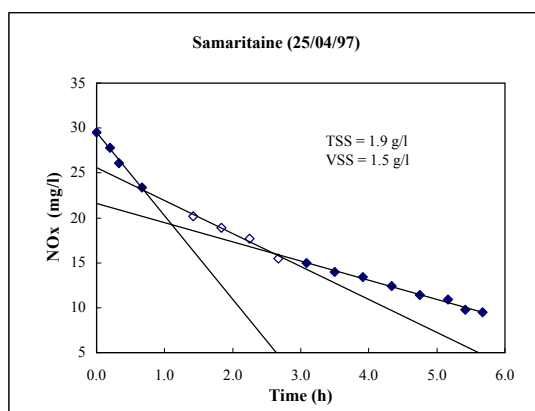
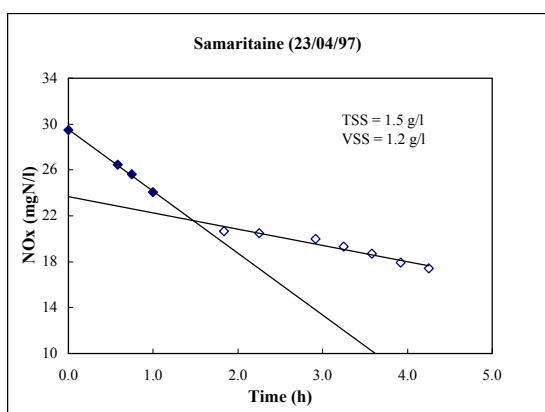


Table III-S2 : Raw data for samples taken from Samaritaine 2 WTP (25/04/97)

Raw data							Experimental conditions		
Time(min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P	St	Sf	Xt
0	0.0	29.5	0.0	29.5	29.5	-	50	50	2405
12	0.2	27.5	0.5	28.0	27.8	-	(mgO <sub>2</sub> /l)	(mgO <sub>2</sub> /l)	(mgO <sub>2</sub> /l)
20	0.3	25.7	0.7	26.4	26.1	-	Xf	12	(mgO <sub>2</sub> /l)
40	0.7	22.9	0.8	23.7	23.4	-	V <sub>ww</sub>	-	(l)
60	1.0	21.6	0.4	22.0	21.8	-	V <sub>x</sub>	1	(l)
85	1.4	20.2	0.0	20.2	20.2	-	V <sub>d</sub>	0.4	(l)
110	1.8	18.9	0.0	18.9	18.9	-	S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
135	2.3	17.7	0.0	17.7	17.7	-	C/N	1.69	
160	2.7	15.5	0.0	15.5	15.5	-			
185	3.1	15.0	0.0	15.0	15.0	-			
210	3.5	14.0	0.0	14.0	14.0	-			
235	3.9	13.4	0.0	13.4	13.4	-			
260	4.3	12.4	0.0	12.4	12.4	-			
285	4.8	11.4	0.0	11.4	11.4	-			
310	5.2	10.9	0.0	10.9	10.9	-			
325	5.4	9.8	0.0	9.8	9.8	-			
340	5.7	9.5	0.0	9.5	9.5	-			

Kinetic data			
k <sub>1</sub>	-6.2	Y1	29.48
k <sub>2</sub>	-2.4	Y2	25.57
k <sub>3</sub>	-1.4	Y3	21.58
		NO <sub>x</sub> 1	3.91
		NO <sub>x</sub> 2	3.99
		Ace 1&2	30+31
		Ace (%) 1&2	60 + 61

S

Table III-S3 : Batch data with samples from Samaritaine 3 WTP (28/04/97)

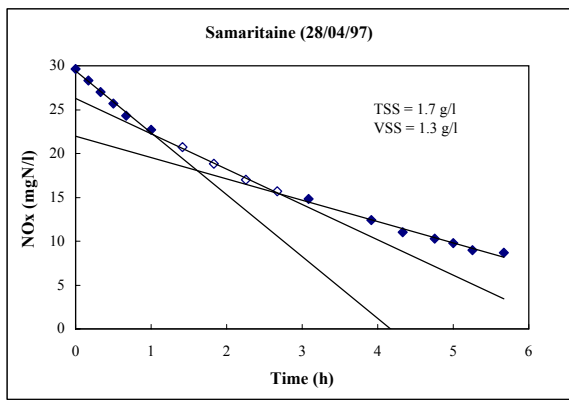
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	29.6	0.0	29.6	29.6	-
10	0.2	27.8	0.5	28.3	28.8	-
20	0.3	26.4	0.6	27.0	27.6	-
30	0.5	25.1	0.6	25.7	26.3	-
40	0.7	23.6	0.7	24.3	25.0	-
60	1.0	22.0	0.7	22.7	23.4	-
85	1.4	20.3	0.4	20.7	21.1	-
110	1.8	18.8	0.0	18.8	18.8	-
135	2.3	17.0	0.0	17.0	17.0	-
160	2.7	15.7	0.0	15.7	15.7	-
185	3.1	14.8	0.0	14.8	14.8	-
235	3.9	12.4	0.0	12.4	12.4	-
260	4.3	11.0	0.0	11.0	11.0	-
285	4.8	10.3	0.0	10.3	10.3	-
300	5.0	9.8	0.0	9.8	9.8	-
315	5.3	9.0	0.0	9.0	9.0	-
340	5.7	8.7	0.0	8.7	8.7	-

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	2397	(mgO <sub>2</sub> /l)
Xf	14	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	1.69	

Kinetic data			
k <sub>1</sub>	-5.4	Y1	29.41
k <sub>2</sub>	-2.9	Y2	25.54
k <sub>3</sub>	-1.8	Y3	21.93
		NOx1	3.87
		NOx2	3.6
		Ace 1&2	30+28
		Ace (%) 1&2	59+55



T

Table III-T1: Batch data with samples from Thivalerval 1 WTP (17/07/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	14.6	0.0	14.6	14.6	4.7
10	0.2	14.8	0.0	14.8	14.8	-
20	0.3	14.2	0.0	14.2	14.2	-
30	0.5	13.3	0.0	13.3	13.3	-
40	0.7	12.6	0.0	12.6	12.6	5.4
50	0.8	11.7	0.0	11.7	11.7	-
60	1.0	11.0	0.0	11.0	11.0	6.5
80	1.3	9.5	0.0	9.5	9.5	-
100	1.7	8.0	0.0	8.0	8.0	-
120	2.0	7.0	0.0	7.0	7.0	-
145	2.4	6.3	0.0	6.3	6.3	-
170	2.8	5.6	0.0	5.6	5.6	-
195	3.3	5.0	0.0	5.0	5.0	6.2
220	3.7	4.3	0.0	4.3	4.3	-
245	4.1	3.7	0.0	3.7	3.7	4.7
270	4.5	3.0	0.0	3.0	3.0	-
290	4.8	2.6	0.0	2.6	2.6	-
310	5.2	2.2	0.0	2.2	2.2	5.0
330	5.5	1.8	0.0	1.8	1.8	-
345	5.8	1.6	0.0	1.6	1.6	-
360	6.0	1.2	0.0	1.2	1.2	5.3

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	3008	(mgO <sub>2</sub> /l)
Xf	45	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	3.42	

Kinetic data			
k <sub>1</sub>	-2.5	Y1	15.62
k <sub>2</sub>	-0.9	Y2	10.07
k <sub>3</sub>	-0.6	Y3	8.21
		NO <sub>x1</sub>	5.55
		NO <sub>x2</sub>	1.86
		Ace 1&2	43+14
		Ace (%) 1&2	85+27

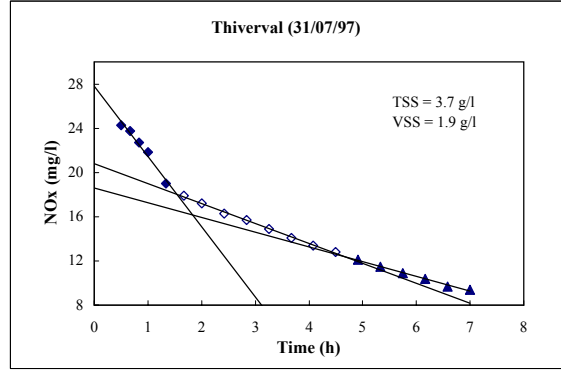
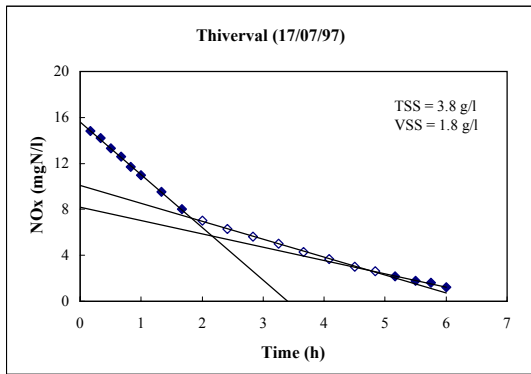


Table III-T2 : Raw data for samples taken from Thivalerval 2 WTP (31/07/97)						
Raw data						
Time(min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	25.6	0.0	25.6	25.6	2.5
10	0.2	24.0	0.0	24.0	24.0	3.5
20	0.3	24.0	0.0	24.0	24.0	5.0
30	0.5	24.0	0.4	24.4	24.2	5.5
40	0.7	23.5	0.4	23.9	23.7	6.5
50	0.8	22.4	0.5	22.9	22.7	7.5
60	1.0	21.5	0.6	22.1	21.9	8.5
80	1.3	18.7	0.5	19.2	19.0	9.0
100	1.7	17.9	0.0	17.9	17.9	8.5
120	2.0	17.2	0.0	17.2	17.2	8.0
145	2.4	16.3	0.0	16.3	16.3	7.5
170	2.8	15.7	0.0	15.7	15.7	7.5
195	3.3	14.9	0.0	14.9	14.9	7.1
220	3.7	14.1	0.0	14.1	14.1	7.0
245	4.1	13.4	0.0	13.4	13.4	6.5
270	4.5	12.8	0.0	12.8	12.8	6.0
295	4.9	12.1	0.0	12.1	12.1	6.5
320	5.3	11.5	0.0	11.5	11.5	6.0
345	5.8	10.9	0.0	10.9	10.9	6.0
370	6.2	10.4	0.0	10.4	10.4	5.5
395	6.6	9.7	0.0	9.7	9.7	5.5
420	7.0	9.4	0.0	9.4	9.4	5.0

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	3476	(mgO <sub>2</sub> /l)
Xf	36	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.01	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	1.95	

Kinetic data			
k <sub>1</sub>	-3.3	Y1	27.81
k <sub>2</sub>	-1.0	Y2	20.79
k <sub>3</sub>	-0.7	Y3	18.59
		NO <sub>x1</sub>	4.81
		NO <sub>x2</sub>	2.2
		Ace 1&2	37+17
		Ace (%) 1&2	74+34

V

Table III-V1: Batch data with samples from Villers (10/09/97)

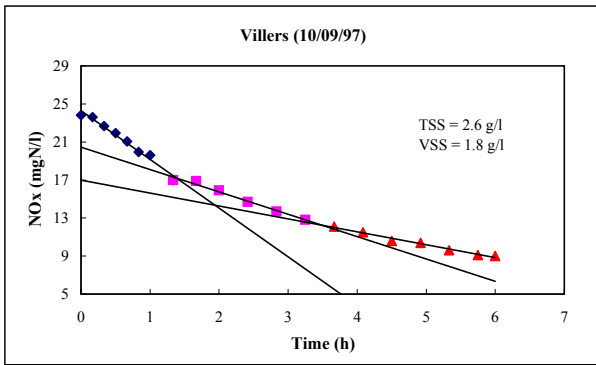
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	23.8	0.0	23.8	23.8	5.0
10	0.2	23.6	0.0	23.6	23.6	-
20	0.3	22.5	0.3	22.8	22.7	7.0
30	0.5	21.7	0.4	22.1	21.9	-
40	0.7	20.7	0.6	21.3	21.1	9.5
50	0.8	19.6	0.6	20.2	20.0	-
60	1.0	19.0	1.0	20.0	19.6	11.0
80	1.3	16.5	0.8	17.3	17.0	-
100	1.7	16.4	0.8	17.2	16.9	11.0
120	2.0	15.5	0.7	16.2	15.9	-
145	2.4	14.4	0.5	14.9	14.7	-
170	2.8	13.7	0.0	13.7	13.7	-
195	3.3	12.8	0.0	12.8	12.8	-
220	3.7	12.1	0.0	12.1	12.1	-
245	4.1	11.5	0.0	11.5	11.5	6.0
270	4.5	10.6	0.0	10.6	10.6	-
295	4.9	10.4	0.0	10.4	10.4	-
320	5.3	9.6	0.0	9.6	9.6	-
345	5.8	9.1	0.0	9.1	9.1	-
360	6.0	9.0	0.0	9.0	9.0	5.0

Experimental conditions		
St	50	(mgO <sub>2</sub> /l)
Sf	50	(mgO <sub>2</sub> /l)
Xt	3746	(mgO <sub>2</sub> /l)
Xf	26	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	-	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.4	(l)
S/X	0.01	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	2.10	

Kinetic data			
k <sub>1</sub>	-3.0	Y1	24.3
k <sub>2</sub>	-1.3	Y2	20.46
k <sub>3</sub>	-0.7	Y3	16.98
		NOx1	3.84
		NOx1	3.49
		Ace 1&2	29+27
		Ace (%) 1&2	59+54



# *APPENDIX IV*

## *RAW DATA FROM NUR TESTS WITH RAW WASTEWATER*

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Appendix IV contains data from tests where raw wastewater was used as a substrate with different sludges. The tests are listed alphabetically and contains the raw data from the NUR tests, the experimental conditions within the batch reactor, and the kinetic data derived from the curves.

### *Abbreviations*

<b>C/N</b>	the initial COD to nitrates as N ratio (within the reactor)
<b>S/X</b>	the initial substrate (acetate) to biomass ratio (within the reactor)
<b>D.F.</b>	Dilution factor (total volume / wastewater volume)
<b>k<sub>1</sub></b>	first rate observed
<b>k<sub>2</sub></b>	second rate observed
<b>k<sub>3</sub></b>	third rate observed
<b>N</b>	sum nitrates and nitrite concentration as defined in equation 4-3
<b>NO<sub>x</sub></b>	sum nitrates and nitrite concentration as defined in equation 4-4
<b>P</b>	ortho-phosphate as P
<b>Y1</b>	first Y intercept in NO <sub>x</sub> vs t curve
<b>Y2</b>	second Y intercept in NO <sub>x</sub> vs t curve
<b>Y3</b>	third Y intercept in NO <sub>x</sub> vs t curve

**A**

Table IV-A1: Batch data with samples from Asnieres-sur-oise (11/09/97)						
Raw data (Substrate-raw wastewater)						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	39.0	0.9	39.9	39.5	1.0
10	0.2	37.5	0.9	38.4	38.0	-
20	0.3	38.0	1.0	39.0	38.6	1.0
30	0.5	37.5	1.0	38.5	38.1	-
40	0.7	36.0	1.0	37.0	36.6	-
50	0.8	35.5	1.1	36.6	36.2	1.0
60	1.0	35.0	1.1	36.1	35.7	-
80	1.3	32.5	1.2	33.7	33.2	1.0
100	1.7	32.5	1.3	33.8	33.3	-
120	2.0	31.0	1.5	32.5	31.9	-
145	2.4	29.5	1.7	31.2	30.5	-
170	2.8	29.0	1.7	30.7	30.0	-
195	3.3	28.0	1.5	29.5	28.9	-
220	3.7	27.0	1.4	28.4	27.8	-
245	4.1	27.0	1.2	28.2	27.7	-
270	4.5	26.0	1.0	27.0	26.6	-
295	4.9	26.0	0.9	26.9	26.5	-
320	5.3	25.5	0.8	26.3	26.0	-
345	5.8	25.0	0.6	25.6	25.4	-
360	6.0	24.5	0.6	25.1	24.9	1.0

Experimental conditions		
St	253	(mgO <sub>2</sub> /l)
Sf	-	(mgO <sub>2</sub> /l)
Xt	1405	(mgO <sub>2</sub> /l)
Xf	-	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.3	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.18	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	6.40	

Kinetic data			
k <sub>1</sub>	-4.9	Y1	39.62
k <sub>2</sub>	-2.6	Y2	36.58
k <sub>3</sub>	-1.3	Y3	32.22
		NO <sub>x1</sub>	3.04
		NO <sub>x2</sub>	4.37
		RBCOD	110 + 158
		%RBCOD	9 + 13

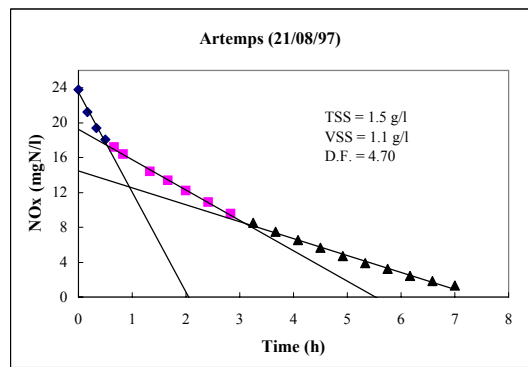
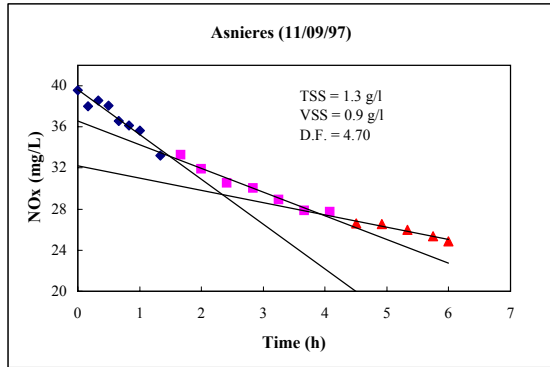


Table III-A2: Batch data with samples from Artemps-Seraucourt 1 (21/08/97)						
Raw data (Substrate-raw wastewater)						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	22.9	1.5	24.4	23.8	15.5
10	0.2	19.4	3.0	22.4	21.2	-
20	0.3	16.8	4.3	21.1	19.4	-
30	0.5	15.1	4.9	20.0	18.0	15.5
40	0.7	14.1	5.1	19.2	17.2	-
50	0.8	13.2	5.3	18.5	16.4	-
80	1.3	11.0	5.7	16.7	14.4	15.4
100	1.7	9.8	5.9	15.7	13.3	-
120	2.0	8.6	6.0	14.6	12.2	-
145	2.4	7.2	6.1	13.3	10.9	-
170	2.8	5.9	6.1	12.0	9.6	-
195	3.3	4.9	6.0	10.9	8.5	-
220	3.7	4.0	5.8	9.8	7.5	-
245	4.1	3.1	5.7	8.8	6.5	-
270	4.5	2.4	5.4	7.8	5.6	-
295	4.9	1.6	5.2	6.8	4.7	-
320	5.3	1.0	4.8	5.8	3.9	-
345	5.8	0.5	4.5	5.0	3.2	-
370	6.2	0.0	4.0	4.0	2.4	-
395	6.6	0.0	3.0	3.0	1.8	-
420	7.0	0.0	2.2	2.2	1.3	14

Experimental conditions		
St	210	(mgO <sub>2</sub> /l)
Sf	88	(mgO <sub>2</sub> /l)
Xt	1881	(mgO <sub>2</sub> /l)
Xf	41	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.3	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.11	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	8.61	

Kinetic data			
k <sub>1</sub>	-10.6	Y1	23.47
k <sub>2</sub>	-3.2	Y2	19.26
k <sub>3</sub>	-1.7	Y3	14.47
		NO <sub>x1</sub>	4.21
		NO <sub>x2</sub>	4.79
		RBCOD	152 + 173
		%RBCOD	15 + 18

**A**

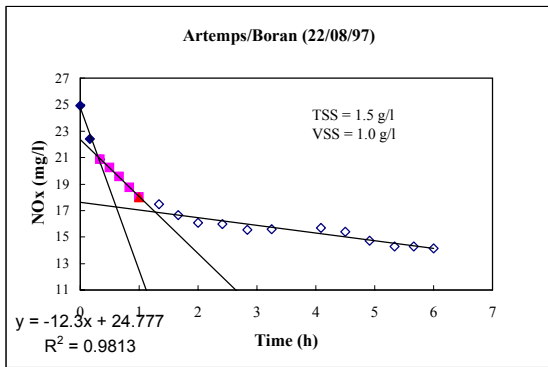
Table IV-A3: Batch data with samples from Artemps/Boran (19/11/97)-acclimatization experiments						
Raw data (Substrate-raw wastewater)						
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>3</sub>	N	NO <sub>x</sub>	P
0	0.0	24.4	0.9	25.3	24.9	12.1
10	0.2	20.9	2.5	23.4	22.4	-
20	0.3	18.8	3.4	22.2	20.8	-
30	0.5	18.0	3.7	21.7	20.2	11.9
40	0.7	17.3	3.8	21.1	19.6	-
50	0.8	16.4	3.9	20.3	18.7	-
60	1.0	15.6	4.0	19.6	18.0	13.2
80	1.3	15.0	4.1	19.1	17.5	-
100	1.7	14.3	3.9	18.2	16.6	-
120	2.0	13.8	3.8	17.6	16.1	12.0
145	2.4	13.8	3.6	17.4	16.0	-
170	2.8	13.5	3.4	16.9	15.5	-
195	3.3	13.6	3.3	16.9	15.6	-
245	4.1	14.0	2.8	16.8	15.7	-
270	4.5	13.9	2.5	16.4	15.4	-
295	4.9	13.4	2.2	15.6	14.7	-
320	5.3	13.1	2.0	15.1	14.3	-
340	5.7	13.1	2.0	15.1	14.3	-
360	6.0	13.0	1.9	14.9	14.1	10.3

Experimental conditions		
St	161	(mgO <sub>2</sub> /l)
Sf	66	(mgO <sub>2</sub> /l)
Xt	1905	(mgO <sub>2</sub> /l)
Xf	36	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.3	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.08	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	6.46	

Kinetic data		
k <sub>1</sub>	-11.2	Y1 24.78
k <sub>2</sub>	-4.1	Y2 22.51
k <sub>3</sub>	-0.5	Y3 17.61
		NO <sub>x1</sub> 2.27
		NO <sub>x2</sub> 4.9
		RBCOD 82 + 177
		%RBCOD 10 + 24



**B**

Table IV-B1: Batch data with samples from Boran WTP (25/02/97)

Raw data (Substrate-centrifuged rw fraction)						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	22.8	1.0	23.8	23.4	-
10	0.2	21.1	1.5	22.6	22.0	-
20	0.3	19.7	1.7	21.4	20.7	-
30	0.5	18.3	2.0	20.3	19.5	-
40	0.7	17.0	2.2	19.2	18.3	-
50	0.8	15.8	2.3	18.1	17.2	-
60	1.0	14.9	2.4	17.3	16.3	-
80	1.3	12.9	2.3	15.2	14.3	-
100	1.7	11.4	2.3	13.7	12.8	-
120	2.0	9.9	2.1	12.0	11.2	-
140	2.3	8.4	2.0	10.4	9.6	-
160	2.7	7.2	1.7	8.9	8.2	-
180	3.0	6.1	1.6	7.7	7.1	-
200	3.3	4.8	1.4	6.2	5.6	-
220	3.7	3.6	1.2	4.8	4.3	-
240	4.0	2.6	1.0	3.6	3.2	-

