

TOTAL NITROGEN REMOVAL USING A PURE-  
OXYGEN PREDENITRIFICATION  
CONFIGURATION

by

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Fulfillment of the Requirements for the Degree of

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CONFIGURATION**

**BY**

**TIBOR TAKACH**

**A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University**

**of Manitoba in partial fulfillment of the requirements of the degree**

**of**

**MASTER OF SCIENCE**

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## ABSTRACT

### TOTAL NITROGEN REMOVAL USING A PURE-OXYGEN PREDENITRIFICATION CONFIGURATION

A study was conducted utilising a pure-oxygen activated sludge system in a predenitrification configuration. The objectives of the study were to: 1) assess the feasibility of a predenitrification configuration at short anoxic and aerobic hydraulic retention times; 2. to determine how predenitrification affects process stability; 3) to determine the potential for total nitrogen removal using short anoxic hydraulic retention times; and 4) to optimise the system by varying the recycle ratio. Two parallel systems were operated at 20°C and with a fixed aerobic hydraulic retention time of 2.5 hours. The hydraulic retention time of the Train B anoxic reactor was decreased from 2.5 hours to 1.5 hours and the recycle ratio was varied from 1 to 2.5  $Q_{R,AN}$ . The study found that a 1.5 hour anoxic hydraulic retention time and a 2.5 hour aerobic hydraulic retention time was sufficient for total nitrogen removals. Total nitrogen removals were dependent on the recycle ratio and the influent carbon loading. Removals approaching the theoretical maximum of 65% at a recycle ratio of 1.5  $Q_{R,AN}$  were observed during the study. Returned dissolved oxygen to the anoxic zone and a lack of a readily available carbon source limited the maximum recycle ratio to 1.8  $Q_{R,AN}$ . Reliable process stability was observed throughout the study and can be attributed to an increase in the buffering capacity of the mixed liquor through alkalinity recovery in the anoxic zone. The effluent pH was observed to be 6.4 and 6.5 for Train A and Train B respectively and the effluent alkalinity remained constant at 195 mg/L and 200 mg/L. Specific nitrification rates

were observed to be 2.6 and 2.7 mgN/gVSS-h while the specific denitrification rates were 3.85 and 4.3 mgN/gVSS-h for Train A and Train B respectively.

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## *Chapter 1*

### INTRODUCTION AND OBJECTIVES

The process of biological nutrient removal has been investigated thoroughly by many researchers. These studies investigated both the operational and economical advantages that could be provided by biological systems. The main driving force for this area of research has been the stricter effluent discharge limits required by governing bodies coupled with the high cost of chemicals required for physical-chemical methods.

Proposed stricter effluent ammonia limits discharging into the Red River prompted the City of Winnipeg to investigate the possibility of biological nutrient removal utilising their existing pure-oxygen treatment facility. A full-scale study indicated that a major capital expenditure would be required for upgrading the facility in order to provide adequate ammonia removal to meet the proposed limits. The study also indicated that process stability might pose problems due to pH and alkalinity suppression inherent in the design of the sealed pure-oxygen reactors. This prompted the City of Winnipeg to investigate nitrification and predenitrification at the laboratory scale in conjunction with the University of Manitoba and private consultants.

This study is the culmination of several projects investigating both nitrification and predenitrification under varying conditions. Results from Sears (1995), Hagar (1995), and Caponnetto (1994) indicated that nitrification appeared to be feasible at a 4h

aerobic hydraulic retention time (HRT) at 24°C, but problems with insufficient alkalinity and nitrite accumulation due to pH suppression may pose a problem. It was concluded that acclimation played an important role in the system and, provided sufficient time was allowed, nitrification would proceed at conditions previously thought to be extremely detrimental to nitrifying micro-organisms (Sears, 1995). Although a 4h HRT exhibited greater process stability, a 2.5 h HRT was shown to be adequate for nitrification at 12°C. This appears to be contradictory to previous findings that indicate a decrease in nitrification performance at lower temperatures. What was found at this temperature was that nitrification appeared to proceed in the clarifier due to the increased solubility of oxygen at lower temperatures coupled with the large amount of biomass contained in the clarifier at this process configuration. The validity of this finding has to be confirmed with pilot scale studies and accurate modelling of the clarifier in order to determine the actual role it would play in nitrification.

In a parallel study conducted by Hagar (1995), predenitrification had been investigated to determine the feasibility of simultaneous carbon-nitrogen removal in a pure-oxygen system. The main results from that study indicated that carbon-limiting conditions exist for denitrification. In existing single-sludge processes, high rates of recycle (300 - 400%) are required for total nitrogen removals approaching 80%. In high purity oxygen systems, a greater driving force exists between the bulk liquid and oxygen allowing for greater oxygen dissolution into the liquid and floc. This oxygen is consequently returned to the anoxic zone thus creating conditions where denitrification is inhibited, limiting the total recycle that could be provided. This study

also indicated that carbon availability is extremely important for efficient nitrogen removal.

Process configuration determines the total nitrogen removal attainable, as well as determining overall process stability. Several pure-oxygen plants have been constructed or retrofitted for biological nitrogen removal which achieve enviable effluent total nitrogen concentrations. Most notably are Hooker's Point in Tampa, Florida and Deer Island in Boston Massachusetts. Both systems utilise a two-stage carbon oxidation, ammonia oxidation system incorporating methanol addition for denitrification. Both the capital and operational costs for these systems can be excessive due to the need of clarifiers after the carbonaceous stage and the methanol requirements for denitrification. Operating a single-sludge system avoids both of these costs as well as significantly decreasing the oxygen requirement by utilising the oxygen obtained from nitrate during the denitrification reaction. Decreased sludge production is also an added benefit from operating in a predenitrification mode.

In retrofit applications, particularly for plants with limited land availability, pure-oxygen systems would prove to be beneficial. Inherent in the pure-oxygen design is the ability to sustain a higher biomass concentration without the corresponding increase in blower capacity and tankage requirements of conventionally aerated systems. As a result of higher oxygen transfer efficiencies in pure-oxygen systems, higher organic loadings can be tolerated without extensive land requirements.

High costs associated with expanding to a two stage pure-oxygen nitrification/denitrification system, along with the costs associated with supplying

alternate carbon sources for denitrification, led to the prospect of utilising a predenitrification configuration to reduce nitrogen discharges to the Red River. Although the principles of nitrification and denitrification are well understood, their application to pure-oxygen systems is not; making this research unique. This study was initiated to investigate the following:

1. Whether predenitrification is feasible at short anoxic and aerobic hydraulic retention times.
2. How predenitrification affects process stability, particularly nitrification.
3. To determine the potential for total nitrogen removal using a short anoxic HRT predenitrification configuration.
4. To optimise the process through activated sludge and mixed liquor recycle.



## FACTORS AFFECTING SINGLE-SLUDGE NITROGEN REMOVAL

The purpose of this chapter is to illustrate the effects of various environmental conditions known to affect nitrification and denitrification processes. As with any biological process, there exist optimum conditions under which the desired bacterial population operates without constraints and because of the variable nature of wastewater, it is desired to operate the plant in such a way that these conditions are maintained close to optimum. Discussed in this chapter are the main parameters which affect nitrification and denitrification: pH, D.O., HRT, sludge recycle, and C/N ratio.

### **Pure-Oxygen Applications in Wastewater Treatment**

Pure-oxygen systems have been investigated since the early 1960's. Investigations led by Union Carbide looked at reactor sizing for systems utilising pure-oxygen (Speece et. al., 1973). Pure-oxygen systems do not affect biomass performance with respect to substrate removal kinetics, cell production, decay rates, and sludge settlability when compared to conventionally aerated system. The main advantage for utilising pure-oxygen is a greater oxygen transfer rate across the gas-liquid interface allowing for higher oxygen uptake rates per unit volume of reactor. This factor can be used to carry significantly higher MLSS concentrations in the plant, increasing the sludge age of the system and thereby decreasing the sludge quantities produced (Speece et. al., 1973).

Greater mixed liquor concentrations and higher gas transfer efficiencies result in a reduction in required reactor volumes when compared to conventionally aerated systems. This makes pure-oxygen system particularly amiable to retrofit applications and for greenfield plants where land availability is a concern.

### **Effects of pH and Alkalinity**

The effect of pH on the active biomass in the treatment system is one of the main problems associated to pure-oxygen systems. Because of their closed headspace design, the entrapment of CO<sub>2</sub> under slight pressure allows it to enter into solution affecting the carbonic acid equilibrium of the water, decreasing the pH and reducing the alkalinity of the mixed liquor. The pH and alkalinity of the solution can be further reduced by alkalinity destruction inherent in the nitrification reaction itself. Operation in a predenitrification configuration produces alkalinity, reducing the effect of alkalinity destruction in nitrification.