Experimental conditions		
St	221	(mgO <sub>2</sub> /l)
Sf	125	(mgO <sub>2</sub> /l)
Xt	2001	(mgO <sub>2</sub> /l)
Xf	8	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.5	(l)
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0	(l)
S/X	0.11	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	9.44	

Kinetic data			
k <sub>1</sub>	-4.9	Y1	23.08
k <sub>2</sub>	-2.9	Y2	19.31
k <sub>3</sub>	-	Y3	-
		NOx1	3.77
		NOx2	-
		RBCOD	93
		%RBCOD	13

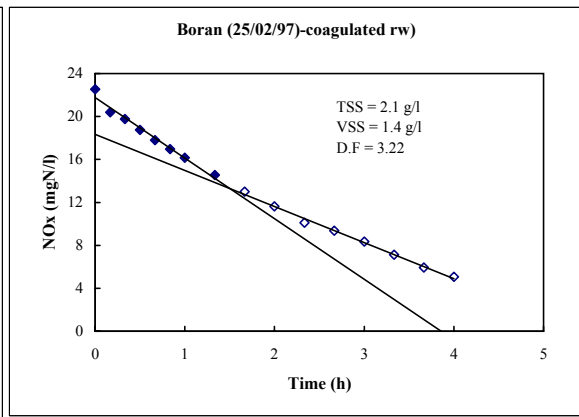
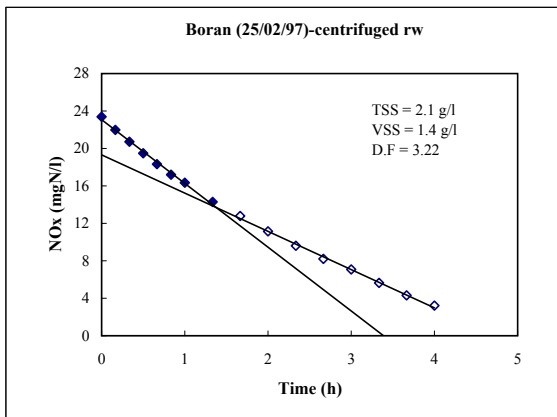


Table IV-B2: Batch data with samples from Boran (25/02/97) - coagulated raw wastewater

Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	22.0	0.9	22.9	22.5	-
10	0.2	19.6	1.3	20.9	20.4	-
20	0.3	18.8	1.6	20.4	19.8	-
30	0.5	17.6	1.9	19.5	18.7	-
40	0.7	16.6	2.0	18.6	17.8	-
50	0.8	15.7	2.1	17.8	17.0	-
60	1.0	14.9	2.1	17.0	16.2	-
80	1.3	13.3	2.1	15.4	14.6	-
100	1.7	11.8	2.0	13.8	13.0	-
120	2.0	10.5	1.9	12.4	11.6	-
140	2.3	9.1	1.7	10.8	10.1	-
160	2.7	8.4	1.6	10.0	9.4	-
180	3.0	7.4	1.6	9.0	8.4	-
200	3.3	6.3	1.4	7.7	7.1	-
220	3.7	5.2	1.2	6.4	5.9	-
240	4.0	4.4	1.1	5.5	5.1	-

Experimental conditions		
St	221	(mgO <sub>2</sub> /l)
Sf	125	(mgO <sub>2</sub> /l)
Xt	2001	(mgO <sub>2</sub> /l)
Xf	8	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.5	-
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0	(l)
S/X	0.11	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	9.65	

Kinetic data			
k <sub>1</sub>	-4	Y1	21.77
k <sub>2</sub>	-2.4	Y2	18.35
k <sub>3</sub>	-	Y3	-
		NOx1	3.43
		NOx2	-
		RBCOD	84
		%RBCOD	12



**B**

Table IV-B3: Batch data with samples from Boves WTP (4/09/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	25.3	0.4	25.7	25.5	14.0
10	0.2	23.0	1.2	24.2	23.7	-
20	0.3	22.0	1.6	23.6	23.0	13.5
30	0.5	21.3	1.8	23.1	22.4	-
40	0.7	20.6	2.2	22.8	21.9	15.5
50	0.8	19.9	2	21.9	21.1	-
60	1.0	19.4	2	21.4	20.6	15.0
80	1.3	18.5	2	20.5	19.7	-
100	1.7	17.6	2	19.6	18.8	-
120	2.0	16.9	1.9	18.8	18.0	-
145	2.4	15.8	1.8	17.6	16.9	-
170	2.8	14.8	1.7	16.5	15.8	-
195	3.3	14.3	1.6	15.9	15.3	-
220	3.7	13.5	1.4	14.9	14.3	-
245	4.1	12.8	1.3	14.1	13.6	-
270	4.5	12.3	1.2	13.5	13.0	-
295	4.9	11.6	1	12.6	12.2	-
320	5.3	10.9	0.8	11.7	11.4	-
345	5.8	10.9	0.7	11.6	11.3	-
360	6.0	10.1	0.6	10.7	10.5	13.5

Experimental conditions	
St	174 (mgO <sub>2</sub> /l)
Sf	70 (mgO <sub>2</sub> /l)
Xt	2714 (mgO <sub>2</sub> /l)
Xf	33 (mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.3 (l)
V <sub>x</sub>	1.0 (l)
V <sub>d</sub>	0.1 (l)
S/X	0.06 (mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	6.81

Kinetic data			
k <sub>1</sub>	-5.0	Y1	25.7
k <sub>2</sub>	-1.0	Y2	21.6
k <sub>3</sub>		Y3	-
		NO <sub>x1</sub>	4.1
		NO <sub>x2</sub>	-
		RBCOD	148
		%RBCOD	18

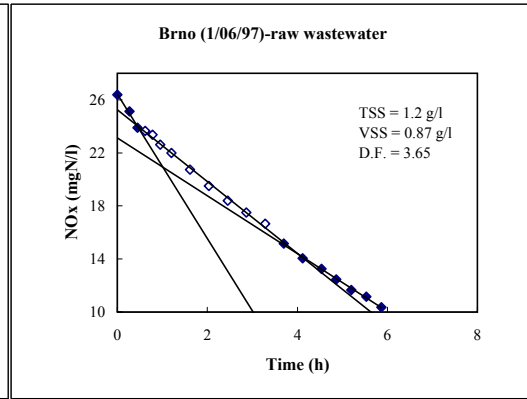
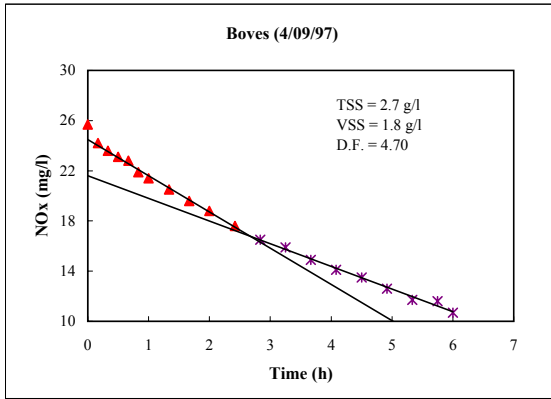


Table IV-B4: Batch data with samples from Brno WTP (1/06/97) - raw wastewater						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	26.2	0.3	26.5	26.4	-
16	0.3	24.9	0.4	25.3	25.1	-
27	0.5	23.6	0.5	24.1	23.9	-
37	0.6	23.3	0.6	23.9	23.7	-
47	0.8	23.0	0.6	23.6	23.4	-
57	1.0	22.2	0.7	22.9	22.6	-
72	1.2	21.5	0.8	22.3	22.0	-
97	1.6	20.2	0.9	21.1	20.7	-
122	2.0	18.9	1.0	19.9	19.5	-
147	2.5	17.8	1.0	18.8	18.4	-
172	2.9	16.9	1.0	17.9	17.5	-
197	3.3	16.0	1.1	17.1	16.7	-
222	3.7	14.5	1.1	15.6	15.2	-
247	4.1	13.4	1.1	14.5	14.1	-
272	4.5	12.6	1.1	13.7	13.3	-
292	4.9	11.8	1.1	12.9	12.5	-
312	5.2	11.0	1.1	12.1	11.7	-
332	5.5	10.5	1.1	11.6	11.2	-
352	5.9	9.7	1.1	10.8	10.4	-

Experimental conditions	
St	68 (mgO <sub>2</sub> /l)
Sf	27 (mgO <sub>2</sub> /l)
Xt	1417 (mgO <sub>2</sub> /l)
Xf	47 (mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.4 (l)
V <sub>x</sub>	1 (l)
V <sub>d</sub>	0 (l)
S/X	0.05 (mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	2.57

Kinetic data			
k <sub>1</sub>	-3.8	Y1	26.44
k <sub>2</sub>	-3.1	Y2	25.24
k <sub>3</sub>	-2.5	Y3	23.13
		NO <sub>x1</sub>	1.2
		NO <sub>x2</sub>	2.1
		RBCOD	34 + 59
		%RBCOD	13 + 24

**B**

Table IV-B5: Batch data with samples from Brno WTP (1/06/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	28.6	0.4	29.0	28.8	-
16	0.3	27.4	0.4	27.8	27.6	-
27	0.5	26.5	0.4	26.9	26.7	-
37	0.6	26.2	0.5	26.7	26.5	-
47	0.8	25.6	0.5	26.1	25.9	-
57	1.0	25.1	0.5	25.6	25.4	-
72	1.2	24.0	0.6	24.6	24.4	-
97	1.6	23.0	0.6	23.6	23.4	-
122	2.0	22.1	0.6	22.7	22.5	-
147	2.5	20.9	0.7	21.6	21.3	-
172	2.9	19.7	0.6	20.3	20.1	-
197	3.3	18.1	0.7	18.8	18.5	-
222	3.7	17.8	0.6	18.4	18.2	-
247	4.1	17.3	0.6	17.9	17.7	-
272	4.5	16.4	0.6	17.0	16.8	-
292	4.9	15.5	0.6	16.1	15.9	-
312	5.2	15.0	0.5	15.5	15.3	-
332	5.5	14.5	0.5	15.0	14.8	-
352	5.9	13.6	0.5	14.1	13.9	-

Experimental conditions		
St	68	(mgO <sub>2</sub> /l)
Sf	27	(mgO <sub>2</sub> /l)
Xt	1417	(mgO <sub>2</sub> /l)
Xf	47	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.4	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.06	(l)
S/X	0.05	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	2.36	

Kinetic data			
k <sub>1</sub>	-3.9	Y1	28.9
k <sub>2</sub>	-2.4	Y2	27.7
k <sub>3</sub>	-2.0	Y3	24.9
		NO <sub>x1</sub>	1.1
		NO <sub>x2</sub>	2.8
		RBCOD	31 + 79
		%RBCOD	12 + 32

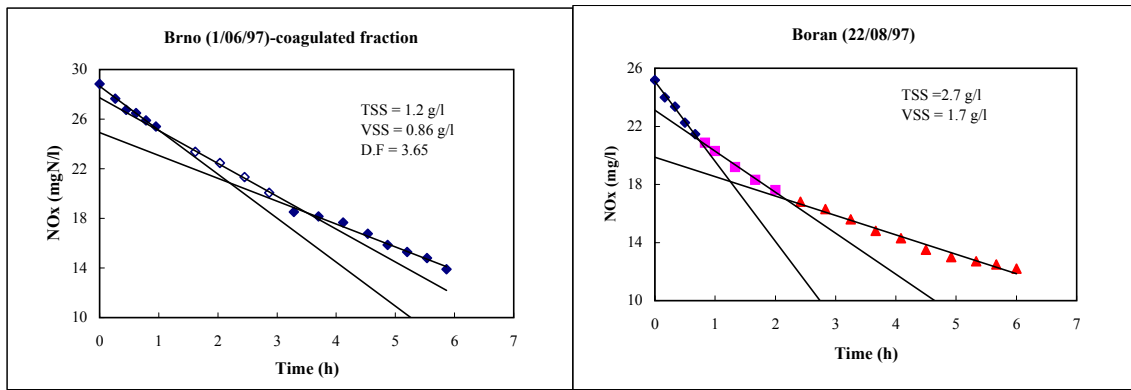


Table IV-B6 : Batch data with samples from Boran WTP (22/08/97)-acclimatization experiment						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	25.0	0.3	25.3	25.2	12.0
10	0.2	23.7	0.5	24.2	24.0	-
20	0.3	23.0	0.6	23.6	23.4	-
30	0.5	21.9	0.6	22.5	22.3	13.5
40	0.7	21.1	0.6	21.7	21.5	-
50	0.8	20.5	0.6	21.1	20.9	-
60	1.0	20.0	0.5	20.5	20.3	13.5
80	1.3	19.0	0.3	19.3	19.2	-
100	1.7	18.3	0.0	18.3	18.3	-
120	2.0	17.6	0.0	17.6	17.6	-
145	2.4	16.8	0.0	16.8	16.8	-
170	2.8	16.3	0.0	16.3	16.3	-
195	3.3	15.6	0.0	15.6	15.6	-
220	3.7	14.8	0.0	14.8	14.8	-
245	4.1	14.3	0.0	14.3	14.3	-
270	4.5	13.5	0.0	13.5	13.5	-
295	4.9	13.0	0.0	13.0	13.0	-
320	5.3	12.7	0.0	12.7	12.7	-
340	5.7	12.5	0.0	12.5	12.5	-
360	6.0	12.2	0.0	12.2	12.2	11.5

Experimental conditions		
St	161	(mgO <sub>2</sub> /l)
Sf	66	(mgO <sub>2</sub> /l)
Xt	3079	(mgO <sub>2</sub> /l)
Xf	23	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.3	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.05	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	6.36	

Kinetic data			
k <sub>1</sub>	-2.8	Y1	25.09
k <sub>2</sub>	-1.0	Y2	23.11
k <sub>3</sub>	-0.5	Y3	19.87
		NO <sub>x1</sub>	1.98
		NO <sub>x2</sub>	5.22
		RBCOD	72 + 189
		%RBCOD	9 + 25

**B**

Table IV-B7: Batch data with samples from Boran/Compiegne WTP (3/06/97)-sludge from Boran and raw wastewater from Compiegne

Raw data							Experimental conditions	
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>3</sub>	N	NOx	P	St	(mgO <sub>2</sub> /l)
0	0.0	27.8	0.4	28.2	28.0	12.0	224	(mgO <sub>2</sub> /l)
11	0.2	25.5	0.7	26.2	25.9	-	Sf	78 (mgO <sub>2</sub> /l)
21	0.4	24.6	0.8	25.4	25.1	-	Xt	3190 (mgO <sub>2</sub> /l)
31	0.5	21.0	0.8	21.8	21.5	11.0	Xf	13 (mgO <sub>2</sub> /l)
44	0.7	20.5	0.8	21.3	21.0	-	V <sub>ww</sub>	0.4 (l)
55	0.9	20.0	0.8	20.8	20.5	-	V <sub>x</sub>	1.0 (l)
75	1.3	18.4	0.6	19.0	18.8	-	V <sub>d</sub>	0 (l)
95	1.6	16.7	0.5	17.2	17.0	11.0	S/X	0.07 (mgO <sub>2</sub> /mgO <sub>2</sub> )
135	2.3	14.3	0.4	14.7	14.5	-	C/N	7.99
175	2.9	11.8	0.3	12.1	12.0	-		
215	3.6	9.4	0.0	9.4	9.4	-		
255	4.3	7.5	0.0	7.5	7.5	-		
295	4.9	5.6	0.0	5.6	5.6	-		
310	5.2	5.1	0.0	5.1	5.1	-		
325	5.4	4.4	0.0	4.4	4.4	10.0		

Kinetic data			
k <sub>1</sub>	-5.1	Y1	27.16
k <sub>2</sub>	-1.9	Y2	21.46
k <sub>3</sub>	-	Y3	-
		NOx1	6.33
		NOx2	-
		RBCOD	172
		%RBCOD	22

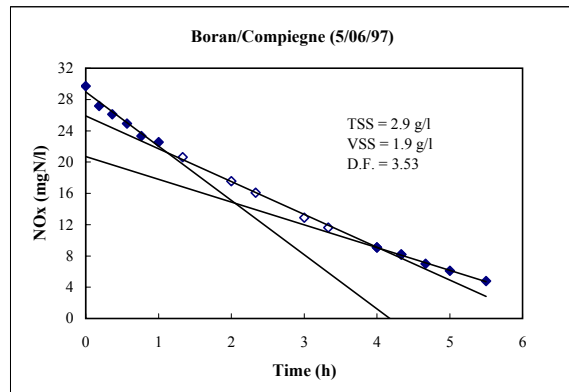
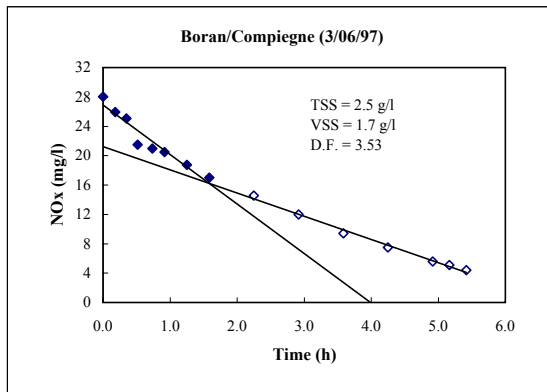


Table IV-B8: Batch data with samples from Boran/Compiegne WTP (5/06/97)-sludge from Boran and raw wastewater from Compiegne

Raw data							Experimental conditions	
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>3</sub>	N	NOx	P	St	(mgO <sub>2</sub> /l)
0	0.0	29.3	0.7	30.0	29.7	13.5	225	(mgO <sub>2</sub> /l)
11	0.2	26.5	1.1	27.6	27.2	-	Sf	65 (mgO <sub>2</sub> /l)
22	0.4	25.4	1.2	26.6	26.1	-	Xt	3190 (mgO <sub>2</sub> /l)
34	0.6	24.1	1.4	25.5	24.9	-	Xf	15 (mgO <sub>2</sub> /l)
46	0.8	22.5	1.4	23.9	23.3	8.5	V <sub>ww</sub>	0.4 (l)
60	1.0	21.7	1.4	23.1	22.5	-	V <sub>x</sub>	1 (l)
80	1.3	19.9	1.2	21.1	20.6	-	V <sub>d</sub>	0 (l)
120	2.0	17.0	0.9	17.9	17.5	13.2	S/X	0.07 (mgO <sub>2</sub> /mgO <sub>2</sub> )
140	2.3	15.6	0.8	16.4	16.1	-	C/N	7.50
180	3.0	12.6	0.5	13.1	12.9	-		
200	3.3	11.4	0.4	11.8	11.6	-		
240	4.0	9.1	0.0	9.1	9.1	-		
260	4.3	8.2	0.0	8.2	8.2	-		
280	4.7	7.0	0.0	7.0	7.0	-		
300	5.0	6.1	0.0	6.1	6.1	-		
330	5.5	4.8	0.0	4.8	4.8	10.0		

Kinetic data			
k <sub>1</sub>	-3.5	Y1	28.97
k <sub>2</sub>	-2.2	Y2	25.91
k <sub>3</sub>	-1.4	Y3	20.7
		NOx1	3.81
		NOx2	5.21
		RBCOD	103 + 142
		%RBCOD	13 + 18

**B**

Table IV-B9: Batch data with samples from Boran/Compiègne WTP (9/06/97)-sludge from Boran and raw wastewater from Compiègne

Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	25.3	0.3	25.6	25.5	5.0
20	0.3	22.4	0.4	22.8	22.6	-
30	0.5	20.4	0.3	20.7	20.6	-
40	0.7	20.2	0.3	20.5	20.4	4.0
50	0.8	18.9	0.3	19.2	19.1	-
65	1.1	18.0	0.0	18.0	18.0	5.3
90	1.5	16.0	0.0	16.0	16.0	-
115	1.9	14.5	0.0	14.5	14.5	-
140	2.3	13.2	0.0	13.2	13.2	4.1
190	3.2	10.5	0.0	10.5	10.5	-
215	3.6	9.4	0.0	9.4	9.4	-
240	4.0	8.1	0.0	8.1	8.1	-
265	4.4	7.0	0.0	7.0	7.0	-
285	4.8	6.0	0.0	6.0	6.0	-
300	5.0	5.5	0.0	5.5	5.5	4.0

Experimental conditions		
St	221	(mgO <sub>2</sub> /l)
Sf	64	(mgO <sub>2</sub> /l)
Xt	4206	(mgO <sub>2</sub> /l)
Xf	33	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.35	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	1.4	(l)
S/X	0.05	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	8.67	

Kinetic data			
k <sub>1</sub>	-3.3	Y1	25.21
k <sub>2</sub>	-1.7	Y2	21.94
k <sub>3</sub>	-1.2	Y3	19.3
		NO <sub>x1</sub>	3.27
		NO <sub>x2</sub>	2.64
		RBCOD	101 + 82
		%RBCOD	11 + 9

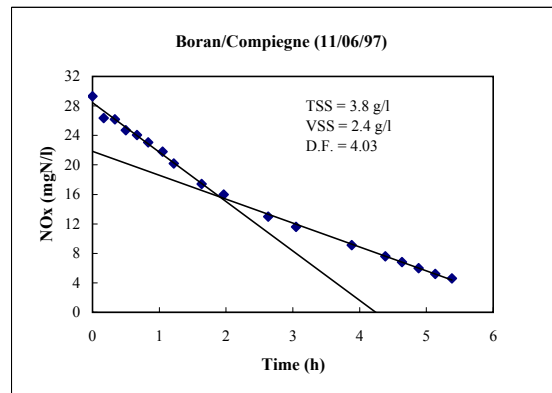
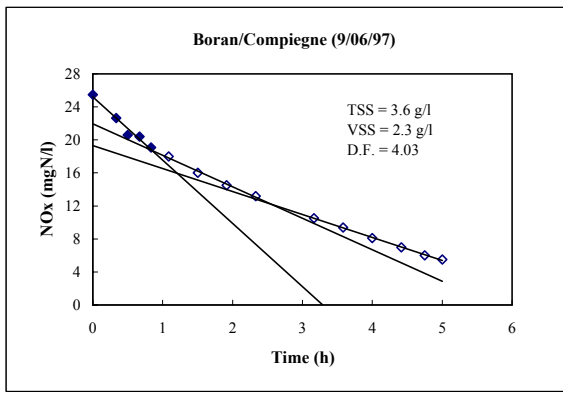


Table IV-B10: Batch data with samples from Boran/Compiègne WTP (11/06/97)-sludge from Boran and raw wastewater from Compiègne

Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	28.9	0.7	29.6	29.3	11.0
10	0.2	25.8	0.9	26.7	26.3	-
20	0.3	25.7	0.8	26.5	26.2	-
30	0.5	24.3	0.7	25.0	24.7	11.0
40	0.7	23.7	0.6	24.3	24.1	-
50	0.8	22.8	0.4	23.2	23.0	-
63	1.1	21.6	0.3	21.9	21.8	9.0
73	1.2	20.0	0.3	20.3	20.2	-
98	1.6	17.4	0.0	17.4	17.4	9.0
118	2.0	16.0	0.0	16.0	16.0	-
158	2.6	13.0	0.0	13.0	13.0	7.5
183	3.1	11.6	0.0	11.6	11.6	-
233	3.9	9.1	0.0	9.1	9.1	8.5
263	4.4	7.6	0.0	7.6	7.6	-
278	4.6	6.8	0.0	6.8	6.8	8.5
293	4.9	6.0	0.0	6.0	6.0	-
308	5.1	5.2	0.0	5.2	5.2	-
323	5.4	4.6	0.0	4.6	4.6	8.5

Experimental conditions		
St	204	(mgO <sub>2</sub> /l)
Sf	71	(mgO <sub>2</sub> /l)
Xt	4015	(mgO <sub>2</sub> /l)
Xf	48	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.35	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.05	(l)
S/X	0.05	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	6.89	

Kinetic data			
k <sub>1</sub>	-2.8	Y1	28.43
k <sub>2</sub>	-1.3	Y2	21.85
k <sub>3</sub>	-	Y3	-
		NO <sub>x1</sub>	6.59
		NO <sub>x2</sub>	-
		RBCOD	204
		%RBCOD	25

**B**

Table IV-B11: Batch data with samples from Boran/Thierval WTP (17/07/97)-sludge from Boran and raw wastewater from Thierval						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	13.5	0.0	13.5	13.5	6.5
10	0.2	12.6	0.0	12.6	12.6	-
30	0.5	11.3	0.0	11.3	11.3	-
40	0.7	10.8	0.0	10.8	10.8	-
50	0.8	10.2	0.0	10.2	10.2	-
60	1.0	9.6	0.0	9.6	9.6	6.0
80	1.3	8.8	0.0	8.8	8.8	-
100	1.7	7.9	0.0	7.9	7.9	-
120	2.0	7.1	0.0	7.1	7.1	6.0
145	2.4	6.2	0.0	6.2	6.2	-
170	2.8	5.3	0.0	5.3	5.3	-
195	3.3	4.5	0.0	4.5	4.5	-
220	3.7	3.6	0.0	3.6	3.6	-
245	4.1	2.8	0.0	2.8	2.8	-
270	4.5	2.1	0.0	2.1	2.1	-
290	4.8	1.4	0.0	1.4	1.4	-
310	5.2	0.9	0.0	0.9	0.9	-
330	5.5	0.4	0.0	0.4	0.4	-
345	5.8	0.0	0.0	0.0	0.0	-
360	6.0	0.0	0.0	0.0	0.0	6.5

Experimental conditions		
St	93	(mgO <sub>2</sub> /l)
Sf	30	(mgO <sub>2</sub> /l)
Xt	3817	(mgO <sub>2</sub> /l)
Xf	28	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.3	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.02	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	6.89	

Kinetic data			
k <sub>1</sub>	-1.2	Y1	13.34
k <sub>2</sub>	-0.7	Y2	12.00
k <sub>3</sub>	-0.5	Y3	9.60
		NO <sub>x1</sub>	1.34
		NO <sub>x2</sub>	2.40
		RBCOD	49 + 87
		%RBCOD	11 + 20

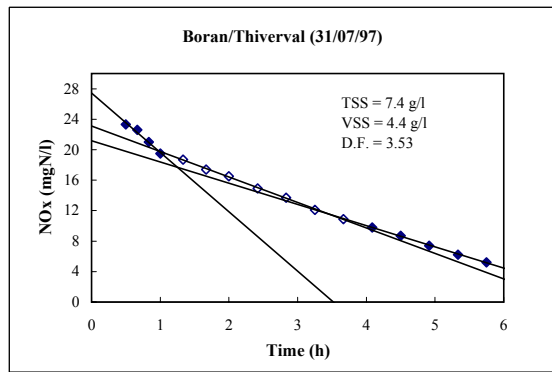
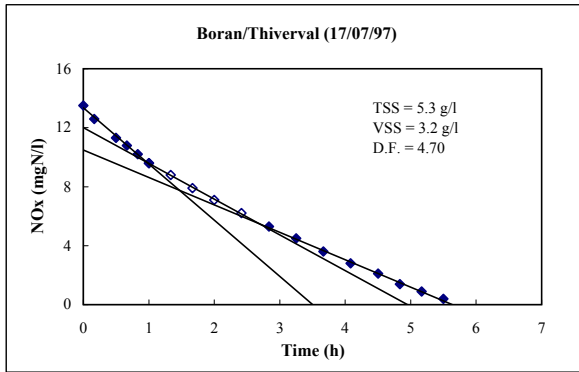


Table IV-B12: Batch data with samples from Boran/Thierval WTP (31/07/97)-sludge from Boran and raw wastewater from Thierval						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	25.4	0.0	25.4	25.4	24.0
10	0.2	23.0	0.0	23.0	23.0	18.0
20	0.3	#N/A	0.0	#N/A	#N/A	19.0
30	0.5	23.3	0.0	23.3	23.3	19.5
40	0.7	22.6	0.0	22.6	22.6	17.0
50	0.8	21.0	0.0	21.0	21.0	16.5
60	1.0	19.5	0.0	19.5	19.5	16.5
80	1.3	18.7	0.0	18.7	18.7	17.0
100	1.7	17.4	0.0	17.4	17.4	15.5
120	2.0	16.5	0.0	16.5	16.5	16.0
145	2.4	14.9	0.0	14.9	14.9	16.0
170	2.8	13.7	0.0	13.7	13.7	16.5
195	3.3	12.1	0.0	12.1	12.1	15.5
220	3.7	10.9	0.0	10.9	10.9	15.0
245	4.1	9.8	0.0	9.8	9.8	15.0
270	4.5	8.7	0.0	8.7	8.7	15.0
295	4.9	7.4	0.0	7.4	7.4	14.0
320	5.3	6.2	0.0	6.2	6.2	15.0
345	5.8	5.2	0.0	5.2	5.2	14.5
370	6.2	4.0	0.0	4.0	4.0	14.5

Experimental conditions		
St	209	(mgO <sub>2</sub> /l)
Sf	43	(mgO <sub>2</sub> /l)
Xt	3788	(mgO <sub>2</sub> /l)
Xf	33	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.4	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0	(l)
S/X	0.06	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	8.23	

Kinetic data			
k <sub>1</sub>	-1.8	Y1	27.45
k <sub>2</sub>	-0.8	Y2	23.09
k <sub>3</sub>	0.6	Y3	21.19
		NO <sub>x1</sub>	4.36
		NO <sub>x2</sub>	1.9
		RBCOD	118 + 52
		%RBCOD	12 + 5

**B**

Table IV-B13: Batch data with samples from Boran WTP (19/11/97)-acclimatization experiment						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	17.3	0.5	17.8	17.6	-
10	0.2	17.5	1.0	18.5	18.1	-
20	0.3	17.6	1.4	19.0	18.5	-
30	0.5	17.8	1.6	19.4	18.8	-
40	0.7	18.0	1.8	19.8	19.0	-
50	0.8	18.1	1.9	20.0	19.3	-
60	1.0	18.3	2.0	20.3	19.5	-
80	1.3	18.6	2.0	20.6	19.8	-
100	1.7	19.0	2.0	21.0	20.2	-
120	2.0	19.3	1.8	21.1	20.4	-
145	2.4	19.7	0.6	20.3	20.1	-
170	2.8	20.1	0.3	20.4	20.3	-
195	3.3	17.3	0.3	17.6	17.5	-
220	3.7	15.4	0.5	15.9	15.7	-
245	4.1	14.5	0.7	15.2	14.9	-
270	4.5	12.8	0.8	13.6	13.3	-
295	4.9	11.5	0.9	12.4	12.0	-
320	5.3	10.3	0.9	11.2	10.8	-
345	5.8	9.2	0.9	10.1	9.7	-
360	6.0	8.6	1.0	9.6	9.2	-

Experimental conditions		
St	202	(mgO <sub>2</sub> /l)
Sf	99	(mgO <sub>2</sub> /l)
Xt	1257	(mgO <sub>2</sub> /l)
Xf	21	(mgO <sub>2</sub> /l)
V <sub>vw</sub>	0.25	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.15	(l)
S/X	0.16	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	11.48	

Kinetic data			
k <sub>1</sub>	-6.3	Y1	31.42
k <sub>2</sub>	-1.9	Y2	24.66
k <sub>3</sub>	-	Y3	-
		NO <sub>x1</sub>	6.76
		NO <sub>x2</sub>	-
		RBCOD	292
		%RBCOD	26

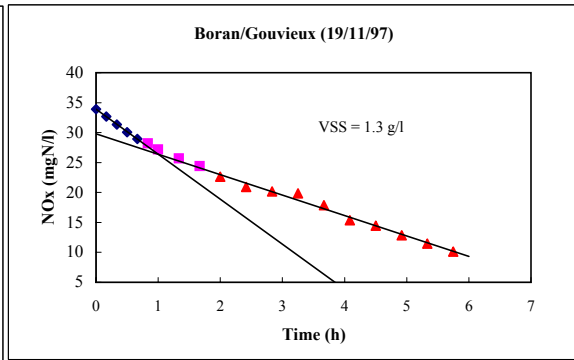
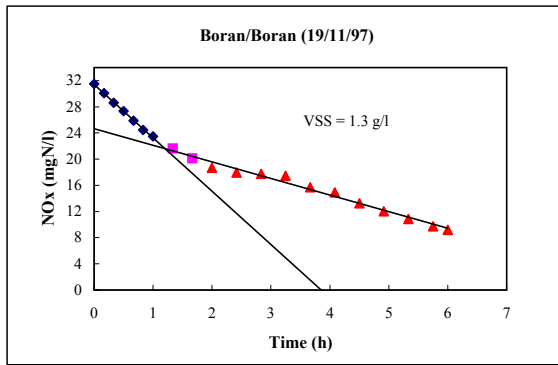


Table IV-B14: Batch data with samples from Boran/Gouvieux WTP (19/11/97)-acclimatization experiment						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	19.7	0.5	20.2	20.0	-
10	0.2	19.9	0.8	20.7	20.3	-
20	0.3	20.0	1.1	21.1	20.7	-
30	0.5	20.2	1.3	21.5	21.0	-
40	0.7	20.4	1.4	21.8	21.2	-
50	0.8	20.5	1.5	22.0	21.4	-
60	1.0	20.7	1.5	22.2	21.6	-
80	1.3	21.0	1.6	22.6	22.0	-
100	1.7	21.4	1.7	23.1	22.4	-
120	2.0	21.7	1.6	23.3	22.7	-
145	2.4	22.1	1.4	23.5	23.0	-
170	2.8	22.5	0.3	22.8	22.7	-
195	3.3	19.7	0.3	20.0	19.9	-
220	3.7	17.6	0.5	18.1	17.9	-
245	4.1	14.9	0.8	15.7	15.4	-
270	4.5	14.0	0.8	14.8	14.5	-
295	4.9	12.4	0.8	13.2	12.9	-
320	5.3	11.0	0.8	11.8	11.5	-
345	5.8	9.7	0.7	10.4	10.1	-
360	6.0	8.9	0.7	9.6	9.3	-

Experimental conditions		
St	150	(mgO <sub>2</sub> /l)
Sf	80	(mgO <sub>2</sub> /l)
Xt	1257	(mgO <sub>2</sub> /l)
Xf	19	(mgO <sub>2</sub> /l)
V <sub>vw</sub>	0.3	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.12	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	7.43	

Kinetic data			
k <sub>1</sub>	-5.8	Y1	33.89
k <sub>2</sub>	-3.5	Y2	29.8
k <sub>3</sub>	-	Y3	-
		NO <sub>x1</sub>	4.1
		NO <sub>x2</sub>	-
		RBCOD	147
		%RBCOD	21

C

Table IV-C1: Batch data with samples from Crespières WTP (24/02/97)-centrifuged fraction

Raw data							Experimental conditions								
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P	St	Sf	Xt	Xf	Vvw	Vx	Vd	S/X	C/N
0	0.0	19.0	2.3	21.3	20.4	-	250	98	3017	47	0.73	1.1	0	0.08	12.27
10	0.2	16.9	2.8	19.7	18.6	-	(mgO <sub>2</sub> /l)	(mgO <sub>2</sub> /l)	(mgO <sub>2</sub> /l)	(mgO <sub>2</sub> /l)	(l)	(l)	(l)	(mgO <sub>2</sub> /mgO <sub>2</sub> )	
20	0.3	14.8	3.2	18.0	16.7	-									
30	0.5	13.4	3.5	16.9	15.5	-									
40	0.7	11.9	3.8	15.7	14.2	-									
50	0.8	10.8	4.0	14.8	13.2	-									
60	1.0	9.8	4.2	14.0	12.3	-									
80	1.3	7.8	4.5	12.3	10.5	-									
100	1.7	5.7	4.9	10.6	8.6	-									
120	2.0	4.1	5.0	9.1	7.1	-									
140	2.3	2.3	5.3	7.6	5.5	-									
164	2.7	0.5	5.3	5.8	3.7	-									
180	3.0	0.0	4.3	4.3	2.6	-									
200	3.3	0.0	2.0	2.0	1.2	-									
220	3.7	0.0	1.2	1.2	0.7	-									

Kinetic data			
k <sub>1</sub>	-5.2	Y1	20.27
k <sub>2</sub>	-2.8	Y2	17.27
k <sub>3</sub>	-	Y3	-
		NOx1	3
		NOx2	-
		RBCOD	51
		%RBCOD	9

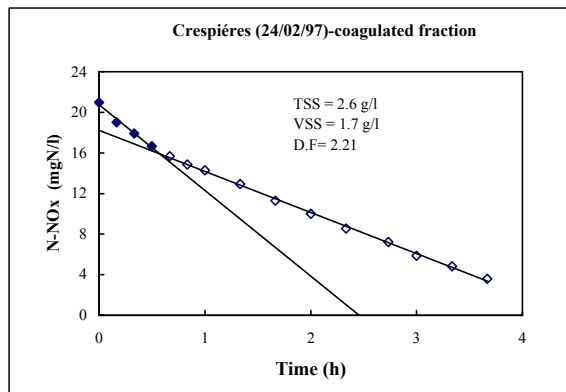
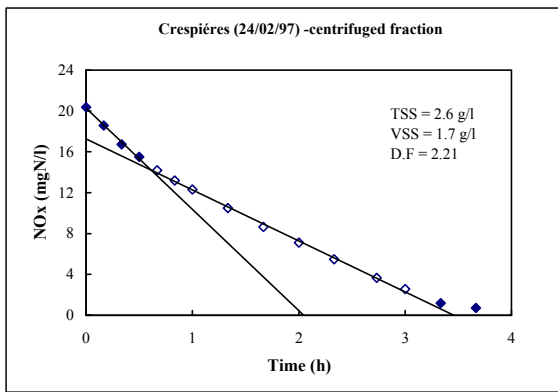


Table IV-C2: Batch data with samples from Crespières WTP (24/02/97) - coagulated fraction

Raw data							Experimental conditions								
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P	St	Sf	Xt	Xf	Vvw	Vx	Vd	S/X	C/N
0	0.0	19.9	1.8	21.7	21.0	-	250	98	3017	47	0.73	1.1	0	0.08	11.52
10	0.2	17.7	2.2	19.9	19.0	-	(mgO <sub>2</sub> /l)	(mgO <sub>2</sub> /l)	(mgO <sub>2</sub> /l)	(mgO <sub>2</sub> /l)	(l)	(l)	(l)	(mgO <sub>2</sub> /mgO <sub>2</sub> )	
20	0.3	16.4	2.5	18.9	17.9	-									
30	0.5	15.1	2.6	17.7	16.7	-									
40	0.7	14.0	2.8	16.8	15.7	-									
50	0.8	13.1	2.9	16.0	14.8	-									
60	1.0	12.5	3.0	15.5	14.3	-									
80	1.3	11.0	3.2	14.2	12.9	-									
100	1.7	9.3	3.3	12.6	11.3	-									
120	2.0	7.9	3.5	11.4	10.0	-									
140	2.3	6.4	3.6	10.0	8.6	-									
164	2.7	5.0	3.7	8.7	7.2	-									
180	3.0	3.6	3.8	7.4	5.9	-									
200	3.3	2.5	3.9	6.4	4.8	-									
220	3.7	1.2	4.0	5.2	3.6	-									

Kinetic data			
k <sub>1</sub>	-4.9	Y1	20.75
k <sub>2</sub>	-2.4	Y2	18.23
k <sub>3</sub>	-	Y3	-
		NOx1	2.67
		NOx2	-
		RBCOD	45
		%RBCOD	8

C

Table IV-C3: Batch data with samples from Creil WTP (28/08/97)-raw wastewater						
Raw data						Experimental conditions
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	31.6	0	31.6	31.6	7.5
10	0.2	30.1	0.8	30.9	30.6	-
20	0.3	28.7	1.5	30.2	29.6	7.5
30	0.5	27.5	2	29.5	28.7	-
40	0.7	26.6	2.2	28.8	27.9	7.5
50	0.8	25.4	2.2	27.6	26.7	-
60	1.0	24.2	2.3	26.5	25.6	-
80	1.3	25.0	2.6	27.6	26.6	-
100	1.7	24.7	2.9	27.6	26.4	-
120	2.0	24.1	3	27.1	25.9	-
170	2.8	20.9	3.3	24.2	22.9	-
195	3.3	20.4	3.4	23.8	22.4	-
220	3.7	19.4	3.5	22.9	21.5	-
270	4.5	18.7	3.5	22.2	20.8	-
295	4.9	17.9	3.6	21.5	20.1	-
320	5.3	17.5	3.5	21.0	19.6	-
345	5.8	17.0	3.5	20.5	19.1	-
360	6.0	16.8	3.5	20.3	18.9	7.5

Kinetic data			
k <sub>1</sub>	-5.2	Y1	31.6
k <sub>2</sub>	-1.2	Y2	26.4
k <sub>3</sub>	-	Y3	-
		NOx1	5.1
		NOx2	-
		RBCOD	186
		%RBCOD	20

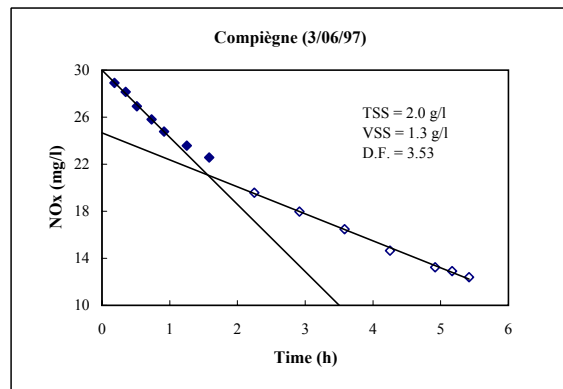
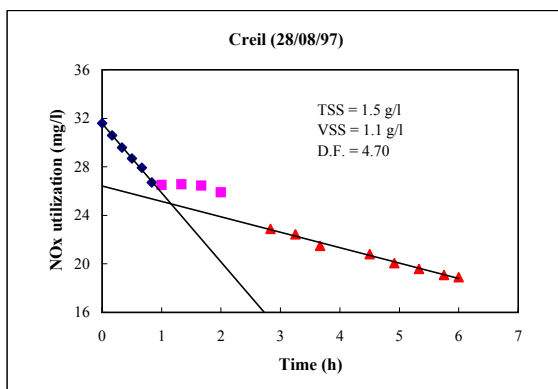


Table IV-C4: Batch data with samples from Compiègne WTP (3/06/97)-raw wastewater						
Raw data						Experimental conditions
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	28.9	0	28.9	28.9	6.5
11	0.2	28.6	0.5	29.1	28.9	-
21	0.4	27.8	0.6	28.4	28.2	-
31	0.5	26.5	0.7	27.2	26.9	-
44	0.7	25.4	0.7	26.1	25.8	-
55	0.9	24.3	0.8	25.1	24.8	10.0
75	1.3	23.1	0.8	23.9	23.6	-
95	1.6	22.1	0.8	22.9	22.6	10.0
135	2.3	19.1	0.8	19.9	19.6	-
175	2.9	17.5	0.8	18.3	18.0	-
215	3.6	16.0	0.8	16.8	16.5	6.5
255	4.3	14.1	0.9	15.0	14.6	-
295	4.9	12.7	0.9	13.6	13.2	5.0
310	5.2	12.3	1	13.3	12.9	-
325	5.4	11.8	1	12.8	12.4	3.0

Kinetic data			
k <sub>1</sub>	-4.4	Y1	30
k <sub>2</sub>	-1.8	Y2	24.67
k <sub>3</sub>	-	Y3	-
		NOx1	5.33
		NOx2	-
		RBCOD	145
		%RBCOD	18



C

Table IV-C5: Batch data with samples from Compiègne WTP (5/06/97)

Raw data							Experimental conditions	
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P	St	
0	0.0	28.1	0	28.1	28.1	4.0	225	(mgO <sub>2</sub> /l)
11	0.2	26.6	0.6	27.2	27.0	-	Sf	65 (mgO <sub>2</sub> /l)
22	0.4	24.9	0.7	25.6	25.3	-	Xt	2222 (mgO <sub>2</sub> /l)
34	0.6	24.0	0.8	24.8	24.5	-	Xf	13 (mgO <sub>2</sub> /l)
46	0.8	23.2	0.9	24.1	23.7	6.5	Vww	0.4 (l)
60	1.0	21.8	1	22.8	22.4	-	Vx	1.0 (l)
80	1.3	21.0	#N/A	#N/A	#N/A	-	Vd	0 (l)
120	2.0	18.0	1.1	19.1	18.7	4.5	S/X	0.10 (mgO <sub>2</sub> /mgO <sub>2</sub> )
140	2.3	17.0	1.2	18.2	17.7	-	C/N	8.01
180	3.0	13.3	1.4	14.7	14.1	3.5		
200	3.3	12.8	1.4	14.2	13.6	-		
240	4.0	11.2	1.6	12.8	12.2	3.0		
260	4.3	10.1	1.7	11.8	11.1	-		
280	4.7	9.2	1.8	11.0	10.3	-		
300	5.0	8.4	1.8	10.2	9.5	-		
330	5.5	7.3	1.9	9.2	8.4	2.5		

Kinetic data			
k <sub>1</sub>	-3.5	Y1	27.85
k <sub>2</sub>	-2.1	Y2	25.28
k <sub>3</sub>	-1.5	Y3	21.8
		NOx1	2.57
		NOx2	3.46
		RBCOD	70 + 94
		%RBCOD	9 + 12