### **Nitrification**

Optimum pH values for biological nitrification have varied widely and depended on the investigator and whether the system studied had been given a sufficient period of time for *Nitrosomonas* and *Nitrobacter* to become acclimated to the new conditions. The majority of reported values suggest that the maximum growth rate for activated sludge lies in the range of 7.5-8.5, but the specific results vary due to the type of culture used and the acclimation period allotted to the micro-organisms. The specific growth rate for a pH of less than 7.2 has been expressed as (US EPA, 1993):

$$\frac{\mu}{\mu_m} = 1 - 0.833(7.2 - pH) \quad \text{Equation 1}$$

where:  $\mu$  specific growth rate of *Nitrosomonas*  
 $\mu_m$ , maximum specific growth rate of *Nitrosomonas*  
 $pH$ , pH of the mixed liquor

Other expressions have been developed in laboratory scale nitrification studies using both synthetic and municipal wastewater.

for synthetic wastewater (Hong and Andersen, 1993)

$$\frac{\mu}{\mu_m} = -0.7166(pH)^2 + 10.415(pH) - 34.8744 \quad \text{Equation 2}$$

All of the above expressions have been developed specifically for *Nitrosomonas* only and it is assumed that pH would have an identical affect on *Nitrobacter*.

Acclimation can play a significant role with regard to the pH effects on nitrification. Stankewich (1972), as well as Haug and McCarty (1972) have shown that nitrification rates can be re-established to their earlier maximum rates provided that sufficient acclimation has been provided. Haug and McCarty (1972) investigated the effect of pH and acclimation using submerged biofilters. They found that nitrification essentially ceased as the pH approached 6.0, but with 1.5 weeks of acclimation, nitrification resumed and the oxidation rate approached that of a pH of 7. Stankewich (1972), on the other hand, reported nitrification at a pH of 5.8.

Sears(1995) has shown this as well when the formation of free nitrous acid (FNA) completely inhibited the nitrification process for a period of about ten days, after which, the system recovered and continued to remove ammonia completely. It was suggested that the bacteria became acclimated to the FNA allowing the reaction to proceed. The FNA concentration is a function of the pH, temperature and total nitrite concentration which suggests that possibly the environmental conditions were such that the formation of FNA was limited during the latter portions of the experiment and that acclimation may have only played a limited role in the recovery of the system. Sears (1995) research is supported by studies conducted by Anthonisen et.al (1976) where the effects of free nitrous acid (FNA) were investigated. They found that FNA concentrations between 0.22 and 2.8 mg/L inhibited nitrifiers.

Sears (1995) did show that full nitrification can be achieved at lower temperatures (12°C) and depressed pH values (<6.0). The above expressions suggest that at pH levels lower than 6.2, nitrification would cease. Actually, this is not the case and full nitrification can occur at depressed pH values, albeit at reduced growth rates signifying the need for increased SRT at low pH levels and temperatures.

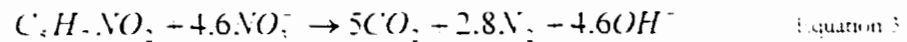
Most pure-oxygen activated sludge systems incorporate a closed headspace into the design of the reactors that can lead to pH suppression of the mixed liquor. The closed headspace design allows for higher pressures in the reactor that allows for greater oxygen dissolution into the liquid phase. It can hinder the nitrification process, however, due to elevated carbon dioxide levels in the headspace, which have the effect of suppressing the pH of the system. One solution to this was illustrated in studies

performed by Hong and Anderson (1993) where different stages of a pure-oxygen reactor were removed allowing the escape of carbon dioxide into the atmosphere resulting in an overall increase in the pH of the mixed liquor.

### **Denitrification**

The effect of pH on denitrification does not cause great concern since alkalinity production occurs in the reaction and the pH is usually maintained. The great variety and larger mixed liquor fraction of heterotrophic biomass responsible for denitrification provides a sort of buffer against depressed pH levels ensuring that a large number of bacteria will still be able to denitrify under adverse conditions.

Sedlak (1991) proposes the following expression for the reduction of nitrates during endogenous respiration:



This equation indicates that 3.57 mg of alkalinity are produced for each gram of nitrate nitrogen reduced.

Most studies indicate that the optimum pH range for denitrification occurs at near neutral conditions; 7.0-8.0. The denitrification rate has shown to decrease linearly between a pH of 8.0-9.5 and 7.0-4.0 (Randall *et al.*, 1992). Dawson and Murphy (1972) have found an optimal pH of 7.0 with half the rate occurring at a pH of 6.0 and 8.0.

The effect of pH on the denitrification system can also be described in terms of the end products produced. Studies have shown that a decrease in pH could result in a

decrease in production of gaseous nitrogen in favour of compounds such as nitrous oxide.

### **Effects of Dissolved Oxygen**

The oxygen requirements for a system depend on several factors including mixing intensity, SRT, organic substrate loading, temperature, size and shape of the biological floc, and the carbon to nitrogen ratio. While elevated D.O. levels are beneficial for nitrification, they can severely inhibit denitrification.

### **Nitrification**

Autotrophs such as *Nitrosomonas* and *Nitrobacter* are obligate aerobes requiring dissolved oxygen, or an aerobic environment in order to carry out their respective reactions. In fact, all oxidative processes require dissolved oxygen in order to complete the reaction and define the oxygen demand of the system. This implies that there must be a minimum D.O. level that must be maintained in order to prevent oxygen from becoming the limiting substrate.

It has been generally accepted that the minimum D.O. in the bulk solution should be above 0.5 *mg/l* in order for nitrification to occur (US EPA, 1993). In activated sludge, the range of minimum D.O. should be maintained between 0.5-2.5 *mg/l* depending on the limitations placed on the bacteria by the system operating parameters and the organic loading (Stenstrom and Song, 1991). The latter may exhibit a great effect on the nitrification of the system. Under high organic loading conditions, oxygen demand increases and thus will require a higher minimum dissolved oxygen concentration, as high as 4.0 *mg/l*, in the bulk solution (Stenstrom and Song, 1991). Hanaki et al. (1990a)

illustrated that a D.O. concentration of 0.5 mg, L. did not affect nitrification in a pure nitrifying culture. The effect of D.O. inhibition was only enhanced in a mixed culture containing heterotrophic organisms.

Several authors have in fact shown that nitrification organisms are capable of surviving extended anoxic (anaerobic) periods with no detrimental effects to their ability to nitrify when reintroduced to an aerobic environment.

Temperature, SRT, and diffusion limitations may also affect the oxygen transfer rate to the floc. The SRT has been shown to increase the oxygen requirements depending on the C/N ratio of the influent (Degyansky and Sherrard, 1977). Increasing the SRT from 4 to 20 days increased the oxygen requirements by 25% due to an increased amount of ammonia being oxidised into nitrate rather than being assimilated into the biomass. This study did not address these topics specifically, but it should be noted that they may have an affect on system performance.

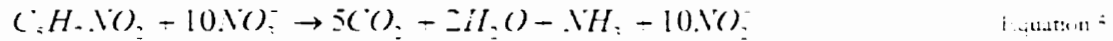
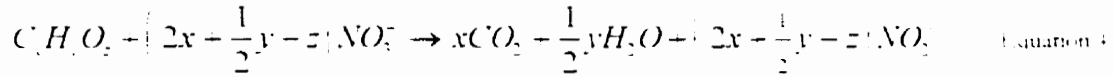
### **Denitrification**

The effects of oxygen, particularly in a single-sludge system, present much concern over the attainable denitrification rate in the anoxic portion of the system. Denitrification, or the reduction of nitrate to nitrite and ultimately nitrogen gas, is a enzyme catalysed heterotrophic process requiring organic carbon as an energy source and oxygen as an electron acceptor. It is essential that purely anoxic conditions be present for nitrate reduction to occur.

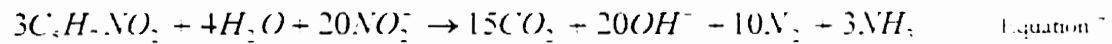
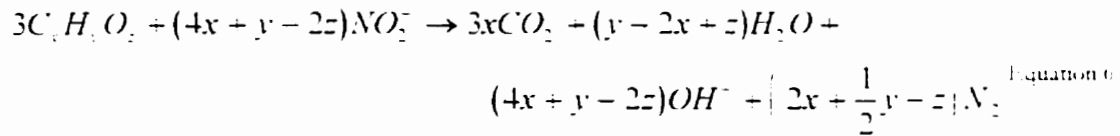
Heterotrophic organisms are capable of both, aerobic and anoxic respiration. Organic substrate for denitrification can be obtained from exogenous organic material

contained in the bulk solution or from endogenous organic material contained in the biomass. Both reactions can be summarised as follows (Drtal et al., 1995):

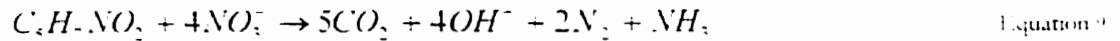
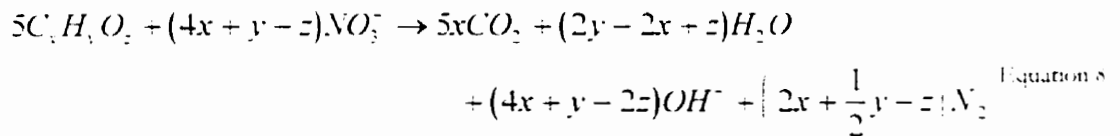
reduction  $NO_3^- \rightarrow N_2^-$ :



reduction  $NO_2^- \rightarrow N_2$ :



reduction  $NO_3^- \rightarrow N_2$ :



The reduction of nitrate follows either an assimilatory or dissimilatory pathway. In assimilation, the nitrate is converted to ammonia that is then used for cell synthesis. In the dissimilatory reaction, nitrate is converted to nitrite and subsequently to nitrogen gas. Other intermediates, such as nitric and nitrous oxides, can form depending on the dissolved oxygen content of the anoxic reactor. These intermediates can have a



detrimental effect on the atmosphere or on the biomass directly, for instance, nitrite and NO are known to be bacteriostatic agents due to their affinity for metal ions in the active centre of enzymes (Schulthess et al., 1994).