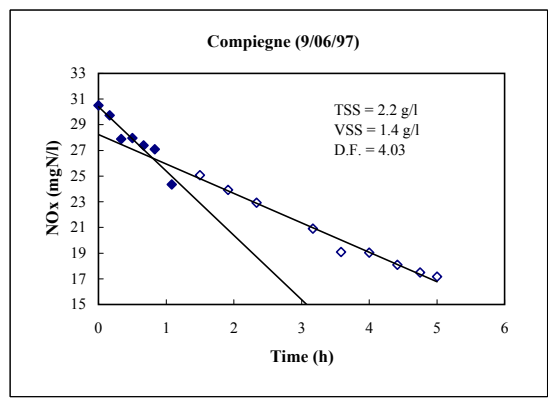
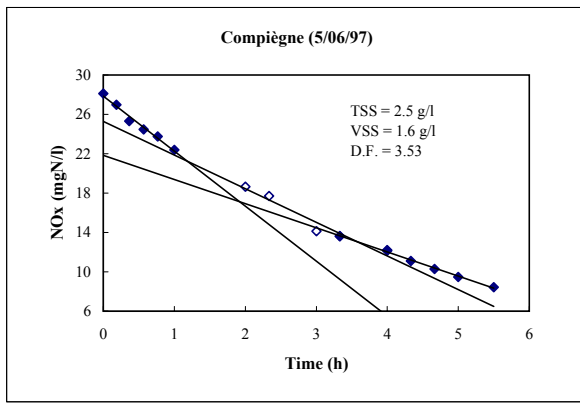


Table IV-C6: Batch data with samples from Compiègne WTP (9/06/97)

Raw data							Experimental conditions	
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P	St	
0	0.0	30.5	0	30.5	30.5	4.0	221	(mgO <sub>2</sub> /l)
10	0.2	29.5	0.4	29.9	29.7	-	Sf	64 (mgO <sub>2</sub> /l)
20	0.3	27.6	0.5	28.1	27.9	-	Xt	2786 (mgO <sub>2</sub> /l)
30	0.5	27.6	0.6	28.2	28.0	-	Xf	45 (mgO <sub>2</sub> /l)
40	0.7	26.9	0.8	27.7	27.4	5.5	Vww	0.35 -
50	0.8	26.6	0.8	27.4	27.1	-	Vx	1 (l)
65	1.1	23.8	0.9	24.7	24.3	8.5	Vd	0.05 (l)
90	1.5	24.4	1.1	25.5	25.1	-	S/X	0.08 (mgO <sub>2</sub> /mgO <sub>2</sub> )
115	1.9	23.2	1.2	24.4	23.9	-	C/N	7.25
140	2.3	22.1	1.4	23.5	22.9	4.5		
190	3.2	19.9	1.7	21.6	20.9	-		
215	3.6	18.0	1.8	19.8	19.1	-		
240	4.0	17.9	1.9	19.8	19.0	4.5		
265	4.4	16.9	2	18.9	18.1	-		
285	4.8	16.3	2	18.3	17.5	-		
300	5.0	15.9	2.1	18.0	17.2	4.0		

Kinetic data			
k <sub>1</sub>	-3.6	Y1	30.41
k <sub>2</sub>	-1.6	Y2	28.23
k <sub>3</sub>	-	Y3	-
		NOx1	2.18
		NOx2	-
		RBCOD	67
		%RBCOD	8

C

Table IV-C7: Batch data with samples from Compiegne WTP (11/06/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	28.9	0.7	29.6	29.3	5.5
10	0.2	25.8	0.9	26.7	26.3	-
20	0.3	25.7	0.8	26.5	26.2	-
30	0.5	24.3	0.7	25.0	24.7	8.0
40	0.7	23.7	0.6	24.3	24.1	-
50	0.8	22.8	0.4	23.2	23.0	-
63	1.1	21.6	0.3	21.9	21.8	10.0
73	1.2	20.0	0.3	20.3	20.2	-
98	1.6	17.4	0.0	17.4	17.4	8.2
118	2.0	16.0	0.0	16.0	16.0	-
158	2.6	13.0	0.0	13.0	13.0	6.0
183	3.1	11.6	0.0	11.6	11.6	-
233	3.9	9.1	0.0	9.1	9.1	7.5
263	4.4	7.6	0.0	7.6	7.6	-
278	4.6	6.8	0.0	6.8	6.8	4.5
293	4.9	6.0	0.0	6.0	6.0	-
308	5.1	5.2	0.0	5.2	5.2	-
323	5.4	4.6	0.0	4.6	4.6	4.5

Experimental conditions		
St	204	(mgO <sub>2</sub> /l)
Sf	71	(mgO <sub>2</sub> /l)
Xt	2659	(mgO <sub>2</sub> /l)
Xf	52	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.35	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.05	(l)
S/X	0.08	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	6.96	

Kinetic data			
k <sub>1</sub>	-3.5	Y1	28.43
k <sub>2</sub>	-1.6	Y2	21.85
k <sub>3</sub>	-	Y3	-
		NOx1	6.59
		NOx2	-
		RBCOD	204
		%RBCOD	25

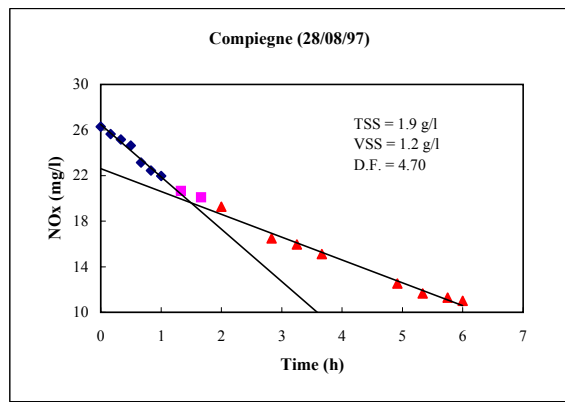
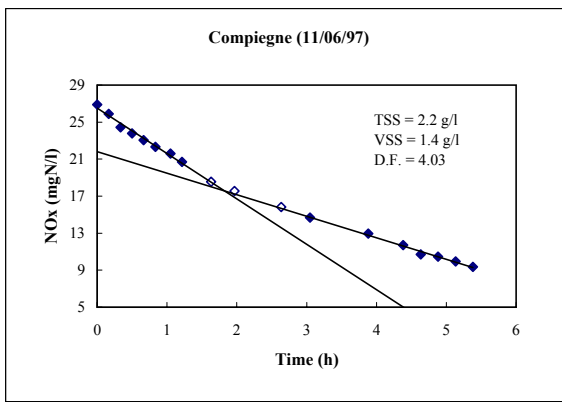


Table IV-C8: Batch data with samples from Compiegne (28/08/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	26.0	0.5	26.5	26.3	4.5
10	0.2	25.4	0.4	25.8	25.6	-
20	0.3	24.8	0.6	25.4	25.2	9.0
30	0.5	24.1	0.9	25.0	24.6	-
40	0.7	22.5	1.1	23.6	23.2	10.0
50	0.8	21.6	1.4	23.0	22.4	-
60	1.0	21.0	1.6	22.6	22.0	10.5
80	1.3	19.5	1.9	21.4	20.6	-
100	1.7	18.7	2.3	21.0	20.1	-
120	2.0	17.7	2.6	20.3	19.3	-
170	2.8	14.5	3.3	17.8	16.5	-
195	3.3	13.8	3.6	17.4	16.0	-
220	3.7	12.7	4	16.7	15.1	-
295	4.9	9.6	4.9	14.5	12.5	-
320	5.3	8.6	5.1	13.7	11.7	-
345	5.8	8.1	5.3	13.4	11.3	-
360	6.0	7.9	5.2	13.1	11.0	4.0

Experimental conditions		
St	269	(mgO <sub>2</sub> /l)
Sf	77	(mgO <sub>2</sub> /l)
Xt	1730	(mgO <sub>2</sub> /l)
Xf	35	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.3	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.16	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	10.15	

Kinetic data			
k <sub>1</sub>	-3.8	Y1	26.48
k <sub>2</sub>	-1.7	Y2	-22.61
k <sub>3</sub>	-	Y3	-
		NOx1	3.87
		NOx2	-
		RBCOD	140
		%RBCOD	11

C

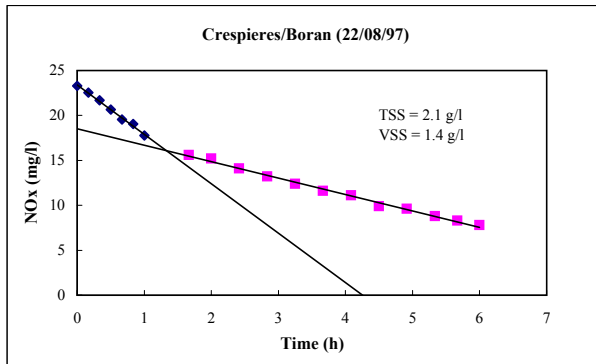
Table IV-C9: Batch data with samples from Crespières/Boran WTP (19/11/97)-acclimatization experiment						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	23.1	0.3	23.4	23.3	10.5
10	0.2	22.3	0.4	22.7	22.5	-
20	0.3	21.4	0.5	21.9	21.7	-
30	0.5	20.4	0.4	20.8	20.6	9.9
40	0.7	19.3	0.4	19.7	19.5	-
50	0.8	18.8	0.4	19.2	19.0	-
60	1.0	17.6	0.3	17.9	17.8	11.2
80	1.3	16.6	0.0	16.6	16.6	-
100	1.7	15.6	0.0	15.6	15.6	-
120	2.0	15.2	0.0	15.2	15.2	-
145	2.4	14.1	0.0	14.1	14.1	11.0
170	2.8	13.2	0.0	13.2	13.2	-
195	3.3	12.4	0.0	12.4	12.4	-
220	3.7	11.6	0.0	11.6	11.6	-
245	4.1	11.1	0.0	11.1	11.1	-
270	4.5	9.9	0.0	9.9	9.9	-
295	4.9	9.6	0.0	9.6	9.6	-
320	5.3	8.8	0.0	8.8	8.8	-
340	5.7	8.3	0.0	8.3	8.3	-
360	6.0	7.8	0.0	7.8	7.8	11.5

Experimental conditions		
St	161	(mgO <sub>2</sub> /l)
Sf	66	(mgO <sub>2</sub> /l)
Xt	2857	(mgO <sub>2</sub> /l)
Xf	22	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.3	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.06	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	6.92	

Kinetic data			
k <sub>1</sub>	-3.9	Y1	23.4
k <sub>2</sub>	-1.3	Y2	18.52
k <sub>3</sub>	-	Y3	-
		NOx1	4.88
		NOx2	-
		RBCOD	176
		%RBCOD	23



**D**

Table IV-D1: Batch data with samples from Darvil WTP (24/07/98)

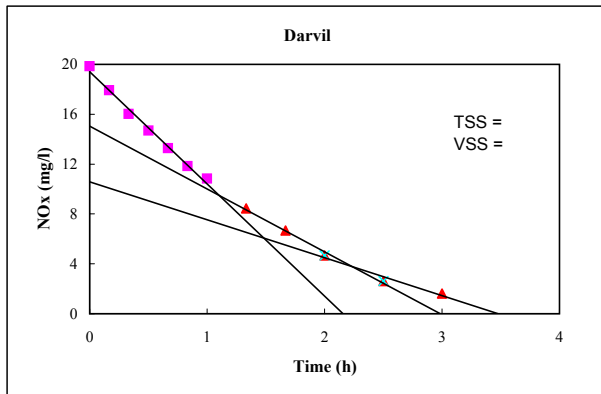
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	12.6	0.7	21.0	13.3	17.3
10	0.2	11.5	1.0	19.2	12.5	18.2
20	0.3	11.5	1.3	18.6	12.8	18.1
30	0.5	11.2	1.4	18.2	12.6	18.0
40	0.7	10.9	1.6	17.9	12.6	18.0
50	0.8	10.7	2.1	17.2	12.8	17.3
60	1.0	10.3	2.2	16.4	12.5	16.7
80	1.3	9.9	2.6	16.0	12.4	16.9
100	1.7	9.6	2.9	14.4	12.5	17.2
120	2.0	8.6	3.2	13.7	11.8	16.6
150	2.5	8.2	2.4	12.6	10.6	19.1
180	3.0	7.5	0.1	11.3	7.6	18.4
200	3.3	6.8	0.0	9.9	6.8	20.3
220	3.7	5.9	0.0	9.4	6.0	22.0
250	4.2	5.6	0.0	8.0	5.7	24.2
280	4.7	4.8	0.1	6.7	4.8	25.9
300	5.0	4.0	0.1	6.0	4.1	25.7
320	5.3	3.6	0.0	5.0	3.6	27.3
340	5.7	3.0	0.0	4.3	3.1	28.9
360	6.0	2.6	0.1	3.3	2.6	33.1

Experimental conditions	
St	342 (mgO <sub>2</sub> /l)
Sf	96 (mgO <sub>2</sub> /l)
Xt	4783 (mgO <sub>2</sub> /l)
Xf	44 (mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.5 (l)
V <sub>x</sub>	1.4 (l)
V <sub>d</sub>	0.1 (l)
S/X	0.07 (mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	25.81

Kinetic data			
k <sub>1</sub>	-3.1	Y1	19.42
k <sub>2</sub>	-2.1	Y2	15.04
k <sub>3</sub>	-1.1	Y3	10.6
		NOx1	4.38
		NOx2	4.47
		RBCOD	135 + 138
		%RBCOD	14 + 14



**E**

Table IV-E1: Batch data with samples from Evry WTP (24/11/97)-raw wastewater-Day 0 of storage experiment						
Raw data						
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>3</sub>	N	NO <sub>x</sub>	P
0	0.0	22.5	2.0	24.5	23.7	-
10	0.2	19.5	3.1	22.6	21.4	-
20	0.3	17.4	3.4	20.8	19.4	-
30	0.5	17.1	3.5	20.6	19.2	-
40	0.7	15.9	3.6	19.5	18.1	-
50	0.8	15.4	3.5	18.9	17.5	-
60	1.0	13.8	3.6	17.4	16.0	-
80	1.3	12.6	3.4	16.0	14.6	-
105	1.8	11.2	3.2	14.4	13.1	-
120	2.0	10.9	3.1	14.0	12.8	-
145	2.4	9.5	2.7	12.2	11.1	-
170	2.8	8.8	2.3	11.1	10.2	-
195	3.3	7.8	1.9	9.7	8.9	-
220	3.7	7.0	1.6	8.6	8.0	-
245	4.1	6.1	1.2	7.3	6.8	-
270	4.5	5.2	0.9	6.1	5.7	-
295	4.9	4.5	0.5	5.0	4.8	-
320	5.3	3.6	0.3	3.9	3.8	-
345	5.8	2.8	0.0	2.8	2.8	-
360	6.0	2.2	0.0	2.2	2.2	-

Experimental conditions	
St	306 (mgO <sub>2</sub> /l)
Sf	98 (mgO <sub>2</sub> /l)
Xt	1622 (mgO <sub>2</sub> /l)
Xf	18 (mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.65 (l)
V <sub>x</sub>	1.0 (l)
V <sub>d</sub>	1.4 (l)
S/X	0.19 (mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	12.91

Kinetic data			
k <sub>1</sub>	-4.9	Y1	23.83
k <sub>2</sub>	-2.3	Y2	19.56
k <sub>3</sub>	-	Y3	-
		NO <sub>x</sub> 1	4.27
		NO <sub>x</sub> 2	-
		RBCOD	71
		%RBCOD	11

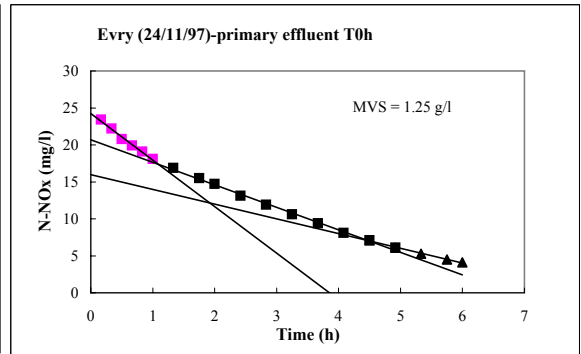
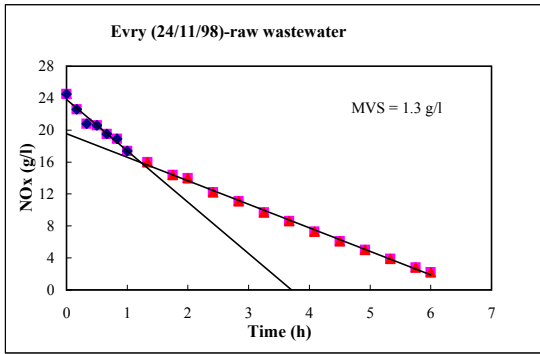


Table IV-E2: Batch data with samples from Evry WTP (24/11/97)-primary effluent-Day 0 of storage experiment						
Raw data						
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>3</sub>	N	NO <sub>x</sub>	P
0	0.0	21.6	2.1	23.7	22.9	-
10	0.2	20.2	3.2	23.4	22.1	-
20	0.3	17.7	4.5	22.2	20.4	-
30	0.5	17.2	3.6	20.8	19.4	-
40	0.7	16.3	3.6	19.9	18.5	-
50	0.8	15.5	3.6	19.1	17.7	-
60	1.0	14.6	3.5	18.1	16.7	-
80	1.3	13.6	3.3	16.9	15.6	-
105	1.8	12.5	3.0	15.5	14.3	-
120	2.0	12.0	2.7	14.7	13.6	-
145	2.4	10.8	2.3	13.1	12.2	-
170	2.8	10.0	1.9	11.9	11.1	-
195	3.3	9.2	1.4	10.6	10.0	-
220	3.7	8.4	1.0	9.4	9.0	-
245	4.1	7.5	0.6	8.1	7.9	-
270	4.5	6.8	0.3	7.1	7.0	-
295	4.9	6.1	0.0	6.1	6.1	-
320	5.3	5.3	0.0	5.3	5.3	-
345	5.8	4.5	0.0	4.5	4.5	-
360	6.0	4.1	0.0	4.1	4.1	-

Experimental conditions	
St	309 (mgO <sub>2</sub> /l)
Sf	98 (mgO <sub>2</sub> /l)
Xt	1622 (mgO <sub>2</sub> /l)
Xf	18 (mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.65 (l)
V <sub>x</sub>	1 (l)
V <sub>d</sub>	0 (l)
S/X	0.19 (mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	13.04

Kinetic data			
k <sub>1</sub>	-5	Y1	24.25
k <sub>2</sub>	-2.4	Y2	20.69
k <sub>3</sub>	-1.6	Y3	15.96
		NO <sub>x</sub> 1	3.56
		NO <sub>x</sub> 2	4.73
		RBCOD	55 + 73
		%RBCOD	8 + 13

E

Table IV-E3: Batch data with samples from Evry WTP (25/11/97)-raw wastewater-Day 1of storage experiment						
Raw data						
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>3</sub>	N	NOx	P
0	0.0	20.9	1.6	22.5	21.9	-
10	0.2	17.9	3.7	21.6	20.1	-
20	0.3	16.2	4.1	20.3	18.7	-
30	0.5	15.4	4.3	19.7	18.0	-
40	0.7	14.1	4.5	18.6	16.8	-
50	0.8	13.0	4.6	17.6	15.8	-
60	1.0	12.2	4.6	16.8	15.0	-
80	1.3	10.6	4.6	15.2	13.4	-
105	1.8	9.6	4.5	14.1	12.3	-
120	2.0	8.4	4.3	12.7	11.0	-
145	2.4	6.9	4.2	11.1	9.4	-
170	2.8	5.9	3.8	9.7	8.2	-
195	3.3	4.7	3.3	8.0	6.7	-
220	3.7	3.9	2.9	6.8	5.6	-
245	4.1	3.0	2.4	5.4	4.4	-
270	4.5	2.2	2.1	4.3	3.5	-
295	4.9	1.6	1.5	3.1	2.5	-
320	5.3	0.8	1.0	1.8	1.4	-
345	5.8	0.0	0.3	0.3	0.2	-
360	6.0	0.0	0.0	0.0	0.0	-

Experimental conditions		
St	318	(mgO <sub>2</sub> /l)
Sf	122	(mgO <sub>2</sub> /l)
Xt	1531	(mgO <sub>2</sub> /l)
Xf	10	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.65	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0	(l)
S/X	0.21	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	14.55	

Kinetic data			
k <sub>1</sub>	-4.7	Y1	21.37
k <sub>2</sub>	-2.0	Y2	16.69
k <sub>3</sub>	-	Y3	-
		NOx1	4.68
		NOx2	-
		RBCOD	78
		%RBCOD	11

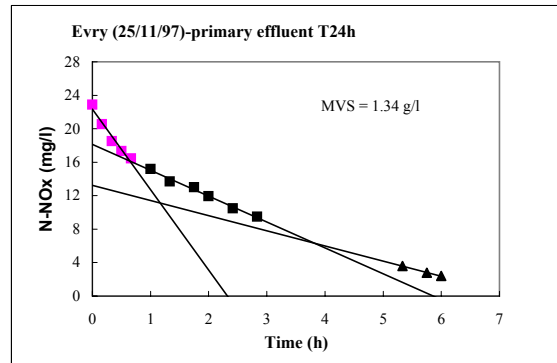
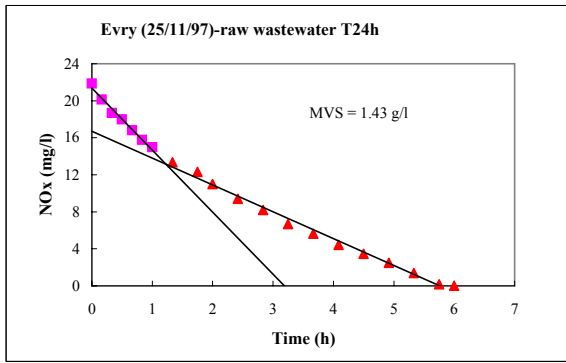


Table IV-E4: Batch data with samples from Evry WTP (25/11/97)-primary effluent-Day 1 of storage experiment						
Raw data						
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>3</sub>	N	NOx	P
0	0.0	21.9	1.6	23.5	22.9	-
10	0.2	18.5	3.4	21.9	20.5	-
20	0.3	16.3	3.7	20.0	18.5	-
30	0.5	15.1	3.7	18.8	17.3	-
40	0.7	14.3	3.6	17.9	16.5	-
50	0.8	14.0	3.6	17.6	16.2	-
60	1.0	13.1	3.5	16.6	15.2	-
80	1.3	11.7	3.3	15.0	13.7	-
105	1.8	11.2	3.0	14.2	13.0	-
120	2.0	10.3	2.7	13.0	11.9	-
145	2.4	9.1	2.3	11.4	10.5	-
170	2.8	8.4	1.8	10.2	9.5	-
195	3.3	7.6	1.3	8.9	8.4	-
220	3.7	6.8	0.9	7.7	7.3	-
245	4.1	6.1	0.6	6.7	6.5	-
270	4.5	5.3	0.3	5.6	5.5	-
295	4.9	4.6	0.0	4.6	4.6	-
320	5.3	3.6	0.0	3.6	3.6	-
345	5.8	2.8	0.0	2.8	2.8	-
360	6.0	2.4	0.0	2.4	2.4	-

Experimental conditions		
St	318	(mgO <sub>2</sub> /l)
Sf	122	(mgO <sub>2</sub> /l)
Xt	1531	(mgO <sub>2</sub> /l)
Xf	10	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.7	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0	(l)
S/X	0.21	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	13.53	

Kinetic data			
k <sub>1</sub>	-7.2	Y1	22.34
k <sub>2</sub>	-2.3	Y2	18.13
k <sub>3</sub>	-1.3	Y3	13.25
		NOx1	4.22
		NOx2	4.88
		RBCOD	65 + 75
		%RBCOD	9 + 11

E

Table IV-E5: Batch data with samples from Evry WTP (27/11/97)-raw wastewater-Day 4 of storage experiment						
Raw data						
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>3</sub>	N	NOx	P
0	0.0	20.5	2.1	22.6	21.8	-
11	0.2	16.7	4.1	20.8	19.2	-
21	0.4	14.6	4.7	19.3	17.4	-
31	0.5	13.1	5.0	18.1	16.1	-
40	0.7	12.0	5.2	17.2	15.1	-
50	0.8	11.5	5.4	16.9	14.7	-
60	1.0	10.4	5.5	15.9	13.7	-
80	1.3	8.5	5.6	14.1	11.9	-
100	1.7	6.6	5.5	12.1	9.9	-
125	2.1	4.6	5.3	9.9	7.8	-
140	2.3	3.7	5.3	9.0	6.9	-
165	2.8	2.5	4.8	7.3	5.4	-
190	3.2	1.2	4.2	5.4	3.7	-
215	3.6	0.3	3.2	3.5	2.2	-
240	4.0	0.0	1.6	1.6	1.0	-
265	4.4	0.0	0.3	0.3	0.2	-
290	4.8	14.6	0.0	14.6	14.6	-
315	5.3	13.4	0.0	13.4	13.4	-
340	5.7	12.3	0.0	12.3	12.3	-
360	6.0	11.5	0.0	11.5	11.5	-

Experimental conditions		
St	318	(mgO <sub>2</sub> /l)
Sf	99	(mgO <sub>2</sub> /l)
Xt	1851	(mgO <sub>2</sub> /l)
Xf	21	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.65	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0	(l)
S/X	0.17	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	14.61	

Kinetic data			
k <sub>1</sub>	-8.0	Y1	36.08
k <sub>2</sub>	-3.1	Y2	31.53
k <sub>3</sub>	-1.5	Y3	23.9
		NOx1	4.55
		NOx2	7.6
		RBCOD	75 + 126
		%RBCOD	11 + 19

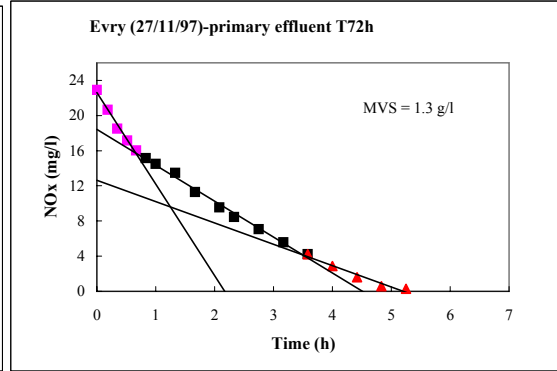
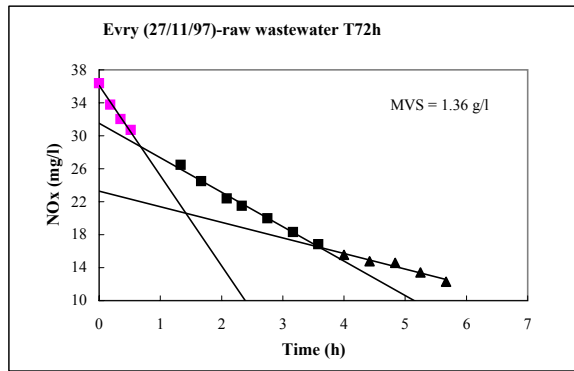


Table IV-E6: Batch data with samples from Evry WTP (27/11/97)-primary effluent-Day 4 of storage experiment						
Raw data						
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>3</sub>	N	NOx	P
0	0.0	21.6	2.2	23.8	22.9	-
11	0.2	18.5	3.6	22.1	20.7	-
21	0.4	16.1	4.0	20.1	18.5	-
31	0.5	14.7	4.1	18.8	17.2	-
40	0.7	13.5	4.2	17.7	16.0	-
50	0.8	12.7	4.1	16.8	15.2	-
60	1.0	12.1	4.0	16.1	14.5	-
80	1.3	11.2	3.8	15.0	13.5	-
100	1.7	9.3	3.3	12.6	11.3	-
125	2.1	7.8	2.9	10.7	9.5	-
140	2.3	7.0	2.4	9.4	8.4	-
165	2.8	6.0	1.8	7.8	7.1	-
190	3.2	4.8	1.3	6.1	5.6	-
215	3.6	3.8	0.7	4.5	4.2	-
240	4.0	2.7	0.3	3.0	2.9	-
265	4.4	1.6	0.0	1.6	1.6	-
290	4.8	0.6	0.0	0.6	0.6	-
315	5.3	0.3	0.0	0.3	0.3	-
340	5.7	0.0	0.0	0.0	0.0	-
360	6.0	0.0	0.0	0.0	0.0	-

Experimental conditions in reactor		
St	318	(mgO <sub>2</sub> /l)
Sf	99	(mgO <sub>2</sub> /l)
Xt	1851	(mgO <sub>2</sub> /l)
Xf	21	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.7	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0	(l)
S/X	0.17	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	13.36	

Kinetic data			
k <sub>1</sub>	-8	Y1	22.63
k <sub>2</sub>	-3.1	Y2	18.44
k <sub>3</sub>	-1.9	Y3	12.65
		NOx1	4.19
		NOx2	5.79
		RBCOD	65 + 89
		%RBCOD	9 + 13

G

Table IV-G1: Batch data with samples from Gouvieux WTP (11/09/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	23.0	0.8	23.8	23.5	5.0
10	0.2	20.6	1.2	21.8	21.3	-
20	0.3	19.1	1.5	20.6	20.0	3.0
30	0.5	17.6	1.8	19.4	18.7	-
40	0.7	16.7	2.0	18.7	17.9	2.0
50	0.8	15.7	2.0	17.7	16.9	-
60	1.0	15.1	2.0	17.1	16.3	-
80	1.3	13.7	2.0	15.7	14.9	2.0
100	1.7	12.6	1.9	14.5	13.7	-
120	2.0	11.4	1.9	13.3	12.5	-
145	2.4	10.0	1.7	11.7	11.0	-
170	2.8	8.6	1.6	10.2	9.6	-
195	3.3	7.2	1.5	8.7	8.1	-
220	3.7	6.3	1.3	7.6	7.1	-
245	4.1	5.2	1.1	6.3	5.9	-
270	4.5	4.0	0.9	4.9	4.5	-
295	4.9	3.2	0.8	4.0	3.7	-
320	5.3	2.3	0.6	2.9	2.7	-
345	5.8	1.4	0.4	1.8	1.6	-
360	6.0	0.9	0.3	1.2	1.1	2.0

Experimental conditions		
St	175	(mgO <sub>2</sub> /l)
Sf	64	(mgO <sub>2</sub> /l)
Xt	3658	(mgO <sub>2</sub> /l)
Xf	29	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.3	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.05	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	7.45	

Kinetic data			
k <sub>1</sub>	-4.7	Y1	23.23
k <sub>2</sub>	-2.0	Y2	20.29
k <sub>3</sub>	-1.3	Y3	17.2
		NOx1	2.93
		NOx2	3.09
		RBCOD	106 + 112
		%RBCOD	13 + 14

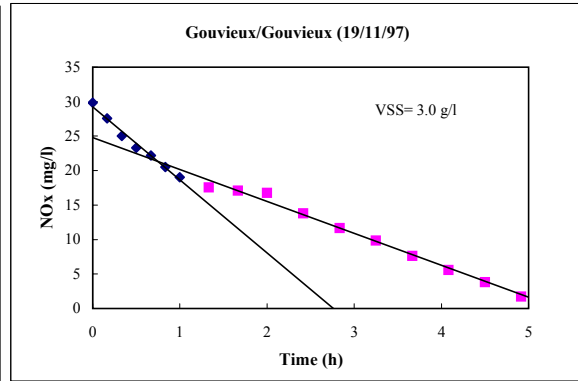
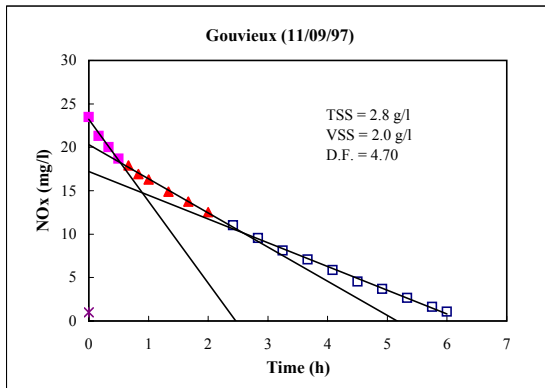


Table IV-G2: Batch data with samples from Gouvieux WTP (19/11/97)-acclimatization experiment						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	16.6	0.9	17.5	17.1	-
10	0.2	16.8	1.8	18.6	17.8	-
20	0.3	16.9	2.4	19.3	18.4	-
30	0.5	17.1	2.7	19.8	18.7	-
40	0.7	17.3	2.8	20.1	18.9	-
50	0.8	17.4	2.9	20.3	19.2	-
60	1.0	17.6	2.7	20.3	19.2	-
80	1.3	17.9	1.1	19.0	18.6	-
100	1.7	18.3	0.3	18.6	18.4	-
120	2.0	16.6	0.3	16.9	16.8	-
145	2.4	13.5	0.5	14.0	13.8	-
170	2.8	11.3	0.6	11.9	11.7	-
195	3.3	9.5	0.6	10.1	9.9	-
220	3.7	7.2	0.7	7.9	7.6	-
245	4.1	5.2	0.6	5.8	5.6	-
270	4.5	3.5	0.5	4.0	3.8	-
295	4.9	1.5	0.4	1.9	1.7	-
320	5.3	0.3	0.3	0.6	0.5	-

Experimental conditions		
St	150	(mgO <sub>2</sub> /l)
Sf	80	(mgO <sub>2</sub> /l)
Xt	3953	(mgO <sub>2</sub> /l)
Xf	19	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.3	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.04	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	8.57	

Kinetic data			
k <sub>1</sub>	-3.5	Y1	29.22
k <sub>2</sub>	-1.6	Y2	24.92
k <sub>3</sub>	-	Y3	-
		NOx1	4.29
		NOx2	-
		RBCOD	154
		%RBCOD	22



**G**

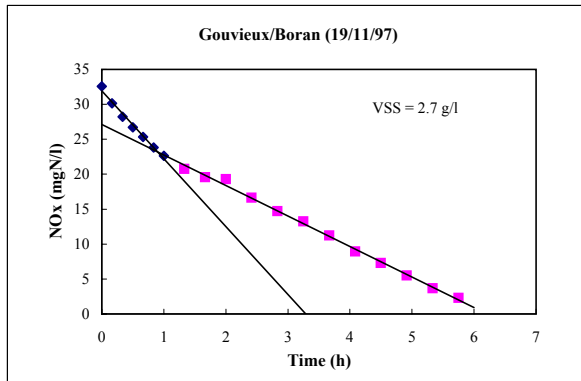
Table IV-G3: Batch data with samples from Gouvieux/Boran WTP (19/11/97)-acclimatization experiment						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	19.1	0.8	19.9	19.6	-
10	0.2	19.3	1.6	20.9	20.2	-
20	0.3	19.4	2.0	21.4	20.6	-
30	0.5	19.6	2.2	21.8	20.9	-
40	0.7	19.8	2.4	22.2	21.2	-
50	0.8	19.9	2.4	22.3	21.4	-
60	1.0	20.1	2.4	22.5	21.5	-
80	1.3	20.4	2.1	22.5	21.7	-
100	1.7	20.8	0.3	21.1	20.9	-
120	2.0	19.1	0.3	19.4	19.3	-
145	2.4	16.4	0.4	16.8	16.6	-
170	2.8	14.4	0.5	14.9	14.7	-
195	3.3	13.0	0.4	13.4	13.2	-
220	3.7	11.0	0.4	11.4	11.2	-
245	4.1	8.7	0.4	9.1	8.9	-
270	4.5	7.1	0.3	7.4	7.3	-
295	4.9	5.3	0.3	5.6	5.5	-
320	5.3	3.5	0.3	3.8	3.7	-
345	5.8	2.1	0.3	2.4	2.3	-
360	6.0	1.1	0.3	1.4	1.3	-

Experimental conditions		
St	202	(mgO <sub>2</sub> /l)
Sf	99	(mgO <sub>2</sub> /l)
Xt	3953	(mgO <sub>2</sub> /l)
Xf	20	(mgO <sub>2</sub> /l)
Vww	0.25	(l)
Vx	1.0	(l)
Vd	0.15	(l)
S/X	0.05	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	10.32	

Kinetic data			
k <sub>1</sub>	-3.6	Y1	31.92
k <sub>2</sub>	-1.6	Y2	27.13
k <sub>3</sub>	-	Y3	-
		NOx1	4.79
		NOx2	-
		RBCOD	207
		%RBCOD	18



# K

Table IV-K1: Batch data with samples from Kwa-Mashu WTP (22/07/97)-South African Treatment plant

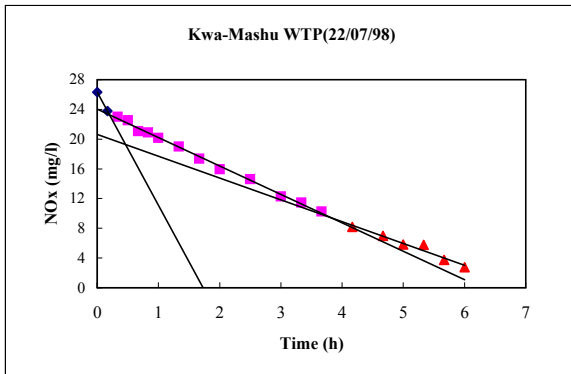
Raw data						
Time (min)	Time (h)	NO3	NO2	NOx	N	P
0	0.0	26.1	0.4	26.3	26.5	6.6
10	0.2	23.2	1.0	23.8	24.2	6.4
20	0.3	22.0	1.7	23.0	23.7	6.3
30	0.5	21.4	1.9	22.5	23.3	6.5
40	0.7	19.8	2.1	21.1	21.9	6.4
50	0.8	19.6	2.2	20.9	21.8	6.4
60	1.0	18.6	2.6	20.1	21.2	6.4
80	1.3	17.6	2.3	19.0	19.9	6.4
100	1.7	15.9	2.4	17.3	18.3	6.5
120	2.0	14.5	2.4	15.9	16.9	6.4
150	2.5	13.1	2.6	14.6	15.6	6.4
180	3.0	10.8	2.5	12.3	13.3	6.5
200	3.3	9.9	2.6	11.5	12.5	6.5
220	3.7	8.8	2.5	10.2	11.2	6.5
250	4.2	6.6	2.6	8.2	9.2	6.6
280	4.7	5.4	2.7	7.0	8.1	6.7
300	5.0	4.3	2.5	5.8	6.8	6.6
320	5.3	4.2	2.6	5.8	6.8	6.6
340	5.7	2.2	2.6	3.8	4.8	6.6
360	6.0	1.3	2.4	2.8	3.7	6.7

Experimental conditions		
St	310	(mgO <sub>2</sub> /l)
Sf	90	(mgO <sub>2</sub> /l)
Xt	2061	(mgO <sub>2</sub> /l)
Xf	54	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.5	(l)
V <sub>x</sub>	1.4	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.15	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	11.70	

Kinetic data			
k <sub>1</sub>	-7.9	Y1	26.34
k <sub>2</sub>	-2.2	Y2	24.02
k <sub>3</sub>	-1.8	Y3	20.6
		NOx1	2.32
		NOx2	3.4
		RBCOD	71 + 105
		%RBCOD	8 + 12



**L**

Table IV-L1: Batch data with samples from Laon WTP (7/08/97)

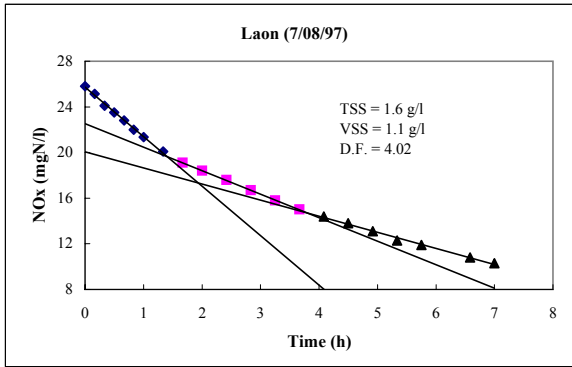
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	25.8	0.0	25.8	25.8	-
10	0.2	24.9	0.4	25.3	25.1	-
20	0.3	23.8	0.5	24.3	24.1	-
30	0.5	23.2	0.5	23.7	23.5	-
40	0.7	22.5	0.5	23.0	22.8	-
50	0.8	21.7	0.5	22.2	22.0	-
60	1.0	21.1	0.4	21.5	21.3	-
80	1.3	19.9	0.3	20.2	20.1	-
100	1.7	19.1	0.0	19.1	19.1	-
120	2.0	18.4	0.0	18.4	18.4	-
145	2.4	17.6	0.0	17.6	17.6	-
170	2.8	16.7	0.0	16.7	16.7	-
195	3.3	15.8	0.0	15.8	15.8	-
220	3.7	15.0	0.0	15.0	15.0	-
245	4.1	14.4	0.0	14.4	14.4	-
270	4.5	13.8	0.0	13.8	13.8	-
295	4.9	13.1	0.0	13.1	13.1	-
320	5.3	12.3	0.0	12.3	12.3	-
345	5.8	11.9	0.0	11.9	11.9	-
395	6.6	10.8	0.0	10.8	10.8	-
420	7.0	10.3	0.0	10.3	10.3	-

Experimental conditions		
St	163	(mgO <sub>2</sub> /l)
Sf	67	(mgO <sub>2</sub> /l)
Xt	2273	(mgO <sub>2</sub> /l)
Xf	15	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.35	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.05	(l)
S/X	0.07	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	6.32	

Kinetic data			
k <sub>1</sub>	-3.9	Y1	25.71
k <sub>2</sub>	-1.9	Y2	22.54
k <sub>3</sub>	-1.2	Y3	20.1
		NOx1	3.3
		NOx2	2.49
		RBCOD	98 + 77
		%RBCOD	15 + 12



M

Table IV-M1: Batch data with samples from Morainvilliers 1 WTP (24/02/97)-centrifuged fraction						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	20.9	1.6	22.5	21.9	-
10	0.2	18.8	2.4	21.2	20.2	-
20	0.3	16.9	2.9	19.8	18.6	-
30	0.5	15.7	3.3	19.0	17.7	-
40	0.7	13.9	3.8	17.7	16.2	-
50	0.8	12.6	4.0	16.6	15.0	-
60	1.0	11.8	4.3	16.1	14.4	-
80	1.3	9.7	4.6	14.3	12.5	-
100	1.7	7.9	4.9	12.8	10.8	-
120	2.0	6.5	5.1	11.6	9.6	-
140	2.3	5.0	5.1	10.1	8.1	-
164	2.7	3.5	5.3	8.8	6.7	-
180	3.0	2.2	5.3	7.5	5.4	-
200	3.3	1.2	5.2	6.4	4.3	-
220	3.7	0.0	4.6	4.6	2.8	-
240	4.0	0.0	3.7	3.7	2.2	-
255	4.3	0.0	2.8	2.8	1.7	-
290	4.8	0.0	1.1	1.1	0.7	-

Experimental conditions		
St	401	(mgO <sub>2</sub> /l)
Sf	105	(mgO <sub>2</sub> /l)
Xt	2796	(mgO <sub>2</sub> /l)
Xf	45	(mgO <sub>2</sub> /l)
V <sub>vw</sub>	0.72	(l)
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0	(l)
S/X	0.14	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	18.34	

Kinetic data			
k <sub>1</sub>	-4.4	Y1	21.66
k <sub>2</sub>	-2.5	Y2	17.71
k <sub>3</sub>	-1.9	Y3	9.4
		NOx1	3.95
		NOx2	8.26
		RBCOD	65 + 137
		%RBCOD	7 + 15

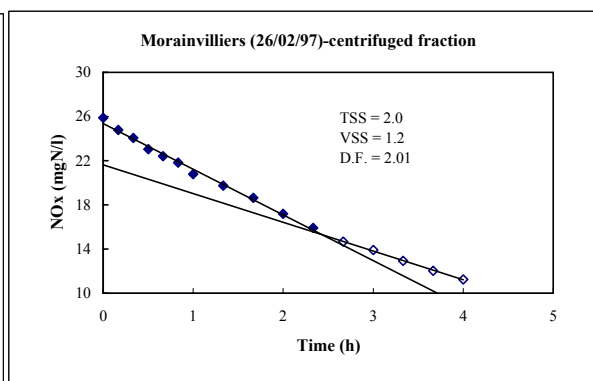
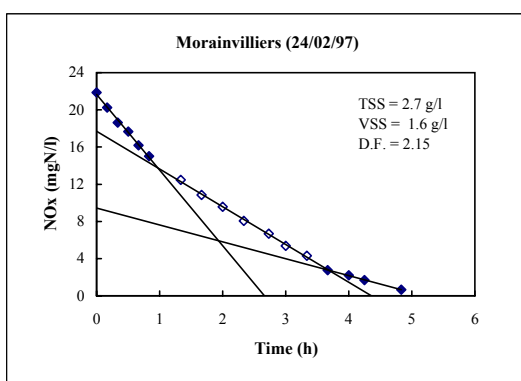


Table IV-M2: Batch data with samples from Morainvilliers 2 (26/02/97)-centrifuged fraction						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	25.4	0.8	26.2	25.9	-
10	0.2	24.0	1.3	25.3	24.8	-
20	0.3	23.1	1.6	24.7	24.1	-
30	0.5	21.9	1.9	23.8	23.0	-
40	0.7	21.2	2.0	23.2	22.4	-
50	0.8	20.5	2.2	22.7	21.8	-
60	1.0	19.4	2.3	21.7	20.8	-
80	1.3	18.3	2.4	20.7	19.7	-
100	1.7	17.2	2.4	19.6	18.6	-
120	2.0	15.8	2.3	18.1	17.2	-
140	2.3	14.6	2.2	16.8	15.9	-
160	2.7	13.4	2.1	15.5	14.7	-
180	3.0	12.7	2.0	14.7	13.9	-
200	3.3	11.8	1.9	13.7	12.9	-
220	3.7	11.0	1.7	12.7	12.0	-
240	4.0	10.3	1.6	11.9	11.3	-