In aerobic respiration, the same series of enzymatic reactions are used for the oxidation of carbonaceous material, therefore, heterotrophic organisms will preferentially select the aerobic pathway which yields more free energy over the anaerobic pathway using nitrate as an electron acceptor. The presence of oxygen in the anoxic zone decreases the specific rate of nitrate reduction and the percentage of heterotrophic organisms utilising the aerobic pathway appears to be greater than the percentage of organisms using the anaerobic pathway for nitrate reduction.

A debate has occurred whether denitrification can occur under aerobic conditions since dissimilatory reactions require that anoxic conditions be present before nitrate reduction can occur. Some research has hypothesised that, depending on the floc size, organic and ammonia loading, a gradient can exist whereby a portion of the floc remains sufficiently anoxic allowing denitrification to proceed (Dawson and Murphy, 1972; Sutton et al., 1979).

Enzymatic inhibition may also determine the denitrification rate in the anoxic zone. Since a large range of activated sludge organisms are capable of both nitrate and oxygen respiration, different enzymes will utilise either nitrate or oxygen as an electron acceptor (Dawson and Murphy, 1972). A degree of enzymatic inhibition in nitrate dissimilation has been observed in several studies using synthetic feed and activated sludge. D.O. concentrations inhibiting nitrate reduction have been reported to be 0.2

mg/l and 0.3-1.5 mg/l for synthetic feed and activated sludge, respectively (Focht and Chang, 1975; Burdick et al., 1982). This has been substantiated by another study where it was found that a substantial number of denitrifiers will produce denitrifying enzymes in the presence of dissolved oxygen which implies that inhibition of enzymatic activity and not the repression of enzyme synthesis is the primary effect of dissolved oxygen (Simpkin and Boyle, 1988). These authors have found that enzymes were synthesised to at least 50% of their maximum levels during alternating anoxic/aerobic regimes found in activated sludge systems.

Other research has shown that in anaerobic/aerobic systems, bacteria can simultaneously use both the nitrate and oxygen pathways (Robertson and Keunen, 1984; Robertson et al., 1988; Kugelman et al., 1991). *Nitrobacter* has also been shown to utilise nitrate as an electron acceptor under anoxic conditions provided that the accumulation of nitrite did not occur (Bock et al., 1988).

### **Effects of Recycle Ratio**

Theoretically, in post denitrification systems or in two and three sludge systems, the amount of total nitrogen removal attainable is 100%. The main disadvantage is that a source of carbon, such as methanol, must be provided for denitrification. Although high total nitrogen removal rates can be achieved in these systems, several disadvantages accompany the design that can be summarised as follows:

- extra costs associated with first stage clarifiers and third stage denitrification units
- methanol and other chemical annual costs

- increased pumping costs
- volatility of chemical costs

Previous studies with nitrogen removal in pure-oxygen systems have resulted in a three-sludge configuration for most retrofits and greenfield construction, for example Hooker's Point in Tampa, Florida, and Deer Island in Boston, Massachusetts. The main concern has been the dissolved oxygen return in the recycle streams to the anoxic zone that decreases the attainable denitrification rate.

### **Nitrification**

In nitrification systems, sludge recycle plays a limited role in the removal of ammonia from the waste stream. The most important role is that it maintains a certain level of mixed liquor solids in the aerated portion of the system and effectively maintains a specific aerobic sludge retention time for the system. Higher recycle ratios will also benefit the system by returning unoxidised ammonia to the headworks effectively increasing the ammonia removal within the system.

### **Denitrification**

In denitrification systems, sludge recycle plays an important role in the removal of total nitrogen from the system. In a predenitrification configuration, the oxidised nitrogen compounds must be returned to the headworks of the process to take full advantage of the available carbon source of the influent stream, thereby requiring sludge recycle as well as internal recycle streams.

The main disadvantage of this process, particularly regarding recycle is that the denitrification process is more complete under anoxic conditions. With the return of

sludge from the clarifier, introduction of oxygen to the system can be avoided by utilising the retention time in the clarifier to ensure all available oxygen has been utilised. Internal recycle streams, however, can not avoid the transport of oxygen dissolved in the bulk solution to the anoxic zone, effectively reducing the denitrification capacity of the anoxic zone.

In a predenitrification configuration, two factors that can determine the overall nitrogen removal in the system are the amount of nitrification in the aerobic zone and the amount of nitrate which can be returned to the anoxic zone. Theoretically, assuming complete nitrification, total nitrogen removals of up to 80% can be achieved employing a recycle ratio of 4Q (Figure 1).

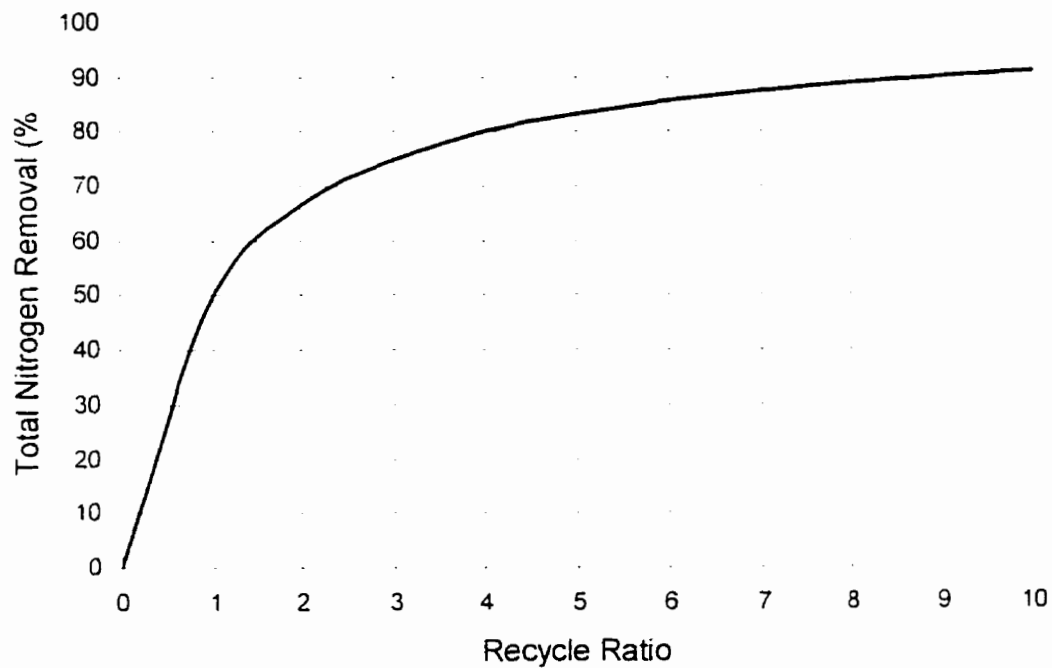


Figure 1 Theoretical total nitrogen removal in a predenitrification system as a function of recycle ratio

Facultative heterotrophic organisms will preferentially select oxygen as the terminal electron acceptor due to the greater free energy available from the aerobic pathway. This also effectively reduces the carbon available for denitrification utilising nitrate as the terminal electron acceptor essentially limiting the maximum total nitrogen removal that can theoretically be obtained in a predenitrification configuration.

Increasing the recycle ratio employed will change the  $COD/NO_3-N_{in}$  ratio in the system. Narkis et al. (1979) looked at nitrification and denitrification in a two stage predenitrification process. The author states that denitrification efficiency depended on the recycle ratio employed and that denitrification performance increased with an increasing  $BOD/NO_3$  ratio until a value of 2.4 was reached after which no increase in denitrification performance was observed.

Several authors have shown that the denitrification reaction is sensitive to dissolved oxygen in the anoxic zone. Because micro-organisms responsible for denitrification have the ability to utilise alternate respiratory pathways, dissolved oxygen levels as low as 0.2 mg/L in the bulk solution have caused a cessation of the denitrification process with the organisms shifting to oxidation of organics through the normal aerobic pathway (Skerman and MacRae, 1957). Others, however have shown that denitrification can take place under, what would be considered, aerobic conditions. Smith and Mulbarger (1970) have shown that rapid denitrification was possible with dissolved oxygen concentrations as high as 1.0 mg/L. This was attributed to floc structure.

### **Effects of Carbon to Nitrogen Ratio**

In any combined nitrogen removal system, one parameter that plays a significant role is the carbon to nitrogen ratio (C/N ratio). Carbon, whether in organic or inorganic form, is required by all micro-organisms for the purpose of cell growth. Autotrophic bacteria in nitrification take advantage of inorganic carbon in the form of  $\text{CO}_2$  dissolved in the mixed liquor, while heterotrophic bacteria consume organic carbon in the substrate introduced to the system by the influent wastewater.

### **Nitrification**

Autotrophic organisms require an inorganic carbon source for their energy requirements. The form commonly associated with this is carbon dioxide ( $\text{CO}_2$ ). Organic carbon, on the other hand can be detrimental to the nitrification process. Hall and Murphy (1985) observed that an increasing C/N ratio produced a marked decrease in the activity of *Nitrosomonas* while decreasing the C/N ratio by increasing the TKN loading produced an increase in *Nitrosomonas* activity.

Hanaki et al. (1990a and 1990b) found that higher carbon loading did not inhibit nitrifying organisms, but that an increased competition between the autotrophic and heterotrophic for available ammonia effectively reduced the formation of nitrite in the system. This was due to several factors: one being the assimilative capacity of the heterotrophic organisms; and the other being the higher growth rate of the heterotrophic organisms effectively crowding out the autotrophs from the bulk solution reducing their access to oxygen and ammonia contained in the bulk solution.

## Denitrification

In a post denitrification configuration, denitrification can proceed under carbon limiting or non-carbon limiting conditions. The organic carbon requirements will be obtained from two sources which will impact the rate and maximum amount of denitrification attainable for a particular system.

Under non-carbon limiting conditions, organic carbon requirements will be obtained from the influent wastewater stream. Here, denitrification will proceed at the maximum rate until carbon-limiting conditions are experienced. Under carbon limiting conditions, the denitrification rate will proceed at the maximum rate until the readily available carbon source is depleted, after which the denitrification rate will reduce to that limited by hydrolysis of non-readily available carbon sources and endogenous respiration. This makes the characteristics of the influent wastewater and recycle streams, as well as, anoxic sludge retention time, important factors when looking at denitrification in a predenitrification system.

For this study the carbon to nitrogen ratio in terms of denitrification can be represented by  $COD/NO_3-N_{eq}$ , where  $NO_3$  includes the returned oxygen component in the recycle stream and is expressed as  $NO_3-N_{rec}$ .  $NO_3-N_{eq}$  is defined as the nitrate equivalent of both the oxidised nitrogen compounds as well as the oxygen in the bulk solution. This factor can illustrate the effect of increased C/N loading on the anoxic portion of the system and can show that denitrification can be inhibited when the fraction of oxygen in the  $NO_3-N_{eq}$  increases.

In a study comparing different single-sludge systems, Sutton et al. (1979) reported a minimum  $\text{COD}/\text{NO}_3\text{-N}_{\text{org}}$  ratio of 8 is required for denitrification to ensure non-carbon limiting conditions. Barnard (1973) and Stern and Marais (1974) found that  $\text{COD}/\text{NO}_3\text{-N}_{\text{org}}$  ratios of 10 and 15, respectively, are required for a predenitrification configuration. In a more recent study, Ekama and Marais (1984) found that 8.6 mg of COD are required to reduce 1 mg of  $\text{NO}_3$  for municipal wastewater.

Many of the micro-organisms in the anoxic (anaerobic) zone will sequentially use terminal electron acceptors in the following order: oxygen, nitrite, nitrate and sulphate. This order is generally maintained due to the thermodynamics involved and the greater amount of energy available to the bacteria when utilising oxygen. Systems incorporating internal recycle are better represented by including both the oxygen and nitrate components.

Wastewater composition will have a marked effect on the rate of denitrification attainable by a single-sludge system. Henze et al. (1994) states that the dominant rate limiting factor is the rate at which the carbon source can be hydrolysed and that a  $\Delta\text{COD}:\Delta\text{N}$  ratio of 3.5 to 4.5 is required for a denitrification process where no part of the carbon source is lost through oxygen related oxidation.

Narkis et al. (1979) investigated denitrification at various C/N ratios and found that a minimum  $\text{BOD}/\text{NO}_x$  ratio of 2.3 was required for complete denitrification. Assuming a  $\text{BOD}/\text{COD}$  ratio of 0.8, this would translate to a  $\text{COD}/\text{NO}_x$  requirement of approximately 2.8.



### **Effects of Hydraulic Retention Time and Sludge Retention Time**

In a single-sludge denitrification system, a optimum balance must be maintained between the time sludge resides under anoxic and aerobic conditions. The fraction of time the sludge resides under these alternating oxidative conditions will have an impact on the composition of the biomass itself and thereby the extent of nitrification and denitrification attainable in the system.

### **Nitrification**

One of the main benefits of a single-sludge denitrification system is that a large portion of the influent carbon can be consumed in the anoxic stage, thereby reducing the aerobic requirements of the system, provided a sufficient fraction of the sludge is maintained under aerobic conditions. A minimum fraction of the sludge must be maintained under aerobic conditions to prevent washout of the nitrification organisms. Marais suggested that there exists a minimum sludge age to achieve nitrification depending on the temperature. His expression for this is:

$$S.A_{\min} = 3.05 \times (1.127)^{T-20} \quad \text{Equation 10}$$

where:  $S.A_{\min}$  is the minimum sludge age for nitrification at a temperature T

McClintock et al. (1993) indicated that a minimum aerobic sludge age for complete nitrification in a single-sludge system is 3 d at 20°C.

### **Denitrification**

In order for denitrification to proceed, the system must have a sufficient anoxic sludge residence (SRT) time so that denitrification can proceed.

Henze (1987) suggested a minimum anoxic solids residence time to aerobic residence time ratio of 0.25. It should be noted that a maximum anoxic sludge residence time is also required to allow for nitrification and the prevention of washout of the nitrifying organisms.

Authors have suggested that a minimum sludge age of 3 days is required for denitrification at higher temperatures and 6 days at 5°C (Sutton et al.), but at higher sludge ages of 3-9 days, denitrification was independent of sludge age (Sutton and Jank).

Stern and Marais have shown that the denitrification rate is inversely proportional to the sludge age. They found that when the sludge age was decreased from 14 days to 10 days, the unit denitrification rate increased. McClintock et al. (1993) has shown that the denitrification rate at a 15 day sludge age ranged from 6-8 mgN/gMLVSS h.

## EXPERIMENTAL MATERIALS AND METHODS

The goal of this chapter is to describe the experimental design, process configuration, process control, operating regime and analytical techniques used in this study of predenitrification in a pure-oxygen activated sludge system.

### **Objectives**

The main objective of this study was to determine the feasibility of predenitrification in a pure-oxygen activated sludge system. Recently, more stringent effluent criteria has required some degree of biological nutrient removal in the design and retrofit of new or existing wastewater treatment plants. This experiment has been designed to investigate:

1. The effect of the anoxic hydraulic retention time on denitrification performance and total nitrogen removal.
2. The optimisation of process performance in terms of total nitrogen removal through internal nitrate recycle.
3. The effects of dissolved oxygen returned to the anoxic zone through sludge and internal recycle.

Although interest in pure-oxygen activated sludge systems has been around for approximately 30 years, design criteria of pure-oxygen treatment plants traditionally

required the removal of carbonaceous organic matter only. Recently throughout the world, effluent criteria has become more stringent, especially in areas where water resources have become limited. This required that nutrient removal be incorporated into the design and retrofit of new and existing wastewater treatment plants.

Since pure-oxygen systems have been designed mainly for carbon removal only, little research has been conducted in the area of nutrient removal using pure-oxygen systems. Previous research (Stankewich, 1972) indicated that nitrogen removal in pure-oxygen systems can be feasible, but inherent problems with pH suppression and possible alkalinity limitations are inevitable with the closed headspace design of most reactors. Anoxic-aerobic systems have long been known to provide process stability through the production of alkalinity in the anoxic zone allowing for a relative comfort zone with regards to the buffering capacity of the wastewater. This was the basis for the initiation of the study of predenitrification.

### **Experimental Methods**

Two laboratory scale pure-oxygen predenitrification systems were used to achieve the objectives of this study. The experiment was conducted in the environmental engineering laboratories of the Department of Civil and Geological Engineering at the University of Manitoba. The duration of the experiment was approximately one year. Activated sludge from a previous predenitrification study was used to inoculate the reactors, after which 3 sludge retention times were provided for the systems to become acclimated to the new conditions. Once steady state had been established and data for the first stage had been collected, the system was optimised through the addition of

internal nitrate recirculation lines. Stage 1 consisted of the study of the effect of two anoxic hydraulic retention times on denitrification performance. Once the optimal HRT had been established from stage 1, stage 2 was initiated and both systems were run in parallel with the same anoxic HRT and different internal recycle ratios. In all, four different internal recycle ratios were investigated.

### Process Configuration

Figure 2 and Figure 3 illustrate the system configuration of the pure-oxygen activated sludge systems used in this experiment. All reactors were constructed of 15 cm inner diameter Plexiglas. Train A utilised a 1.9 l anoxic and 3.1 l aerobic liquid volume which corresponded to a 1.5 h and 2.5 h HRT respectively. Train B utilised a 3.1 l liquid volume which corresponded to a 2.5 h HRT for both the anoxic and aerobic units. Headspace volume of approximately 1 l was provided for all reactors. Sampling ports were located approximately 5 cm from the bottom of the reactors.