Experimental conditions		
St	172	(mgO <sub>2</sub> /l)
Sf	83	(mgO <sub>2</sub> /l)
Xt	1879	(mgO <sub>2</sub> /l)
Xf	17	(mgO <sub>2</sub> /l)
V <sub>vw</sub>	0.8	(l)
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0	(l)
S/X	0.09	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	6.56	

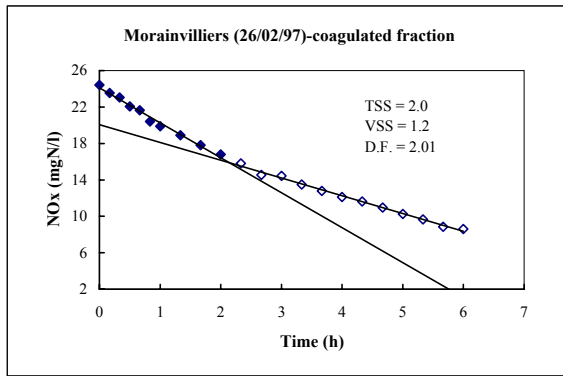
Kinetic data			
k <sub>1</sub>	-3.3	Y1	25.37
k <sub>2</sub>	-2.3	Y2	21.64
k <sub>3</sub>	-	Y3	-
		NOx1	3.73
		NOx2	-
		RBCOD	58
		%RBCOD	17

**M**

Table IV-M3: Batch data with samples from Morainvilliers 2 (24/02/97)-coagulated fraction						
Raw data						Experimental conditions
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	24.0	0.7	24.7	24.4	-
10	0.2	23.0	0.9	23.9	23.5	-
20	0.3	22.4	1.1	23.5	23.1	-
30	0.5	21.3	1.3	22.6	22.1	-
40	0.7	20.8	1.4	22.2	21.6	-
50	0.8	19.5	1.5	21.0	20.4	-
60	1.0	19.0	1.5	20.5	19.9	-
80	1.3	18.0	1.5	19.5	18.9	-
100	1.7	16.9	1.5	18.4	17.8	-
120	2.0	15.9	1.5	17.4	16.8	-
140	2.3	14.9	1.5	16.4	15.8	-
160	2.7	13.7	1.4	15.1	14.5	-
180	3.0	13.6	1.4	15.0	14.4	-
200	3.3	12.7	1.3	14.0	13.5	-
220	3.7	12.0	1.3	13.3	12.8	-
240	4.0	11.4	1.2	12.6	12.1	-
260	4.3	10.9	1.2	12.1	11.6	-
280	4.7	10.3	1.1	11.4	11.0	-
300	5.0	9.6	1.1	10.7	10.3	-
320	5.3	9.0	1.1	10.1	9.7	-
340	5.7	8.2	1.1	9.3	8.9	-
360	6.0	8.0	1.0	9.0	8.6	-

Kinetic data			
k <sub>1</sub>	-3.1	Y1	24.12
k <sub>2</sub>	-1.6	Y2	20.01
k <sub>3</sub>	-	Y3	-
		NOx1	4.11
		NOx2	-
		RBCOD	64
		%RBCOD	18



**N**

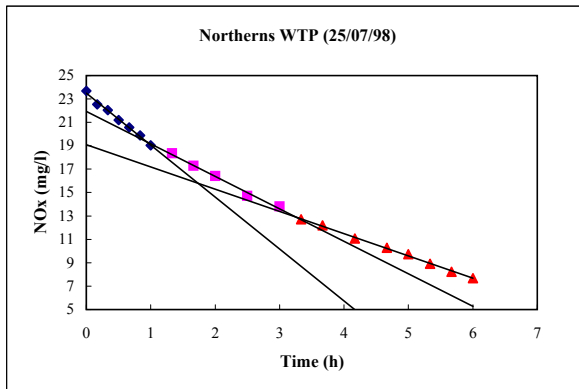
Table IV-N1: Batch data with samples from Northern WTP (25/07/98)-South African						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	23.5	0.3	23.7	23.8	6.6
10	0.2	22.2	0.6	22.5	22.8	6.6
20	0.3	21.7	0.9	22.0	22.6	6.3
30	0.5	20.7	1.1	21.2	21.8	6.0
40	0.7	19.9	1.3	20.6	21.2	5.9
50	0.8	19.1	1.5	19.9	20.6	6.0
60	1.0	18.2	1.6	19.0	19.8	5.7
80	1.3	17.4	1.8	18.3	19.1	5.7
100	1.7	16.2	2.0	17.3	18.2	5.4
120	2.0	15.2	2.0	16.4	17.2	5.4
150	2.5	13.5	2.2	14.7	15.7	5.3
180	3.0	12.5	2.3	13.8	14.8	5.0
200	3.3	11.3	2.5	12.7	13.8	5.1
220	3.7	10.7	2.5	12.2	13.2	5.2
250	4.2	9.6	2.7	11.1	12.2	5.0
280	4.7	8.7	2.8	10.3	11.4	5.3
300	5.0	8.1	2.8	9.7	10.8	5.1
320	5.3	7.3	2.8	8.9	10.1	5.1
340	5.7	6.6	2.9	8.2	9.5	5.1
360	6.0	6.0	2.9	7.7	8.9	5.1

Experimental conditions		
St	251	(mgO <sub>2</sub> /l)
Sf	90	(mgO <sub>2</sub> /l)
Xt	2419	(mgO <sub>2</sub> /l)
Xf	51	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.5	(l)
V <sub>x</sub>	1.4	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.10	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	10.54	

Kinetic data			
k <sub>1</sub>	-2.8	Y1	23.51
k <sub>2</sub>	-1.9	Y2	21.95
k <sub>3</sub>	-1.3	Y3	19.1
		NOx1	1.56
		NOx2	2.86
		RBCOD	48 + 88
		%RBCOD	7 + 13



O

Table IV-O1: Batch data with samples from Orense WTP (18/05/97)-raw wastewater						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	29.7	0.0	29.7	29.7	-
10	0.2	25.5	0.0	25.5	25.5	-
20	0.3	24.8	0.0	24.8	24.8	-
30	0.5	24.1	0.0	24.1	24.1	-
42	0.7	23.4	0.0	23.4	23.4	-
52	0.9	22.6	0.0	22.6	22.6	-
65	1.1	21.6	0.0	21.6	21.6	-
85	1.4	20.3	0.0	20.3	20.3	-
110	1.8	19.0	0.0	19.0	19.0	-
135	2.3	17.2	0.0	17.2	17.2	-
160	2.7	15.6	0.0	15.6	15.6	-
185	3.1	14.7	0.0	14.7	14.7	-
210	3.5	13.8	0.0	13.8	13.8	-
235	3.9	12.6	0.0	12.6	12.6	-
260	4.3	11.4	0.0	11.4	11.4	-
285	4.8	10.5	0.0	10.5	10.5	-
310	5.2	9.7	0.0	9.7	9.7	-
325	5.4	9.1	0.0	9.1	9.1	-
340	5.7	8.5	0.0	8.5	8.5	-
360	6.0	7.7	0.0	7.7	7.7	-

Experimental conditions	
St	145 (mgO <sub>2</sub> /l)
Sf	26 (mgO <sub>2</sub> /l)
Xt	1952 (mgO <sub>2</sub> /l)
Xf	24 (mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.5 (l)
V <sub>x</sub>	1.0 (l)
V <sub>d</sub>	0 (l)
S/X	0.07 (mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	4.88

Kinetic data			
k <sub>1</sub>	-21.0	Y1	29.7
k <sub>2</sub>	-3.2	Y2	26.05
k <sub>3</sub>	-2.0	Y3	22.0
		NOx1	3.65
		NOx2	4.05
		RBCOD	79 + 88
		%RBCOD	19 + 21

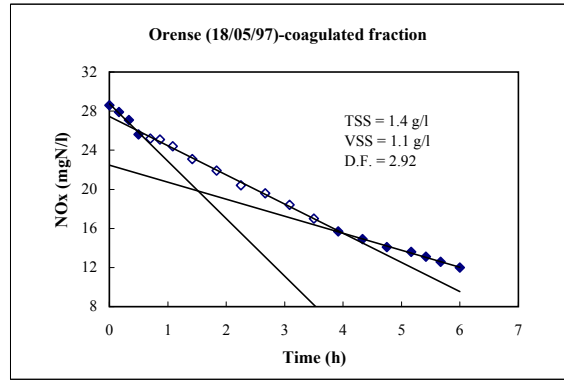
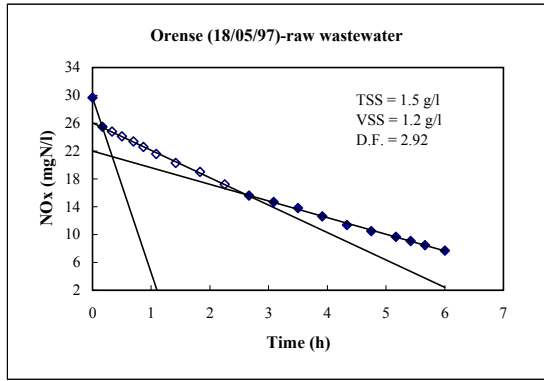


Table IV-O2 :Batch data with samples from Orense (18/05/97)-coagulated fraction						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	28.6	0.0	28.6	28.6	-
10	0.2	27.9	0.0	27.9	27.9	-
20	0.3	27.1	0.0	27.1	27.1	-
30	0.5	25.6	0.0	25.6	25.6	-
42	0.7	25.2	0.0	25.2	25.2	-
52	0.9	25.1	0.0	25.1	25.1	-
65	1.1	24.4	0.0	24.4	24.4	-
85	1.4	23.1	0.0	23.1	23.1	-
110	1.8	21.9	0.0	21.9	21.9	-
135	2.3	20.4	0.0	20.4	20.4	-
160	2.7	19.6	0.0	19.6	19.6	-
185	3.1	18.4	0.0	18.4	18.4	-
210	3.5	17.0	0.0	17.0	17.0	-
235	3.9	15.7	0.0	15.7	15.7	-
260	4.3	14.9	0.0	14.9	14.9	-
285	4.8	14.1	0.0	14.1	14.1	-
310	5.2	13.6	0.0	13.6	13.6	-
325	5.4	13.1	0.0	13.1	13.1	-
340	5.7	12.6	0.0	12.6	12.6	-
360	6.0	12	0.0	12.0	12.0	-

Experimental conditions	
St	145 (mgO <sub>2</sub> /l)
Sf	26 (mgO <sub>2</sub> /l)
Xt	1952 (mgO <sub>2</sub> /l)
Xf	24 (mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.5 (l)
V <sub>x</sub>	1 (l)
V <sub>d</sub>	0 (l)
S/X	0.07 (mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	5.07

Kinetic data			
k <sub>1</sub>	-5.3	Y1	28.8
k <sub>2</sub>	-2.7	Y2	27.4
k <sub>3</sub>	-1.5	Y3	22.47
		NOx1	1.32
		NOx2	4.97
		RBCOD	29 + 108
		%RBCOD	7 + 26

**P**

Table IV-P1: Batch data with samples from Plaisir WTP (25/02/97)-centrifuged fraction

Raw data							Experimental conditions								
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>3</sub>	N	NOx	P	St	Sf	Xt	Xf	Vvw	Vx	Vd	S/X	C/N
0	0.0	20.4	0.6	21.0	20.8	-	259 (mgO <sub>2</sub> /l)	77 (mgO <sub>2</sub> /l)	2001 (mgO <sub>2</sub> /l)	8 (mgO <sub>2</sub> /l)	0.6 (l)	1.1 (l)	0 (l)	0.13 (mgO <sub>2</sub> /mgO <sub>2</sub> )	12.48
10	0.2	18.8	0.9	19.7	19.3	-									
20	0.3	17.5	1.1	18.6	18.2	-									
30	0.5	16.4	1.2	17.6	17.1	-									
40	0.7	15.5	1.3	16.8	16.3	-									
50	0.8	14.8	1.3	16.1	15.6	-									
60	1.0	13.9	1.4	15.3	14.7	-									
80	1.3	12.6	1.2	13.8	13.3	-									
100	1.7	11.4	1.0	12.4	12.0	-									
120	2.0	10.5	0.9	11.4	11.0	-									
140	2.3	9.3	0.7	10.0	9.7	-									
160	2.7	8.5	0.6	9.1	8.9	-									
180	3.0	7.8	0.5	8.3	8.1	-									
200	3.3	7.0	0.4	7.4	7.2	-									
220	3.7	6.1	0.4	6.5	6.3	-									
240	4.0	5.4	0.3	5.7	5.6	-									

Kinetic data			
k <sub>1</sub>	-4.2	Y1	20.45
k <sub>2</sub>	-2.2	Y2	15.54
k <sub>3</sub>	-	Y3	-
		NOx1	5.2
		NOx2	
		RBCOD	108
		%RBCOD	16

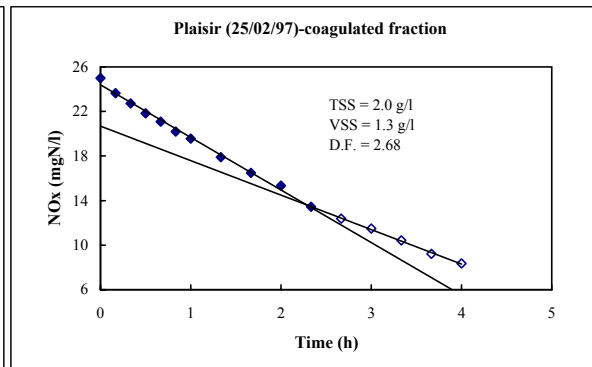
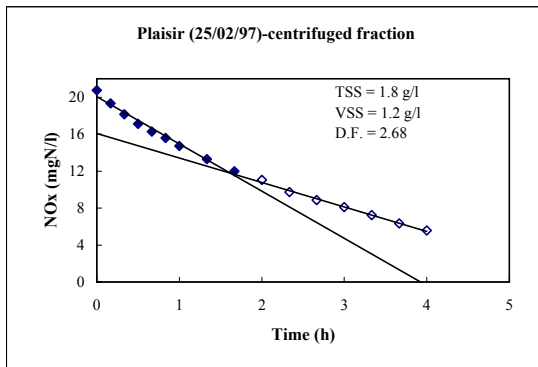


Table IV-P2: Batch data with samples from Plaisir (25/02/97)-coagulated fraction

Raw data							Experimental conditions								
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>3</sub>	N	NOx	P	St	Sf	Xt	Xf	Vvw	Vx	Vd	S/X	C/N
0	0.0	24.7	0.5	25.2	25.0	-	(mgO <sub>2</sub> /l)	(mgO <sub>2</sub> /l)	(mgO <sub>2</sub> /l)	(mgO <sub>2</sub> /l)	(l)	(l)	(l)	#DIV/0! (mgO <sub>2</sub> /mgO <sub>2</sub> )	0.00
10	0.2	23.1	0.9	24.0	23.6	-									
20	0.3	22.0	1.2	23.2	22.7	-									
30	0.5	21.0	1.4	22.4	21.8	-									
40	0.7	20.2	1.5	21.7	21.1	-									
50	0.8	19.3	1.5	20.8	20.2	-									
60	1.0	18.6	1.6	20.2	19.6	-									
80	1.3	17.0	1.5	18.5	17.9	-									
100	1.7	15.6	1.5	17.1	16.5	-									
120	2.0	14.5	1.4	15.9	15.3	-									
140	2.3	12.6	1.4	14.0	13.4	-									
160	2.7	11.6	1.3	12.9	12.4	-									
180	3.0	10.7	1.3	12.0	11.5	-									
200	3.3	9.7	1.2	10.9	10.4	-									
220	3.7	8.5	1.2	9.7	9.2	-									
240	4.0	7.7	1.1	8.8	8.4	-									

Kinetic data			
k <sub>1</sub>	-3.6	Y1	24.78
k <sub>2</sub>	-2.4	Y2	20.67
k <sub>3</sub>	-	Y3	-
		NOx1	4.3
		NOx2	-
		RBCOD	89
		%RBCOD	13



R

Table IV-R1: Batch data with samples from Rostock WTP (17/03/97)-raw wastewater						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	31.3	0.3	31.6	31.5	-
10	0.2	27.5	0.6	28.1	27.9	-
20	0.3	25.2	1.1	26.3	25.9	-
30	0.5	24.0	1.3	25.3	24.8	-
40	0.7	22.7	1.3	24.0	23.5	-
50	0.8	21.5	1.3	22.8	22.3	-
60	1.0	20.5	1.2	21.7	21.2	-
70	1.2	19.3	1.2	20.5	20.0	-
90	1.5	18.0	1.1	19.1	18.7	-
110	1.8	16.7	0.9	17.6	17.2	-
130	2.2	15.2	0.8	16.0	15.7	-
150	2.5	13.9	0.7	14.6	14.3	-
170	2.8	12.8	0.4	13.2	13.0	-
190	3.2	12.8	0.0	12.8	12.8	-
210	3.5	11.7	0.4	12.1	11.9	-
230	3.8	10.4	0.4	10.8	10.6	-
250	4.2	9.5	0.4	9.9	9.7	-
270	4.5	8.3	0.4	8.7	8.5	-
290	4.8	7.2	0.4	7.6	7.4	-
310	5.2	8.5	0.4	8.9	8.7	-
330	5.5	7.8	0.3	8.1	8.0	-
350	5.8	7.3	0.4	7.7	7.5	-
370	6.2	6.4	0.4	6.8	6.6	-
385	6.4	6	0.4	6.4	6.2	-
400	6.7	5.3	0.4	5.7	5.5	-

Experimental conditions			
St	298	(mgO <sub>2</sub> /l)	
Sf	81	(mgO <sub>2</sub> /l)	
Xt	2445	(mgO <sub>2</sub> /l)	
Xf	46	(mgO <sub>2</sub> /l)	
V <sub>ww</sub>	0.5	(l)	
V <sub>x</sub>	1.1	(l)	
V <sub>d</sub>	0	(l)	
S/X	0.12	(mgO <sub>2</sub> /mgO <sub>2</sub> )	
C/N	9.47		

Kinetic data			
k <sub>1</sub>	-13.6	Y1	31.5
k <sub>2</sub>	-4.4	Y2	25
k <sub>3</sub>	-2.6	Y3	17.9
k <sub>4</sub>	-1.1	NOx1	6.48
		NOx2	7.12
		RBCOD	161 + 176
		%RBCOD	17 + 18

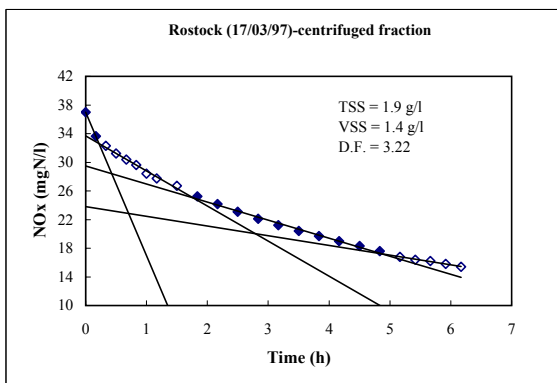
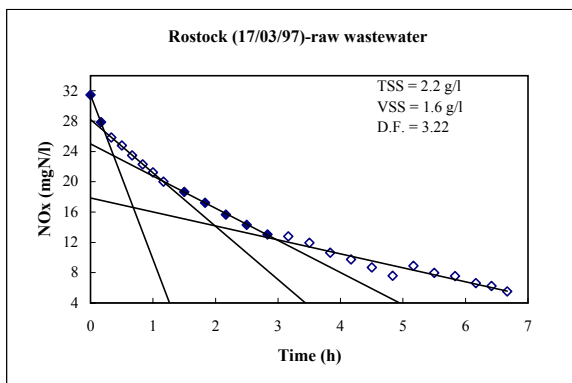


Table IV-R2: Batch data with samples from Rostock (17/03/97)-centrifuged fraction						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	36.8	0.3	37.1	37.0	-
10	0.2	33.4	0.4	33.8	33.6	-
20	0.3	31.8	0.8	32.6	32.3	-
30	0.5	30.7	0.9	31.6	31.2	-
40	0.7	29.9	0.8	30.7	30.4	-
50	0.8	29.2	0.7	29.9	29.6	-
60	1.0	28.0	0.7	28.7	28.4	-
70	1.2	27.4	0.6	28.0	27.8	-
90	1.5	26.4	0.5	26.9	26.7	-
110	1.8	25.0	0.4	25.4	25.2	-
130	2.2	24.0	0.3	24.3	24.2	-
150	2.5	23.1	0.0	23.1	23.1	-
170	2.8	22.1	0.0	22.1	22.1	-
190	3.2	21.2	0.0	21.2	21.2	-
210	3.5	20.4	0.0	20.4	20.4	-
230	3.8	19.7	0.0	19.7	19.7	-
250	4.2	19.0	0.0	19.0	19.0	-
270	4.5	18.3	0.0	18.3	18.3	-
290	4.8	17.6	0.0	17.6	17.6	-
310	5.2	16.8	0.0	16.8	16.8	-
325	5.4	16.4	0.0	16.4	16.4	-
340	5.7	16.2	0.0	16.2	16.2	-
355	5.9	15.8	0.0	15.8	15.8	-
370	6.2	15.4	0.0	15.4	15.4	-

Experimental conditions			
St	298	(mgO <sub>2</sub> /l)	
Sf	81	(mgO <sub>2</sub> /l)	
Xt	2445	(mgO <sub>2</sub> /l)	
Xf	46	(mgO <sub>2</sub> /l)	
V <sub>ww</sub>	0.5	(l)	
V <sub>x</sub>	1.1	(l)	
V <sub>d</sub>	0	(l)	
S/X	0.12	(mgO <sub>2</sub> /mgO <sub>2</sub> )	
C/N	8.03		

Kinetic data			
k <sub>1</sub>	-14.3	Y1	36.98
k <sub>2</sub>	-3.5	Y2	29.5
k <sub>3</sub>	-1.8	Y3	23.8
k <sub>4</sub>	-1	NOx1	7.51
		NOx2	5.64
		RBCOD	186 + 140
		%RBCOD	19 + 15

## R

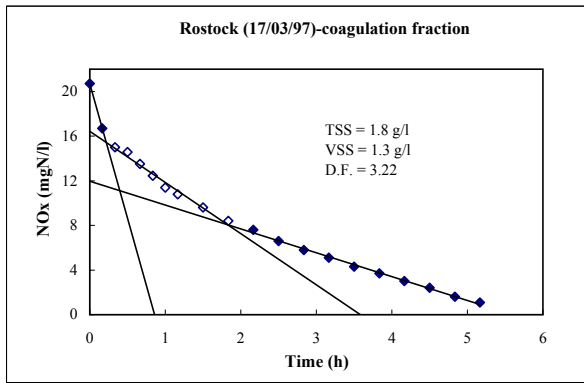
Table IV-R3: Batch data with samples from Rostock WTP (17/03/97)- coagulated fraction						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	20.7	0.0	20.7	20.7	-
10	0.2	16.5	0.3	16.8	16.7	-
20	0.3	14.7	0.5	15.2	15.0	-
30	0.5	14.2	0.6	14.8	14.6	-
40	0.7	13.2	0.5	13.7	13.5	-
50	0.8	12.2	0.4	12.6	12.4	-
60	1.0	11.2	0.3	11.5	11.4	-
70	1.2	10.6	0.3	10.9	10.8	-
90	1.5	9.6	0.0	9.6	9.6	-
110	1.8	8.4	0.0	8.4	8.4	-
130	2.2	7.6	0.0	7.6	7.6	-
150	2.5	6.6	0.0	6.6	6.6	-
170	2.8	5.8	0.0	5.8	5.8	-
190	3.2	5.1	0.0	5.1	5.1	-
210	3.5	4.3	0.0	4.3	4.3	-
230	3.8	3.7	0.0	3.7	3.7	-
250	4.2	3.0	0.0	3.0	3.0	-
270	4.5	2.4	0.0	2.4	2.4	-
290	4.8	1.6	0.0	1.6	1.6	-
310	5.2	1.1	0.0	1.1	1.1	-

Experimental conditions	
St	298 (mgO <sub>2</sub> /l)
Sf	81 (mgO <sub>2</sub> /l)
Xt	2445 (mgO <sub>2</sub> /l)
Xf	46 (mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.5 (l)
V <sub>x</sub>	1.1 (l)
V <sub>d</sub>	0 (l)
S/X	0.12 (mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	14.40

Kinetic data			
k <sub>1</sub>	-18.5	Y1	20.7
k <sub>2</sub>	-3.5	Y2	16.4
k <sub>3</sub>	1.6	Y3	11.9
		NOx1	4.3
		NOx2	4.5
		RBCOD	105 + 112
		%RBCOD	11 + 12



S

Table IV-S1: Batch data with samples from Samaritaine 1 WTP (23/04/97)-raw wastewater						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	27.5	0.5	28.0	27.8	-
25	0.4	25.0	1.1	26.1	25.7	-
35	0.6	23.5	1.1	24.6	24.2	-
45	0.8	23.4	1.2	24.6	24.1	-
60	1.0	22.3	1.2	23.5	23.0	-
85	1.4	20.3	1.1	21.4	21.0	-
110	1.8	#N/A	#N/A	#N/A	#N/A	-
135	2.3	17.1	0.9	18.0	17.6	-
155	2.6	16.2	0.8	17.0	16.7	-
175	2.9	15.0	0.8	15.8	15.5	-
195	3.3	13.9	0.7	14.6	14.3	-
215	3.6	12.9	0.7	13.6	13.3	-
235	3.9	11.9	0.6	12.5	12.3	-
255	4.3	10.9	0.6	11.5	11.3	-

Experimental conditions	
St	216 (mgO <sub>2</sub> /l)
Sf	85 (mgO <sub>2</sub> /l)
Xt	2451 (mgO <sub>2</sub> /l)
Xf	12 (mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.35 (l)
V <sub>x</sub>	1.0 (l)
V <sub>d</sub>	0.05 (l)
S/X	0.09 (mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	7.77

Kinetic data			
k <sub>1</sub>	-3.8	Y1	27.56
k <sub>2</sub>	-2.7	Y2	24.92
k <sub>3</sub>	-	Y3	-
		NO <sub>x</sub> 1	2.64
		NO <sub>x</sub> 2	-
		RBCOD	85
		%RBCOD	9

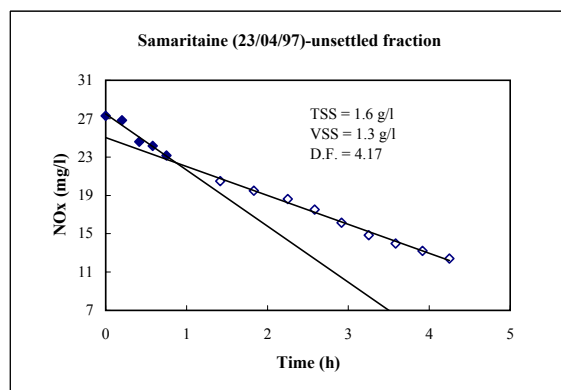
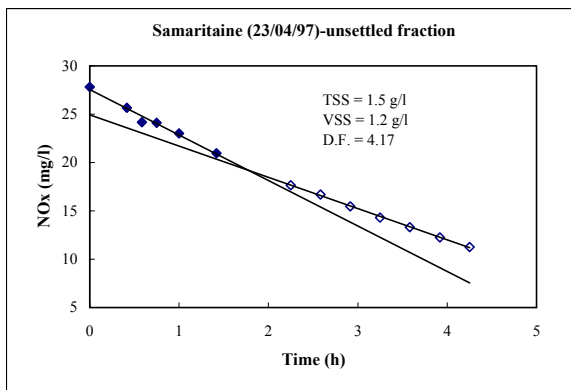


Table IV-S2: Batch data with samples from Samaritaine 1 (23/04/97)-unsettled fraction						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	27.0	0.5	27.5	27.3	-
12	0.2	26.3	0.9	27.2	26.8	-
25	0.4	24.0	1.0	25.0	24.6	-
35	0.6	23.5	1.1	24.6	24.2	-
45	0.8	22.5	1.1	23.6	23.2	-
85	1.4	20.5	0.0	20.5	20.5	-
110	1.8	19.0	0.8	19.8	19.5	-
135	2.3	18.2	0.7	18.9	18.6	-
155	2.6	17.1	0.7	17.8	17.5	-
175	2.9	15.8	0.6	16.4	16.2	-
195	3.3	14.5	0.6	15.1	14.9	-
215	3.6	13.6	0.6	14.2	14.0	-
235	3.9	12.9	0.5	13.4	13.2	-
255	4.3	12.1	0.5	12.6	12.4	-

Experimental conditions	
St	216 (mgO <sub>2</sub> /l)
Sf	85 (mgO <sub>2</sub> /l)
Xt	2451 (mgO <sub>2</sub> /l)
Xf	12 (mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.35 (l)
V <sub>x</sub>	1 (l)
V <sub>d</sub>	0.05 (l)
S/X	0.09 (mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	7.85

Kinetic data			
k <sub>1</sub>	-4.3	Y1	27.49
k <sub>2</sub>	-2.3	Y2	25.01
k <sub>3</sub>	-	Y3	-
		NO <sub>x</sub> 1	2.48
		NO <sub>x</sub> 2	-
		RBCOD	80
		%RBCOD	9

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Table IV-S3: Batch data with samples from Samaritaine 2 WTP (25/04/97)-raw wastewater						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	27.8	0.4	28.2	28.0	-
20	0.3	22.5	1.0	23.5	23.1	-
30	0.5	21.0	1.0	22.0	21.6	-
40	0.7	18.8	1.0	19.8	19.4	-
60	1.0	18.0	0.9	18.9	18.5	-
85	1.4	17.8	0.8	18.6	18.3	-
110	1.8	15.5	0.7	16.2	15.9	-
135	2.3	14.0	0.6	14.6	14.4	-
160	2.7	11.8	0.5	12.3	12.1	-
185	3.1	10.0	0.5	10.5	10.3	-
210	3.5	9.0	0.4	9.4	9.2	-
235	3.9	7.4	0.5	7.9	7.7	-
260	4.3	6.1	0.4	6.5	6.3	-
285	4.8	4.5	0.4	4.9	4.7	-
310	5.2	3.1	0.4	3.5	3.3	-
325	5.4	2.4	0.3	2.7	2.6	-
340	5.7	1.6	0.3	1.9	1.8	-

Experimental conditions		
St	180	(mgO <sub>2</sub> /l)
Sf	75	(mgO <sub>2</sub> /l)
Xt	2404	(mgO <sub>2</sub> /l)
Xf	12	(mgO <sub>2</sub> /l)
V <sub>vw</sub>	0.35	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.07	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	6.42	

Kinetic data			
k <sub>1</sub>	-8.3	Y1	27.85
k <sub>2</sub>	-2.7	Y2	23.3
k <sub>3</sub>	-2.2	Y3	21.1
		NOx1	4.55
		NOx2	2.24
		RBCOD	146 + 72
		%RBCOD	19 + 9

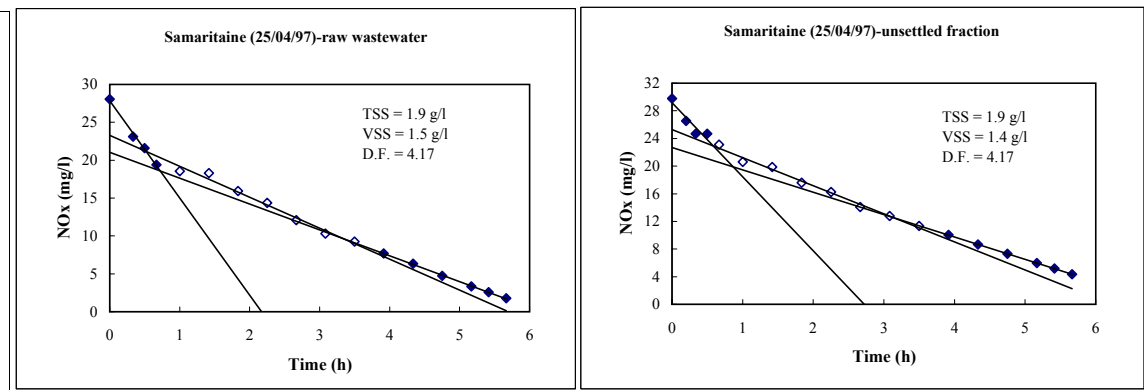


Table IV-S4: Batch data with samples from Samaritaine 2 (25/04/97)-unsettled fraction						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	29.5	0.5	30.0	29.8	-
12	0.2	26.0	0.9	26.9	26.5	-
20	0.3	24.0	1.1	25.1	24.7	-
30	0.5	24.0	1.1	25.1	24.7	-
40	0.7	22.5	1.0	23.5	23.1	-
60	1.0	20.0	1.0	21.0	20.6	-
85	1.4	19.4	0.8	20.2	19.9	-
110	1.8	17.2	0.7	17.9	17.6	-
135	2.3	15.9	0.6	16.5	16.3	-
160	2.7	13.8	0.5	14.3	14.1	-
185	3.1	12.5	0.5	13.0	12.8	-
210	3.5	11.1	0.4	11.5	11.3	-
235	3.9	9.8	0.4	10.2	10.0	-
260	4.3	8.4	0.4	8.8	8.6	-
285	4.8	7.1	0.4	7.5	7.3	-
310	5.2	5.8	0.3	6.1	6.0	-
325	5.4	5.0	0.3	5.3	5.2	-
340	5.7	4.1	0.4	4.5	4.3	-

Experimental conditions		
St	180	(mgO <sub>2</sub> /l)
Sf	75	(mgO <sub>2</sub> /l)
Xt	2404	(mgO <sub>2</sub> /l)
Xf	12	(mgO <sub>2</sub> /l)
V <sub>vw</sub>	0.35	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.07	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	6.00	

Kinetic data			
k <sub>1</sub>	-7.6	Y1	29.18
k <sub>2</sub>	-2.9	Y2	25.3
k <sub>3</sub>	-2.3	Y3	22.71
		NOx1	3.88
		NOx2	2.58
		RBCOD	125 + 83
		%RBCOD	17 + 11

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Table IV-S5: Batch data with samples from Samaritaine 3 WTP (28/04/97)-raw wastewater						
Raw data						
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	26.7	0.3	27.0	26.9	-
10	0.2	24.5	0.6	25.1	24.9	-
20	0.3	23.1	0.7	23.8	23.5	-
30	0.5	21.6	0.8	22.4	22.1	-
40	0.7	20.9	0.9	21.8	21.4	-
60	1.0	19.3	1.0	20.3	19.9	-
85	1.4	17.1	1.0	18.1	17.7	-
110	1.8	14.7	1.0	15.7	15.3	-
135	2.3	13.1	1.0	14.1	13.7	-
160	2.7	11.5	1.0	12.5	12.1	-
185	3.1	9.8	1.0	10.8	10.4	-
210	3.5	8.2	1.0	9.2	8.8	-
235	3.9	6.6	1.0	7.6	7.2	-
260	4.3	5.8	0.0	5.8	5.8	-
285	4.8	4.3	0.9	5.2	4.8	-
300	5.0	3.5	0.9	4.4	4.0	-
315	5.3	2.9	0.8	3.7	3.4	-
340	5.7	2.1	0.8	2.9	2.6	-

Experimental conditions		
St	197	(mgO <sub>2</sub> /l)
Sf	69	(mgO <sub>2</sub> /l)
Xt	2397	(mgO <sub>2</sub> /l)
Xf	14	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.4	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.05	(l)
S/X	0.08	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	7.33	

Kinetic data			
k <sub>1</sub>	-5.8	Y1	26.49
k <sub>2</sub>	-3.0	Y2	23.65
k <sub>3</sub>	1.8	Y3	16.5
		NO <sub>x1</sub>	2.84
		NO <sub>x2</sub>	7.14
		RBCOD	80 + 201
		%RBCOD	11 + 26

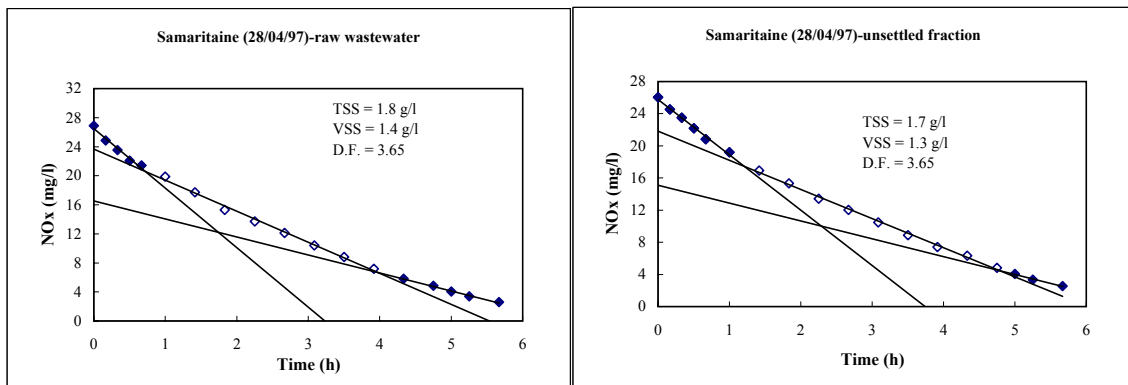


Table IV-S6: Batch data with samples from Samaritaine 3 WTP (28/04/97)-unsettled fraction						
Raw data						
Time (min)	Time (h)	NO <sub>2</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	25.8	0.4	26.2	26.0	-
10	0.2	24.1	0.7	24.8	24.5	-
20	0.3	23.0	0.8	23.8	23.5	-
30	0.5	21.7	0.8	22.5	22.2	-
40	0.7	20.3	0.9	21.2	20.8	-
60	1.0	18.6	1.0	19.6	19.2	-
85	1.4	16.4	0.9	17.3	16.9	-
110	1.8	14.8	0.9	15.7	15.3	-
135	2.3	12.9	0.9	13.8	13.4	-
160	2.7	11.5	0.9	12.4	12.0	-
185	3.1	10.0	0.8	10.8	10.5	-
210	3.5	8.4	0.8	9.2	8.9	-
235	3.9	7.0	0.7	7.7	7.4	-
260	4.3	5.9	0.7	6.6	6.3	-
285	4.8	4.4	0.7	5.1	4.8	-
300	5.0	3.7	0.6	4.3	4.1	-
315	5.3	3.0	0.6	3.6	3.4	-
340	5.7	2.2	0.6	2.8	2.6	-

Experimental conditions		
St	197	(mgO <sub>2</sub> /l)
Sf	69	(mgO <sub>2</sub> /l)
Xt	2397	(mgO <sub>2</sub> /l)
Xf	14	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.4	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.05	(l)
S/X	0.08	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	7.52	

Kinetic data			
k <sub>1</sub>	-5.3	Y1	25.77
k <sub>2</sub>	-2.8	Y2	21.82
k <sub>3</sub>	-1.7	Y3	15.09
		NO <sub>x1</sub>	3.95
		NO <sub>x2</sub>	6.74
		RBCOD	111 + 189
		%RBCOD	15 + 26

**S**

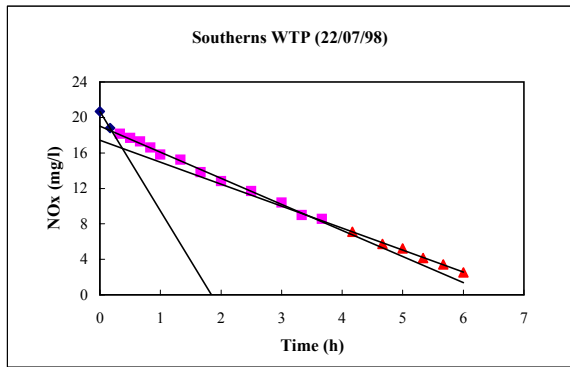
Table IV-S7: Batch data with samples from Southern WTP (28/04/97)-raw wastewater(South African)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	NO <sub>x</sub>	N	P
0	0.0	20.3	0.7	20.7	21.0	6.1
10	0.2	18.2	1.0	18.8	19.2	6.0
20	0.3	17.5	1.1	18.1	18.6	6.0
30	0.5	17.1	1.2	17.7	18.2	6.0
40	0.7	16.6	1.3	17.3	17.9	6.1
50	0.8	15.9	1.4	16.6	17.2	6.2
60	1.0	15.0	1.4	15.8	16.4	6.1
80	1.3	14.4	1.6	15.2	16.0	6.1
100	1.7	12.8	1.5	13.8	14.4	5.8
120	2.0	11.9	1.8	12.8	13.7	6.2
150	2.5	10.6	2.0	11.7	12.6	6.2
180	3.0	9.2	2.1	10.4	11.3	6.2
200	3.3	7.7	2.1	9.0	9.9	6.2
220	3.7	7.3	2.1	8.5	9.4	6.3
250	4.2	5.8	2.2	7.1	8.0	6.3
280	4.7	4.4	2.3	5.7	6.7	6.4
300	5.0	3.9	2.1	5.2	6.0	6.4
320	5.3	2.9	2.2	4.1	5.0	6.5
340	5.7	2.1	2.2	3.4	4.3	6.5
360	6.0	1.2	2.1	2.5	3.3	6.6

Experimental conditions		
St	267	(mgO <sub>2</sub> /l)
Sf	106	(mgO <sub>2</sub> /l)
Xt	3049	(mgO <sub>2</sub> /l)
Xf	37	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.6	(l)
V <sub>x</sub>	1.4	(l)
V <sub>d</sub>	0	(l)
S/X	0.09	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	12.74	

Kinetic data			
k <sub>1</sub>	-4.9	Y1	20.68
k <sub>2</sub>	-1.4	Y2	19.03
k <sub>3</sub>	-1.1	Y3	17.4
		NO <sub>x1</sub>	1.65
		NO <sub>x2</sub>	1.61
		RBCOD	42 + 41
		%RBCOD	7 + 7



T

Table IV-T1: Batch data with samples from Thiverval 1 WTP (17/07/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	14.4	0.0	14.4	14.4	4.2
10	0.2	13.6	0.0	13.6	13.6	-
20	0.3	12.8	0.0	12.8	12.8	4.4
30	0.5	12.3	0.0	12.3	12.3	-
40	0.7	12.0	0.0	12.0	12.0	4.4
50	0.8	11.7	0.0	11.7	11.7	-
60	1.0	11.2	0.0	11.2	11.2	4.4
80	1.3	10.6	0.0	10.6	10.6	-
100	1.7	10.1	0.0	10.1	10.1	-
120	2.0	9.5	0.0	9.5	9.5	4.3
145	2.4	8.8	0.0	8.8	8.8	-
170	2.8	8.2	0.0	8.2	8.2	-
195	3.3	7.6	0.0	7.6	7.6	4.1
220	3.7	7.1	0.0	7.1	7.1	-
245	4.1	6.6	0.0	6.6	6.6	4.3
270	4.5	6.1	0.0	6.1	6.1	-
290	4.8	5.6	0.0	5.6	5.6	-
310	5.2	5.3	0.0	5.3	5.3	4.1
330	5.5	4.9	0.0	4.9	4.9	-
345	5.8	4.6	0.0	4.6	4.6	-
360	6.0	4.4	0.0	4.4	4.4	4.3

Experimental conditions		
St	94	(mgO <sub>2</sub> /l)
Sf	30	(mgO <sub>2</sub> /l)
Xt	3008	(mgO <sub>2</sub> /l)
Xf	45	(mgO <sub>2</sub> /l)
V <sub>vw</sub>	0.3	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.03	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	6.53	

Kinetic data			
k <sub>1</sub>	-2.6	Y1	14.4
k <sub>2</sub>	-1.0	Y2	13.16
k <sub>3</sub>	-0.6	Y3	11.5
		NOx1	1.24
		NOx2	1.63
		RBCOD	45 + 59
		%RBCOD	10 + 13

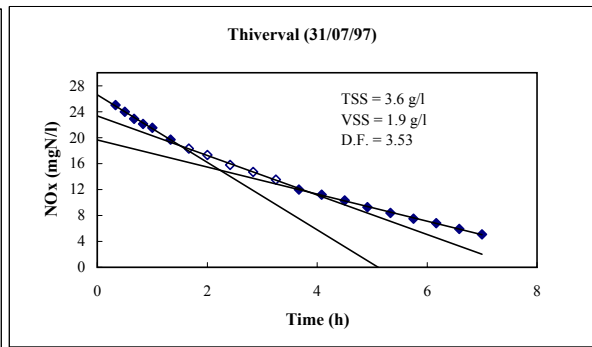
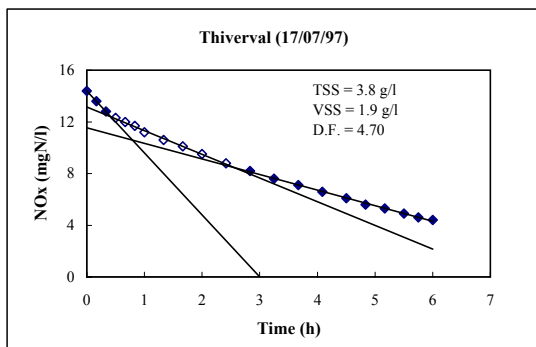


Table IV-T2: Batch data with samples from Thiverval (31/07/97)						
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NOx	P
0	0.0	24.5	0.4	24.9	24.7	6.0
10	0.2	-	0.6	#VALUE!	#VALUE!	6.5
20	0.3	24.3	0.7	25.0	24.7	7.5
30	0.5	23.3	0.7	24.0	23.7	8.0
40	0.7	22.2	0.7	22.9	22.6	8.0
50	0.8	21.5	0.6	22.1	21.9	7.5
60	1.0	20.9	0.6	21.5	21.3	7.5
80	1.3	19.2	0.5	19.7	19.5	7.0
100	1.7	17.8	0.5	18.3	18.1	7.0
120	2.0	16.9	0.4	17.3	17.1	6.5
145	2.4	15.5	0.3	15.8	15.7	6.5
170	2.8	14.4	0.3	14.7	14.6	6.0
195	3.3	13.2	0.3	13.5	13.4	6.0
220	3.7	12.0	0.0	12.0	12.0	5.5
245	4.1	11.2	0.0	11.2	11.2	5.5
270	4.5	10.3	0.0	10.3	10.3	5.5
295	4.9	9.3	0.0	9.3	9.3	5.5
320	5.3	8.4	0.0	8.4	8.4	5.5
345	5.8	7.5	0.0	7.5	7.5	5.0
370	6.2	6.8	0.0	6.8	6.8	5.0
395	6.6	5.9	0.0	5.9	5.9	5.0
420	7.0	5.1	0.0	5.1	5.1	5.0