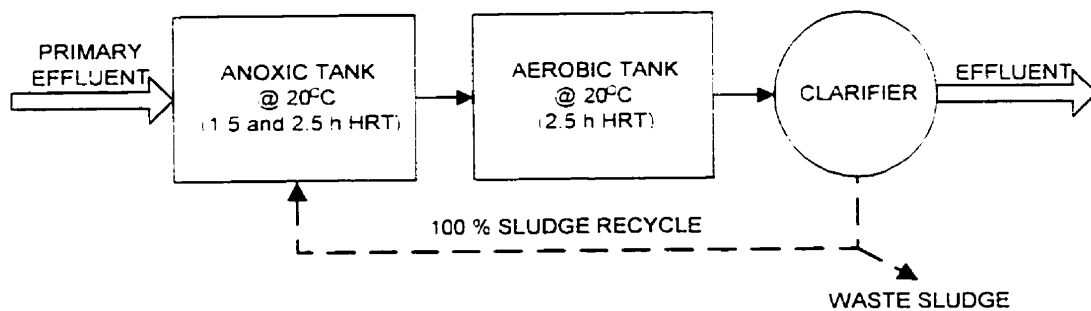


Figure 2. Predenitrification Flow Diagram without Nitrate Recycle

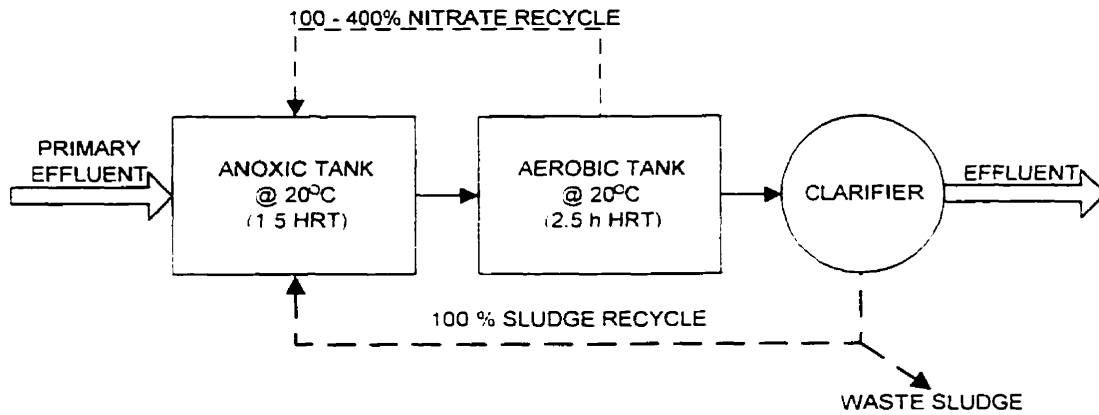


Figure 3. Predenitrification Flow Diagram with Nitrate Recycle

Each unit contained several openings in the top plate of the assembly to allow for influent line, effluent line, air supply, dissolved oxygen and ORP probe locations. All reactors contained a magnetic stirring bar and rested on a Can-Lab magnetic stirrer to provide adequate mixing to keep the sludge in suspension. Both systems utilised a 5 l (4 h HRT) Plexiglas clarifier with sampling ports located at various points along the side. A mechanical scraper arm was inserted into the clarifier to prevent accumulation of sludge along the sides of the clarifier and to ensure that all biomass was returned to the reactors. Even with the use of the scraper, biomass accumulation occurred throughout the day and had to be dislodged by hand with a hand scraper.

Aeration was provided to the aerobic reactor by means of a porous air stone which was located through one of the ports in the top plate. Oxygen was delivered through a pressure relief valve to the aerobic unit by Tygon™ tubing. Enough aeration could not be provided strictly by the air stones to maintain a dissolved oxygen concentration of 3 mg/l without excessive oxygen usage. In full scale, most pure-oxygen systems consist

of four stages and vent gas purity is maintained at approximately 50% oxygen. This ensures that approximately 95% of the oxygen is utilised prior to discharge through the exhaust vent. This type of control was not available for these systems and in order to circumvent this problem an air recirculation line was incorporated into the aerobic reactors. Headspace pressure was monitored by means of a manometer and maintained by a vent gas tube that extended into a flask partially filled with water. This maintained the headspace pressure at approximately 7 cm H<sub>2</sub>O gage. Figure 4 illustrates the typical experimental set up used for this study.

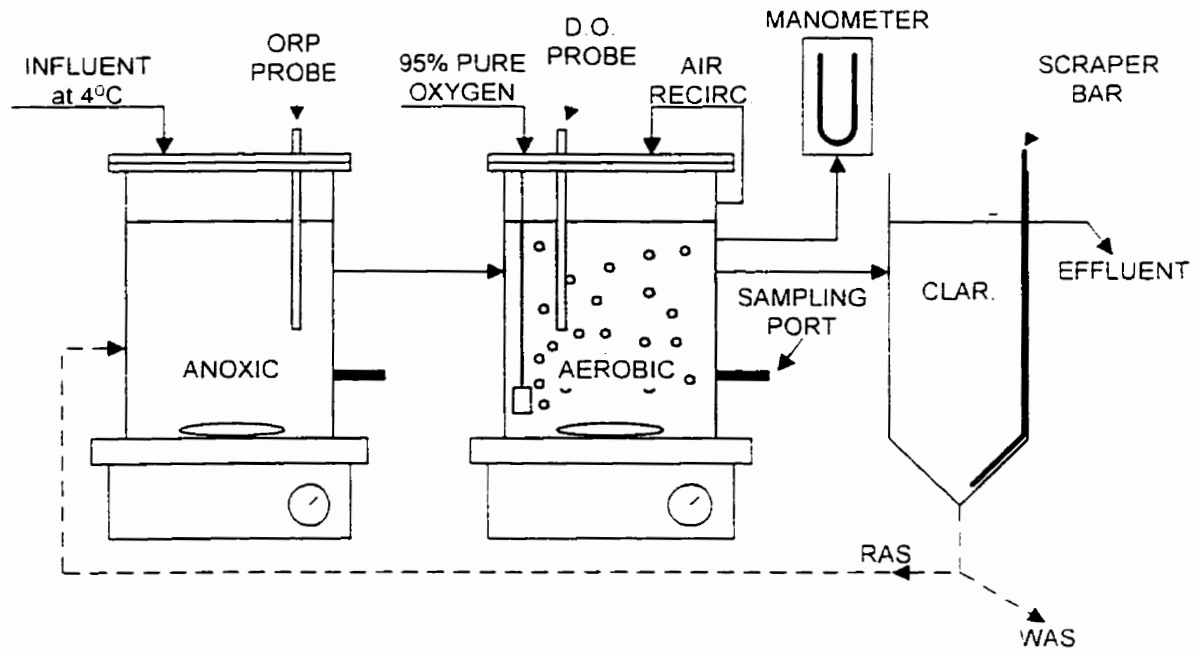


Figure 4. Typical Reactor Configuration

Two household refrigerators were used to hold the primary effluent at a temperature of approximately 4°C. Primary effluent was held in 40 l PVC buckets which contained a magnetic stirring bar and rested on a Can-Lab magnetic stirrer. The primary effluent was stirred continuously to keep the solids in suspension. Solids build-up did occur

along the sides of the buckets and required occasional cleaning. An opening was provided in the side of the refrigerator for the insertion of a Tygon™ influent line to the reactors. The influent line was weighted down by means of a small weight.

Cole-Palmer peristaltic pumps outfitted with Mastertflex heads (size 7016) and variable speed controllers provided all liquid and sludge transportation requirements. Previous studies by Sears (1995) and Hagar (1995) determined that at least no.16 tubing was required for the pumpheads to minimize plugging problems. No. 14 Tygon™ tubing was used between pumpheads to maintain adequate sludge velocity in order to prevent sludge deposition or settling within the tubes themselves. Biomass growth along the length of the tubing and could not be prevented and required that the tubing be massaged on a regular basis to remove this growth. Variable speed controllers were monitored by a hand tachometer and calibrated to the required flow rates.

Reactor volumes were maintained at the 3.1 l and 1.9 l marks by means of effluent ports inserted through the top plate to a predetermined depth. Variable speed controllers were calibrated to maintain pump speeds at slightly more revolutions per minute than was required in order to prevent liquid accumulation due to flow variations caused by biomass build-up in the tubing. Occasionally clogging did occur which required attention to prevent a spill. These systems performed adequately throughout the experiment and only two spills due to this cause were reported for the duration of the experiment.



### **Primary Effluent Characteristics**

The City of Winnipeg's North End Wastewater Pollution Control Centre (NEWPCC) provided the primary effluent for the purpose of this study. Grab samples were collected three times weekly at approximately 1:00 pm that corresponded to a 7:00 am flush time peak flow. The samples were collected in 20 l polyethylene canisters dedicated specifically for this purpose and were delivered to the University of Manitoba via a courier service. The primary effluent was then transferred to 20 l plastic buckets and stored in a walk-in environmental chamber. All samples were kept at 4°C to prevent degradation prior to use. The primary effluent was then transferred to the refrigerators where 50% of each bucket was transferred to each refrigerator to ensure an even distribution of the feed.

Winnipeg experiences a fairly wide range of flow conditions throughout the year. In the beginning of this study, uncharacteristically wet weather due to extreme rainfalls during the summer months of 1992 and 1993 produced primary effluent that was more dilute with respect to normal conditions and contributed significantly to difficulties in maintaining conditions conducive for denitrification. Table 1 illustrates the NEWPCC primary effluent characteristics throughout the duration of the study.

Table 1. NEWPCO primary effluent wastewater characteristics

		TRAIN A	TRAIN B
MLVSS (mg/l)	period 1	4350 ± 340	4730 ± 630
	period 2	4890 ± 930	4690 ± 420
	period 3	4490 ± 700	4150 ± 300
	period 4	4190 ± 440	3510 ± 370
Influent COD sol. (mg/L)	period 1	143 ± 51	139 ± 24
	period 2	150 ± 35	154 ± 25
	period 3	135 ± 36	135 ± 35
	period 4	126 ± 50	128 ± 48
Influent Suspended Solids (mg/L)	period 1	80 ± 18	81 ± 16
	period 2	84 ± 30	84 ± 26
	period 3	85 ± 31	82 ± 31
	period 4	58 ± 15	58 ± 13
Influent Ammonia sol. (mg/L)	period 1	28.6 ± 4.5	27.7 ± 4.0
	period 2	34.2 ± 12.4	36.9 ± 7.5
	period 3	29.1 ± 7.4	28.0 ± 7.3
	period 4	15.9 ± 2.8	15.7 ± 3.6
Influent TKN sol. (mg/L)	period 1	36.2 ± 5.3	34.9 ± 4.8
	period 2	41.1 ± 15.0	44.8 ± 8.2
	period 3	32.6 ± 7.8	32.6 ± 7.8
	period 4	25.9 ± 8.6	25.4 ± 8.7
Influent Alkalinity (mg/l as CaCO <sub>3</sub> )	period 1	334 ± 65	353 ± 41
	period 2	264 ± 70	286 ± 23
	period 3	307 ± 30	307 ± 29
	period 4	226 ± 21	224 ± 21
Influent pH	period 1	7.3 ± 0.7	7.3 ± 0.7
	period 2	7.5 ± 0.2	7.5 ± 0.2
	period 3	7.4 ± 0.1	7.4 ± 0.1
	period 4	7.3 ± 0.1	7.2 ± 0.1

### Operating Regime and Process Control

The operating parameters for this experiment were decided from earlier works conducted by Sears (1995) and Hagar (1995). It was shown that complete nitrification could be achieved at an aerobic HRT of 4.0 h, a 15 d SRT and a temperature of 20°C.

Biological nutrient removal systems have been shown to require less aerobic volume than do conventionally aerated systems (McClintock et al., 1993). The total HRT of the both conventional and BNR systems remain similar, although approximately 40-50% of the total volume was dedicated to the anaerobic and anoxic volumes in the BNR system. This study looked at systems with 37% and 50% anoxic fractions which correspond to a 1.5 and 2.5 h anoxic HRT. Both systems used a 2.5 h HRT aerobic unit for nitrification purposes. Table 2 illustrates the operating regime throughout the entire experimental period. Flow to both systems was maintained at 30 l/d throughout the experiment.

### **Solids and Hydraulic Retention Time Control**

One of the main operating parameters essential for process control is the SRT. This is maintained through the wasting of excess biosolids produced from the treatment process. SRT analysis and calculations, based on volatile solids, was conducted three times weekly and excess biomass was removed from the system on a daily basis.

For this study a 20 d SRT was chosen based on previous studies conducted by Capponetto (1994), Sears (1995) and Hagar (1995). Wasting occurred by withdrawing excess biomass from a port located in the side of the aerobic vessel.

### **Dissolved Oxygen Control**

Dissolved oxygen was introduced to the system by means of bottled industrial grade oxygen. A flow regulator provided a minimum flow to the system in order to maintain a DO concentration in excess of 2 mg/L at all times. Oxygen was fed through a port

located in the top of the reactor and then through a porous air stone located in the reactor.

Table 2 Operational parameters

		TRAIN A	TRAIN B
System SRT (d)	all periods)	20	20
Anoxic SRT (d)	period 1	4.7 ± 0.3	7.4 ± 0.6
	period 2	3.8 ± 0.1	6.4 ± 0.4
	period 3	4.0 ± 0.2	3.4 ± 0.4
	period 4	4.4 ± 0.3	3.5 ± 0.3
Aerobic SRT (d)	period 1	7.3 ± 0.4	7.5 ± 0.7
	period 2	6.7 ± 1.0	6.5 ± 0.5
	period 3	6.8 ± 0.5	5.6 ± 0.5
	period 4	7.2 ± 0.3	5.6 ± 0.6
Recycle Rate (based on $Q_{RAW}$ )	period 1	1.0	1.0
	period 2	1.0	1.0
	period 3	1.0	1.5
	period 4	1.0	2.5
Anoxic HRT (h)	period 1	1.5	2.5
	period 2	1.5	2.5
	period 3	1.5	1.5
	period 4	1.5	1.5
Aerobic HRT (h)	all periods)	2.5	2.5
MLSS <sub>aerobic</sub> (mg/L)	period 1	5688 ± 364	6462 ± 736
	period 2	6404 ± 1197	6233 ± 537
	period 3	6555 ± 1021	6340 ± 600
	period 4	5992 ± 507	5253 ± 303
MLVSS <sub>aerobic</sub> (mg/L)	period 1	4353 ± 341	4734 ± 626
	period 2	4894 ± 931	4692 ± 421
	period 3	4490 ± 704	4147 ± 298
	period 4	4194 ± 444	3516 ± 369

Sufficient oxygen could not be provided to the mixed liquor by means of the air stone alone necessitating the use of a air recycle line on which withdrew headspace gasses from the top of the reactor and reintroduced them to the bulk solution through

another porous air stone. Higher oxygen feed rates were not provided due to the potential of stripping CO<sub>2</sub> from the bulk solution and thereby artificially affecting the carbonic acid balance within the system.

Problems were encountered in maintaining the oxygen feed rate throughout the day resulting in periods of low DO concentrations, particularly in the mornings. Adjustments would be made to the at the start of the day to maintain a minimum DO concentration of 2 mg/L, however, suspected temperature dependent contraction of the equipment restricted air flow to the system resulting in periods of low DO.

DO was continually monitored by means of a submersed DO sensor and a YSI DO meter. Probe fouling due to biomass growth resulted in a gradual decrease in the recorded DO concentration of the bulk solution. Probe membranes were cleaned on a daily basis. Probe membranes were replaced every second to fourth day to ensure accurate DO measurements. DO probes and meters were calibrated using the Winkler method whenever membranes were replaced or cleaned.

### **Analytical Methods**

All methods were conducted according to the 18th edition Standard Methods 1992.. The following table illustrates the sampling frequency and type of analysis being conducted for this study:

Table 3 Sampling Methods and Frequency

Parameter	Method	Frequency
Flow	Manual based on level measurements	Daily
Temperature	Manual with thermometer	Daily
ORP	On-line ORP measurement	Daily
Pressure	Manual measurement of water column depth	Daily
Headspace CO <sub>2</sub>	Thermal conductivity gas chromatography	Three times weekly
Alkalinity	Standard Methods #2320B	Daily
Dissolved Oxygen	YSI Meter and submersible probe	Daily
pH	Fisher pH probe	Daily
Suspended Solids	Standard Methods #2540D	Three times weekly
Volatile Suspended Solids	Standard Methods #2540E	Three times weekly
SOC	Standard Methods #5310C	Three times weekly
COD	Standard Methods #5660D	Three times weekly
TKN	Standard Methods 4500-Norg; Standard Methods 4500-NH <sub>4</sub>	Three times weekly
Ammonia	Standard Methods 4500-NH <sub>4</sub>	Three times weekly
Nitrate	Cadmium Reduction Method	Three times weekly
Oxygen Uptake Rate	Standard Methods #2710B	As required

## RESULTS AND DISCUSSION

### PROCESS PERFORMANCE

This study was conducted over a one-year, beginning in August 1994 and continuing until September 1995. Four distinct operating periods were characterised throughout the entire study. The first period (day 0 to day 139) was described as the acclimation period where the process underwent start-up and sufficient biomass was allowed to accumulate to bring the system to a system SRT of 20 d. At least three SRT's were included during this period ensuring "pseudo-steady state" conditions throughout the study. Actual steady state could not be realised due to the use of actual wastewater and the variations involved with it.

The second period (day 140 to day 242) of operation can be characterised with poorer process performance. Figure 5 illustrates the ammonia removals obtained during this period. Ammonia removals declined throughout the winter period beginning about day 140 and continuing through to day 242. This "winter period" drop was also experienced in a parallel nitrification study conducted by R. George (1996). Changing wastewater characteristics were suspected as a contributing factor. Suspected inhibition due to changing wastewater characteristics could not be determined from this study.