Experimental conditions		
St	209	(mgO <sub>2</sub> /l)
Sf	31	(mgO <sub>2</sub> /l)
Xt	3476	(mgO <sub>2</sub> /l)
Xf	36	(mgO <sub>2</sub> /l)
V <sub>vw</sub>	0.4	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0	(l)
S/X	0.06	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	8.39	

Kinetic data			
k <sub>1</sub>	-2.7	Y1	26.58
k <sub>2</sub>	-1.4	Y2	23.34
k <sub>3</sub>	-1	Y3	19.66
		NOx1	3.24
		NOx2	3.68
		RBCOD	117 + 133
		%RBCOD	12 + 14

V

Table IV-V1: Batch data with samples from Villers WTP (10/09/97)

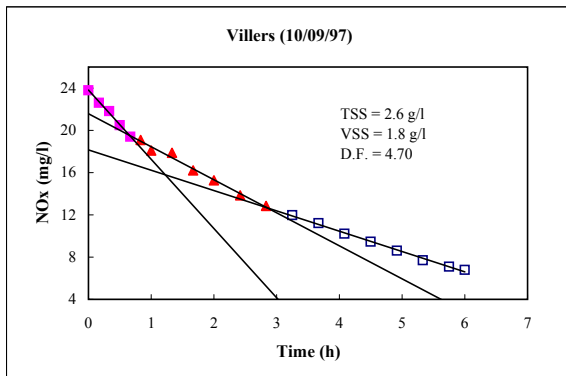
Raw data						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	23.8	0.0	23.8	23.8	6.5
10	0.2	22.3	0.5	22.8	22.6	-
20	0.3	21.4	0.7	22.1	21.8	9.0
30	0.5	20.0	0.8	20.8	20.5	-
40	0.7	18.8	1.0	19.8	19.4	8.5
50	0.8	18.5	1.0	19.5	19.1	-
60	1.0	17.5	1.0	18.5	18.1	7.5
80	1.3	17.4	0.8	18.2	17.9	-
100	1.7	15.6	1.0	16.6	16.2	11.5
120	2.0	14.6	1.1	15.7	15.3	-
145	2.4	13.2	1.1	14.3	13.9	-
170	2.8	12.2	1.1	13.3	12.9	-
195	3.3	11.3	1.1	12.4	12.0	-
220	3.7	10.6	1.0	11.6	11.2	-
245	4.1	9.6	1.0	10.6	10.2	5.0
270	4.5	8.8	1.1	9.9	9.5	-
295	4.9	8.0	1.0	9.0	8.6	-
320	5.3	7.1	1.0	8.1	7.7	-
345	5.8	6.5	1.0	7.5	7.1	-
360	6.0	6.2	1.0	7.2	6.8	4.5

Experimental conditions		
St	198	(mgO <sub>2</sub> /l)
Sf	81	(mgO <sub>2</sub> /l)
Xt	3746	(mgO <sub>2</sub> /l)
Xf	26	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0.3	(l)
V <sub>x</sub>	1.0	(l)
V <sub>d</sub>	0.1	(l)
S/X	0.05	(mgO <sub>2</sub> /mgO <sub>2</sub> )
C/N	8.32	

Kinetic data			
k <sub>1</sub>	-3.6	Y1	23.8
k <sub>2</sub>	-1.7	Y2	21.58
k <sub>3</sub>	-1.0	Y3	18.2
		NO <sub>x1</sub>	2.22
		NO <sub>x2</sub>	3.43
		RBCOD	80 + 124
		%RBCOD	9 + 13





# ***APPENDIX V***

## ***RAW DATA FROM NUR TESTS WITH ENDOGENOUS CARBON***

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Appendix V contains data from tests where the endogenous carbon of sludge was used as a substrate. The tests are listed alphabetically and contains the raw data from the NUR tests, the experimental conditions within the batch reactor, and the kinetic data derived from the curves.

### ***Abbreviations***

<b>k<sub>1</sub></b>	first rate observed
<b>k<sub>2</sub></b>	second rate observed
<b>N</b>	sum nitrates and nitrite concentration as defined in equation 4-3
<b>NO<sub>x</sub></b>	sum nitrates and nitrite concentration as defined in equation 4-4
<b>P</b>	ortho-phosphate as P
<b>Y1</b>	first Y intercept in NO <sub>x</sub> vs t curve
<b>Y2</b>	second Y intercept in NO <sub>x</sub> vs t curve

**B**

Table V-B1: Batch data with samples from Boran (25/02/97)						
Raw data (Substrate-raw wastewater)						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	22.8	0.3	23.1	23.0	-
20	0.3	22.1	0.4	22.5	22.3	-
30	0.5	22.1	0.4	22.5	22.3	-
50	0.8	20.9	0.4	21.3	21.1	-
60	1.0	20.6	0.4	21.0	20.8	-
100	1.7	20.0	0.4	20.4	20.2	-
120	2.0	19.5	0.5	20.0	19.8	-
140	2.3	18.5	0.5	19.0	18.8	-
160	2.7	19.2	0.5	19.7	19.5	-
180	3.0	18.5	0.5	19.0	18.8	-
200	3.3	18.0	0.5	18.5	18.3	-
220	3.7	17.6	0.5	18.1	17.9	-
240	4.0	17.3	0.5	17.8	17.6	-

Experimental conditions		
Xt	2001	(mgO <sub>2</sub> /l)
Xf	8	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0	(l)
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0.5	(l)

Kinetic data			
k <sub>1</sub>	-1	Y1	-
k <sub>2</sub>	-	Y2	-
		NO <sub>x</sub> 1	-
		RBCOD	-
		%RBCOD	-

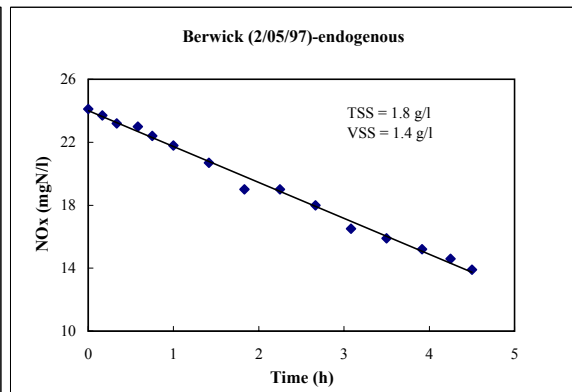
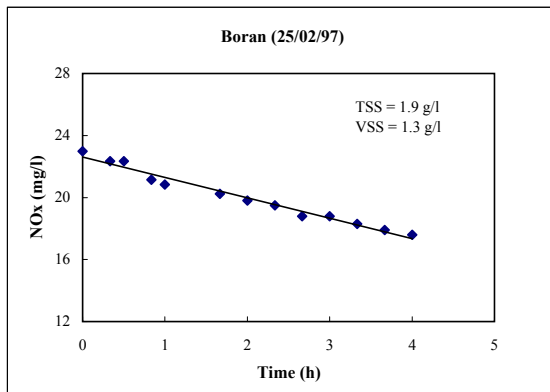


Table V-B2: Batch data with samples from Berwick(2/05/97)						
Raw data (Substrate-raw wastewater)						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	24.1	0.0	24.1	24.1	-
10	0.2	23.7	0.0	23.7	23.7	-
20	0.3	23.2	0.0	23.2	23.2	-
35	0.6	23.0	0.0	23.0	23.0	-
45	0.8	22.4	0.0	22.4	22.4	-
60	1.0	21.8	0.0	21.8	21.8	-
85	1.4	20.7	0.0	20.7	20.7	-
110	1.8	19.0	0.0	19.0	19.0	-
135	2.3	19.0	0.0	19.0	19.0	-
160	2.7	18.0	0.0	18.0	18.0	-
185	3.1	16.5	0.0	16.5	16.5	-
210	3.5	15.9	0.0	15.9	15.9	-
235	3.9	15.2	0.0	15.2	15.2	-
255	4.3	14.6	0.0	14.6	14.6	-
270	4.5	13.9	0.0	13.9	13.9	-

Experimental conditions		
Xt	2671	(mgO <sub>2</sub> /l)
Xf	82	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.45	(l)

Kinetic data			
k <sub>1</sub>	-1.6	Y1	-
k <sub>2</sub>	-	Y2	-
		Y3	-
		NO <sub>x</sub> 1	-
		NO <sub>x</sub> 2	-
		RBCOD	-
		%RBCOD	-

**B**

Table V-B3: Batch data with samples from Boran (25/02/97)						
Raw data (Substrate-raw wastewater)						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	20.9	0.3	21.2	21.1	-
60	1.0	19.2	0.7	19.9	19.6	-
120	2.0	17.0	1.2	18.2	17.7	-
180	3.0	15.2	1.7	16.9	16.2	-
240	4.0	12.8	2.1	14.9	14.1	-
300	5.0	11.2	2.6	13.8	12.8	-
360	6.0	9.8	3.0	12.8	11.6	-
420	7.0	8.0	3.4	11.4	10.0	-
480	8.0	6.4	3.8	10.2	8.7	-

Experimental conditions		
Xt	1729	(mgO <sub>2</sub> /l)
Xf	39	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0	(l)
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0.5	(l)

Kinetic data		
k <sub>1</sub>	-1.3	Y1 -
k <sub>2</sub>	-	Y2 -
		NO <sub>x</sub> 1 -
		RBCOD -
		%RBCOD -

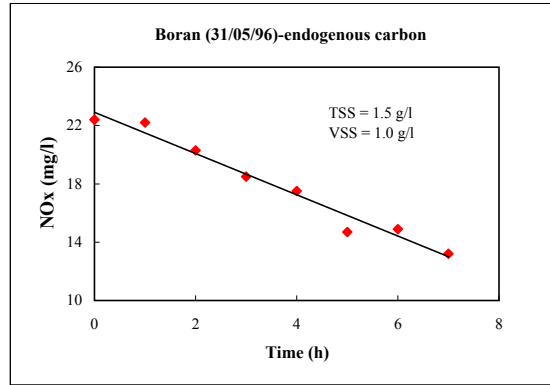
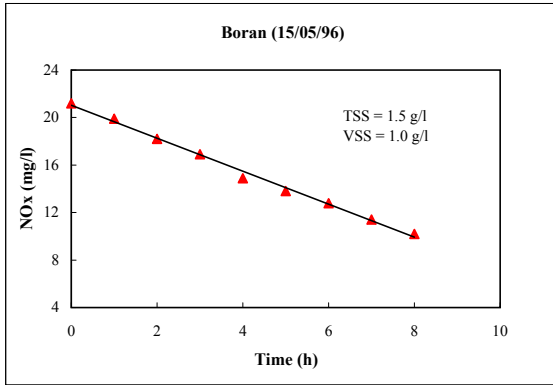


Table V-B4: Batch data with samples from Berwick(2/05/97)						
Raw data (Substrate-raw wastewater)						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	22.0	0.4	22.4	22.2	-
60	1.0	21.5	0.7	22.2	21.9	-
120	2.0	19.5	0.8	20.3	20.0	-
180	3.0	17.5	1.0	18.5	18.1	-
240	4.0	16.5	1.0	17.5	17.1	-
300	5.0	13.5	1.2	14.7	14.2	-
360	6.0	13.9	1.0	14.9	14.5	-
420	7.0	12.0	1.2	13.2	12.7	-
480	8.0	#N/A	1.0	#N/A	#N/A	-

Experimental conditions		
Xt	1881	(mgO <sub>2</sub> /l)
Xf	27	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0	(l)
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0.5	(l)

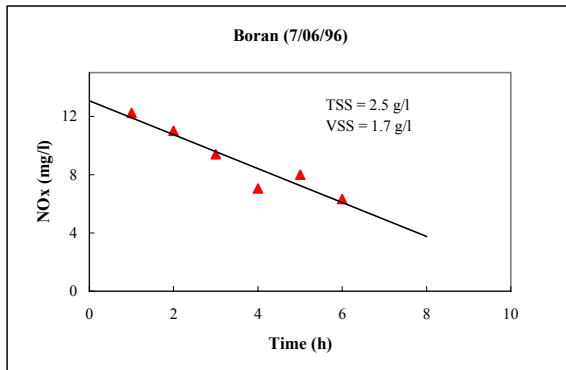
Kinetic data		
k <sub>1</sub>	-1.3	Y1 -
k <sub>2</sub>	-	Y2 -
		Y3 -
		NO <sub>x</sub> 1 -
		NO <sub>x</sub> 2 -
		RBCOD -
		%RBCOD -

## B

Table V-B%: Batch data with samples from Boran (7/06/96)						
Raw data (Substrate-raw wastewater)						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	22.8	0.0	22.8	22.8	-
60	1.0	21.7	0.3	22.0	21.9	-
120	2.0	19.4	0.4	19.8	19.6	-
180	3.0	12.4	0.3	12.7	12.6	-
240	4.0	16.5	0.4	16.9	16.7	-
300	5.0	14.0	0.4	14.4	14.2	-
360	6.0	11.0	0.4	11.4	11.2	-
420	7.0	11.8	0.5	12.3	12.1	-
480	8.0	9.9	0.7	10.6	10.3	-

Experimental conditions		
Xt	2556	(mgO <sub>2</sub> /l)
Xf	20	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0	(l)
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0.5	(l)

Kinetic data		
k <sub>1</sub>	1.2	Y1 -
k <sub>2</sub>	-	Y2 -
		NO <sub>x</sub> 1 -
		RBCOD -
		%RBCOD -



E

Table V-E1: Batch data with samples from Evry (24/11/97)-storage experiment							
Raw data						Experimental conditions	
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P	
0	0.0	24.1	0.0	24.1	24.1	-	x 1622 (mgO <sub>2</sub> /l)
10	0.2	24.3	0.0	24.3	24.3	-	Xf 18 (mgO <sub>2</sub> /l)
20	0.3	23.3	0.0	23.3	23.3	-	V <sub>ww</sub> 0 (l)
30	0.5	23.7	0.0	23.7	23.7	-	V <sub>x</sub> 1 (l)
40	0.7	22.6	0.0	22.6	22.6	-	V <sub>d</sub> 0.4 (l)
50	0.8	22.5	0.0	22.5	22.5	-	
60	1.0	23.0	0.0	23.0	23.0	-	
80	1.3	21.8	0.0	21.8	21.8	-	
100	1.7	21.2	0.0	21.2	21.2	-	
120	2.0	21.1	0.0	21.1	21.1	-	
145	2.4	20.5	0.0	20.5	20.5	-	
170	2.8	20.1	0.0	20.1	20.1	-	
195	3.3	19.1	0.0	19.1	19.1	-	
220	3.7	18.7	0.0	18.7	18.7	-	
245	4.1	18.5	0.0	18.5	18.5	-	
270	4.5	18.1	0.0	18.1	18.1	-	
295	4.9	18.1	0.0	18.1	18.1	-	
320	5.3	17.1	0.0	17.1	17.1	-	
345	5.8	16.8	0.0	16.8	16.8	-	
360	6.0	16.8	0.0	16.8	16.8	-	

Kinetic data			
k <sub>1</sub>	-1.0	Y1	-
k <sub>2</sub>	-	Y2	-
		NO <sub>x</sub> 1	-
		RBCOD	-
		%RBCOD	-

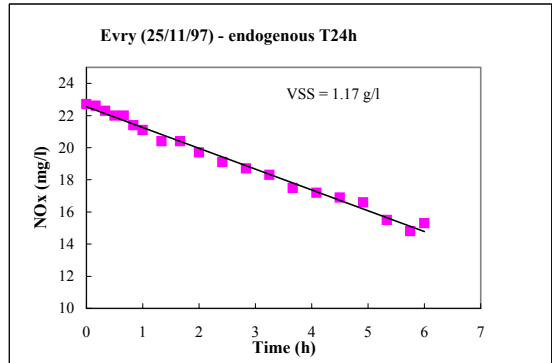
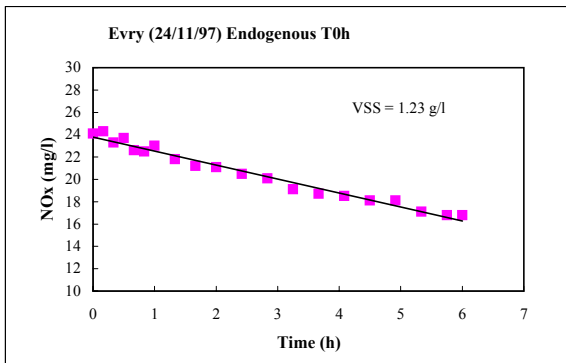


Table V-E2: Batch data with samples from Evry (25/11/97/97)-storage experiment							
Raw data (Substrate-raw wastewater)						Experimental conditions	
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P	
0	0.0	22.7	0.0	22.7	22.7	-	x 1531 (mgO <sub>2</sub> /l)
10	0.2	22.6	0.0	22.6	22.6	-	Xf 16 (mgO <sub>2</sub> /l)
20	0.3	22.3	0.0	22.3	22.3	-	V <sub>ww</sub> 0 (l)
30	0.5	22.0	0.0	22.0	22.0	-	V <sub>x</sub> 1 (l)
40	0.7	22.0	0.0	22.0	22.0	-	V <sub>d</sub> 0.4 (l)
50	0.8	21.4	0.0	21.4	21.4	-	
60	1.0	21.1	0.0	21.1	21.1	-	
80	1.3	20.4	0.0	20.4	20.4	-	
100	1.7	20.4	0.0	20.4	20.4	-	
120	2.0	19.7	0.0	19.7	19.7	-	
145	2.4	19.1	0.0	19.1	19.1	-	
170	2.8	18.7	0.0	18.7	18.7	-	
195	3.3	18.3	0.0	18.3	18.3	-	
220	3.7	17.5	0.0	17.5	17.5	-	
245	4.1	17.2	0.0	17.2	17.2	-	
270	4.5	16.9	0.0	16.9	16.9	-	
295	4.9	16.6	0.0	16.6	16.6	-	
320	5.3	15.5	0.0	15.5	15.5	-	
345	5.8	14.8	0.0	14.8	14.8	-	
360	6.0	15.3	0.0	15.3	15.3	-	

Kinetic data			
k <sub>1</sub>	-1.0	Y1	-
k <sub>2</sub>	-	Y2	-
		NO <sub>x</sub> 1	-
		RBCOD	-
		%RBCOD	-

**E**

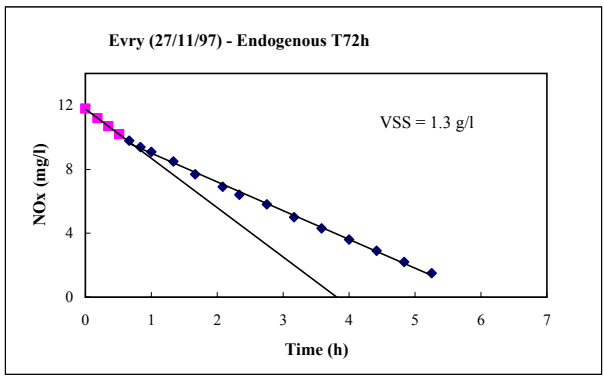
Table V-E3: Batch data with samples from Evry (27/11/97)-storage experiment						
Raw data (Substrate-raw wastewater)						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	11.8	0.0	11.8	11.8	-
11	0.2	11.2	0.0	11.2	11.2	-
21	0.4	10.7	0.0	10.7	10.7	-
31	0.5	10.2	0.0	10.2	10.2	-
40	0.7	9.8	0.0	9.8	9.8	-
50	0.8	9.4	0.0	9.4	9.4	-
60	1.0	9.1	0.0	9.1	9.1	-
80	1.3	8.5	0.0	8.5	8.5	-
100	1.7	7.7	0.0	7.7	7.7	-
125	2.1	6.9	0.0	6.9	6.9	-
140	2.3	6.4	0.0	6.4	6.4	-
165	2.8	5.8	0.0	5.8	5.8	-
190	3.2	5.0	0.0	5.0	5.0	-
215	3.6	4.3	0.0	4.3	4.3	-
240	4.0	3.6	0.0	3.6	3.6	-
265	4.4	2.9	0.0	2.9	2.9	-
290	4.8	2.2	0.0	2.2	2.2	-
315	5.3	1.5	0.0	1.5	1.5	-
340	5.7	1.1	0.0	1.1	1.1	-
360	6.0	0.5	0.0	0.5	0.5	-

Experimental conditions		
x	1850	(mgO <sub>2</sub> /l)
Xf	21	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0	(l)
V <sub>x</sub>	1	(l)
V <sub>d</sub>	0.4	(l)

Kinetic data			
k <sub>1</sub>	-2.4	Y1	11.79
k <sub>2</sub>	-1.3	Y2	10.31
		NO <sub>x1</sub>	1.47
		RBCOD	16
		%RBCOD	2



## R

Table V-R1: Batch data with samples from Rostock (17/03/97)						
Raw data (Substrate-raw wastewater)						
Time (min)	Time (h)	NO <sub>3</sub>	NO <sub>2</sub>	N	NO <sub>x</sub>	P
0	0.0	22.4	0.0	22.4	22.4	-
20	0.3	20.8	0.0	20.8	20.8	-
40	0.7	19.6	0.0	19.6	19.6	-
60	1.0	18.8	0.0	18.8	18.8	-
80	1.3	18.2	0.0	18.2	18.2	-
100	1.7	17.4	0.0	17.4	17.4	-
120	2.0	16.8	0.0	16.8	16.8	-
140	2.3	16.1	0.0	16.1	16.1	-
160	2.7	15.6	0.0	15.6	15.6	-
180	3.0	14.7	0.0	14.7	14.7	-
200	3.3	14.3	0.0	14.3	14.3	-
220	3.7	14.1	0.0	14.1	14.1	-
240	4.0	13.3	0.0	13.3	13.3	-
260	4.3	12.8	0.0	12.8	12.8	-
280	4.7	12.2	0.0	12.2	12.2	-
305	5.1	11.7	0.0	11.7	11.7	-
320	5.3	11.3	0.0	11.3	11.3	-
335	5.6	10.8	0.0	10.8	10.8	-
350	5.8	10.4	0	10.4	10.4	-

Experimental conditions		
x	2444	(mgO <sub>2</sub> /l)
Xf	46	(mgO <sub>2</sub> /l)
V <sub>ww</sub>	0	(l)
V <sub>x</sub>	1.1	(l)
V <sub>d</sub>	0.5	(l)

Kinetic data		
k <sub>1</sub>	-1.1	Y1 -
k <sub>2</sub>	-	Y2 -
		NO <sub>x</sub> 1 -
		RBCOD -
		%RBCOD -