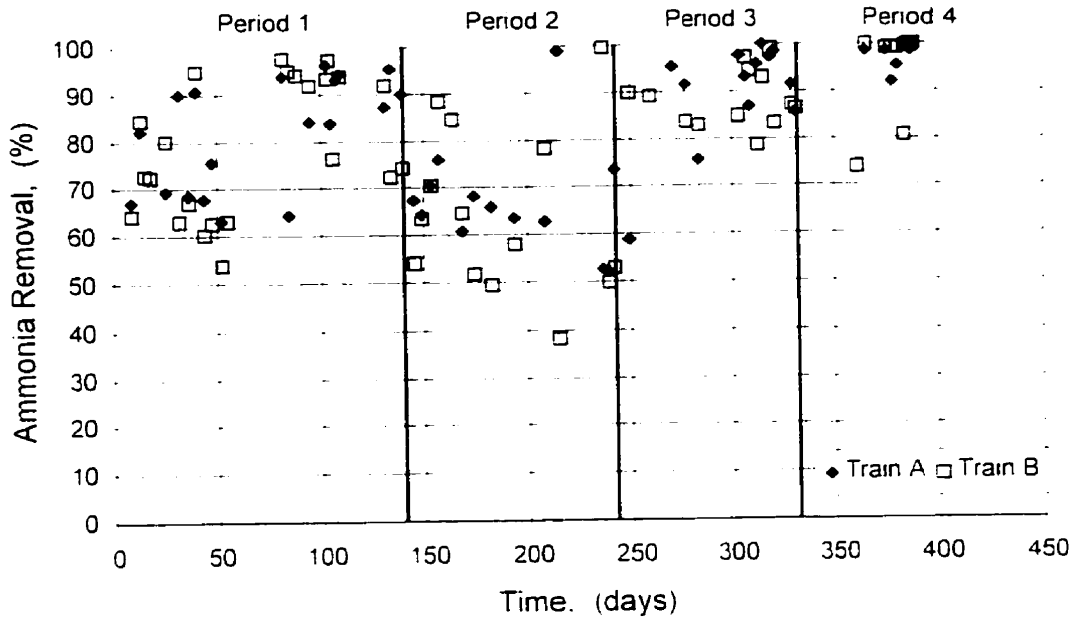


Figure 5 Ammonia removal histogram. Train B, 1.5h anoxic HRT for phase 3&4.

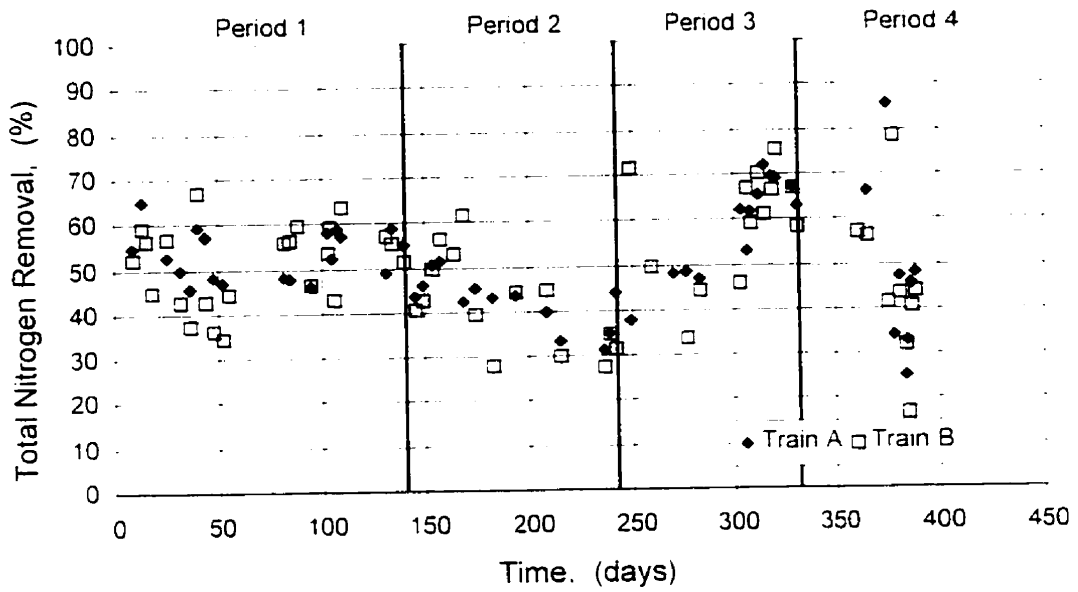


Figure 6 Total nitrogen removal histogram. Train B, 1.5h anoxic HRT for phase 3&4.



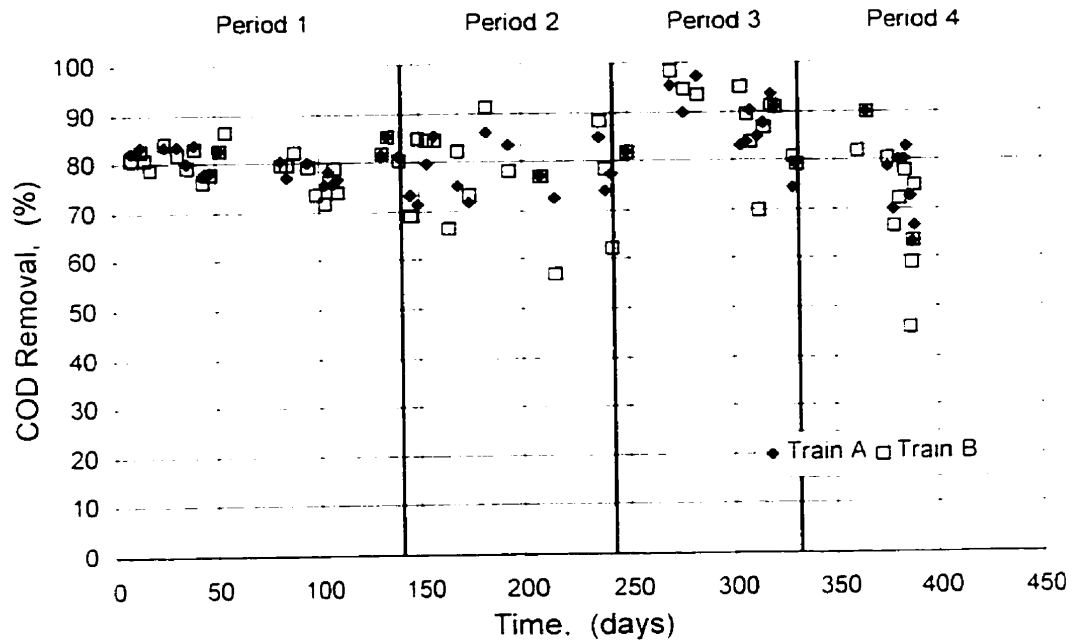


Figure 7 COD removal histogram. Train B, 1.5h anoxic HRT for phase 3&4

Period three (day 243 to day 331) can be characterised as typical summer wastewater operating conditions. Wastewater quality was fairly consistent throughout this phase which allowed the system to approach maximum nitrification and denitrification performance, as illustrated in Figure 5 and Figure 6. Almost complete carbon removal was also noted (Figure 7). Period 4 (day 332 to day 389) was characterised by variable performance in terms of COD removal in both systems. The influent COD decreased slightly from an average of 135 mg/L in period 3 to 128 in period 4. A change in the influent refractory organic content is suspected for the decrease in COD removal since nitrification did not appear to be affected during period 4.

Throughout the study Train A was operated using the same operational parameters. In Train B, operational parameters were the same as Train A for periods 1 and 2, but

for periods 3 and 4 the recycle ratio was increased to 1.5 and  $2.5 \cdot Q_{RAW}$  respectively. The operational parameters for the systems are presented in Table 2.

Overall, process performance was good throughout the study and depended greatly on influent wastewater characteristics. The availability of carbon was suspected to be the major factor contributing to poor process performance.

## **DENITRIFICATION**

### **Denitrification Performance**

Denitrification performance for both Train A and Train B was consistent and virtually identical for periods 1 and 2, indicating that a 1.5 h anoxic HRT was sufficient for denitrification at a recycle of  $1 \cdot Q_{RAW}$ . The higher recycle rate for Train B indicated that carbon limiting conditions persisted while Train A, which was operated at the same parameters throughout, only exhibited carbon limiting conditions during period 4 (Figure 8).

Table 4 Operational parameters - all periods

		TRAIN A	TRAIN B
System SRT (d)		20	20
Anoxic HRT (h)		1.5	2.5 (per. 1 & 2, 1.5 (per 3 & 4)
Aerobic HRT (h)		2.5	2.5
F/M (gCOD/g·d)		0.26	0.27
OUR (mg O <sub>2</sub> /gVSS <sub>reactor</sub> ·h)		4.5	5.0
Recycle Rate (based on Q <sub>RAW</sub> )	period 1 period 2 period 3 period 4	1.0 1.0 1.0 1.0	1.0 1.0 1.5 2.5
C/N (gCOD <sub>deg</sub> /gTKN <sub>deg</sub> )	period 1 period 2 period 3 period 4	0.65 0.65 0.8 0.7	0.7 0.65 0.9 0.8
SVI (mL/g)	period 1 period 2 period 3 period 4	164 ± 11 253 ± 39 193 ± 50 216 ± 24	148 ± 7 286 ± 29 179 ± 43 214 ± 57
SNR (mgN/gVSS·h)	period 1 period 2 period 3 period 4	2.5 ± 0.5 2.2 ± 0.8 2.6 ± 0.5 2.1 ± 0.9	2.3 ± 0.4 2.2 ± 0.5 2.7 ± 0.6 2.6 ± 1.2
SDNR (mgN/gVSS·h)	period 1 period 2 period 3 period 4	3.1 ± 0.6 3.1 ± 1.1 3.9 ± 0.8 2.0 ± 1.3	1.9 ± 0.3 2.1 ± 0.5 4.3 ± 1.3 2.3 ± 1.5
Total N Removed (%)	period 1 period 2 period 3 period 4	52 ± 6 43 ± 5 65 ± 5 44 ± 23	54 ± 7 45 ± 12 65 ± 6 40 ± 19
Effluent Alkalinity (mg/l as CaCO <sub>3</sub> )	period 1 period 2 period 3 period 4	246 ± 47 165 ± 43 173 ± 24 124 ± 19	242 ± 33 193 ± 49 190 ± 28 119 ± 23
Effluent pH	period 1 period 2 period 3 period 4	6.3 ± 0.6 6.3 ± 0.2 6.3 ± 0.1 6.3 ± 0.1	6.2 ± 0.6 6.5 ± 0.2 6.3 ± 0.1 6.3 ± 0.1

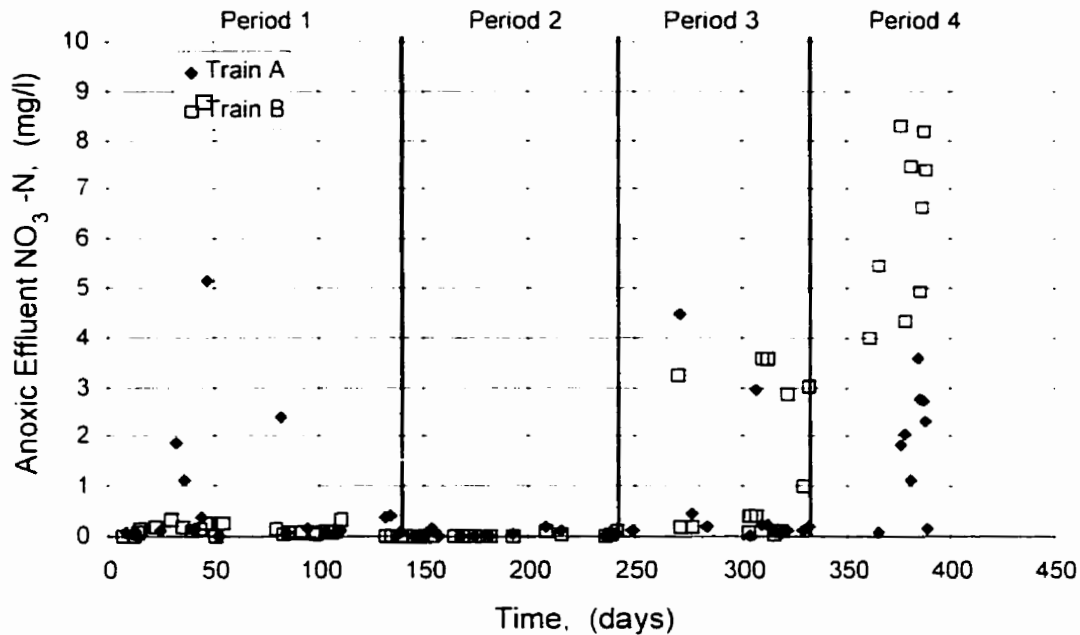


Figure 8. Anoxic effluent nitrate concentration histogram

Higher recycle rates are needed for adequate total nitrogen removals. Unfortunately, recycle brings back not only nitrate, but oxygen as well, which has been shown to be inhibitory to denitrification processes.

### Effects of Oxygen on Denitrification

The effect of dissolved oxygen is detrimental to any anaerobic process. In general, the presence of dissolved oxygen reduces the denitrification efficiency due to the preference of the heterotrophic organisms for the higher energy (aerobic) pathway. Some studies state that enzyme suppression is the cause for decreased removal efficiencies (Dawson and Murphy, 1972). The effect of oxygen on Train B can be seen in Figure 9 which shows that higher oxygen returned to the anoxic reactor through internal recycle decreases the nitrate removal efficiency.

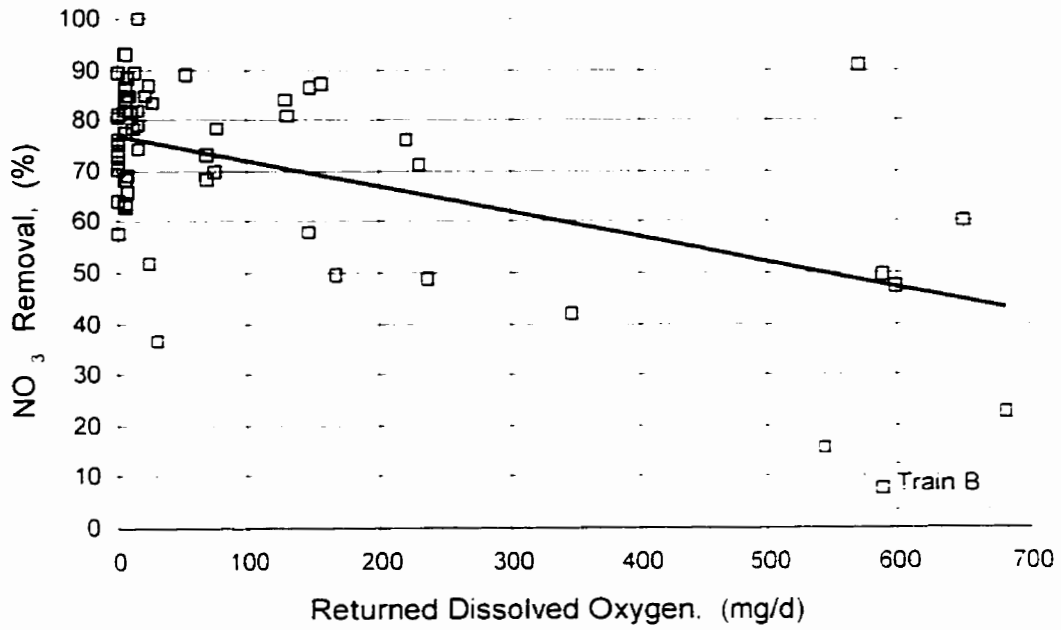


Figure 9 Denitrification efficiency as a function of returned dissolved oxygen to the anoxic reactor

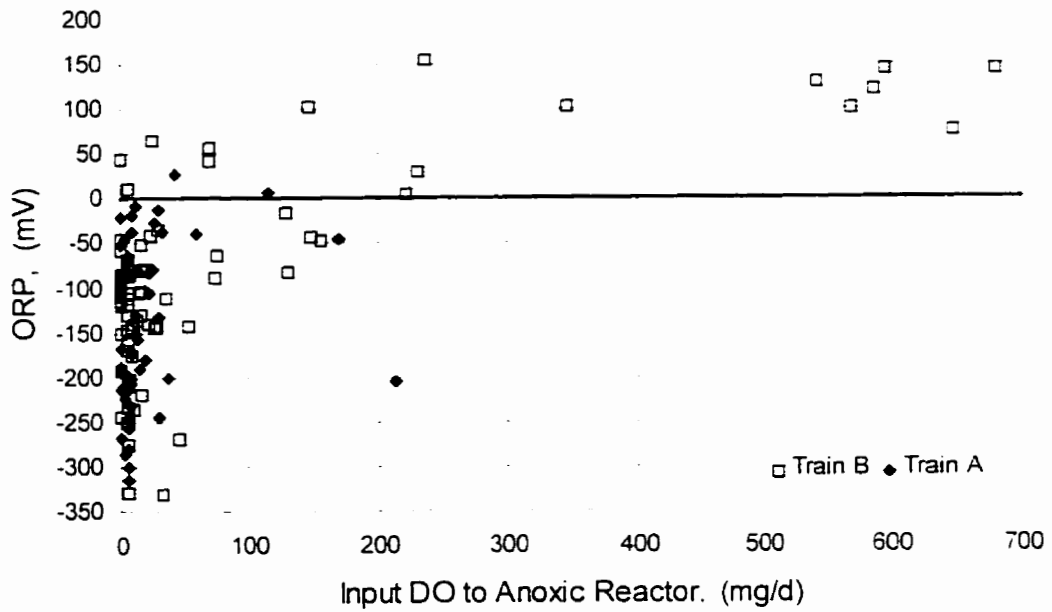


Figure 10 Oxidation reduction potential as a function of returned dissolved oxygen

The effect of dissolved oxygen can also be seen in Figure 10 which shows the ORP increases with increasing dissolved oxygen returned to the anoxic reactor. The ORP is a general measure of the half reactions taking place within the bulk solution and gives an indication of the reducing conditions present. In general, the conversion of nitrate to nitrogen gas requires conditions of approximately -150mV.

Due to the affinity of the heterotrophic organisms for higher energy yielding reactions, the presence of oxygen quickly consumes a large portion of the readily available carbon contained in the influent stream by aerobic respiration. Figure 11 shows that the anoxic effluent contained zero dissolved oxygen throughout all phases of the study indicating that carbon was preferentially utilised for deoxygenation of the recycle streams in both trains. The exception in period 4 indicates that the wastewater did not contain sufficient carbon to fully remove all of the oxygen from Train B essentially shutting down the denitrification process altogether. The smallest unit of measure on the D.O. meter was 0.2 mg/l. Verification with the manufacturer confirmed that a reading of zero would be extremely difficult to achieve due to background electronic noise within the meter and probe itself. Readings of 0.1 mg/l were considered to be zero and can be verified by the degree of denitrification obtained and low ORP values that would indicate anaerobic reactions were taking place.

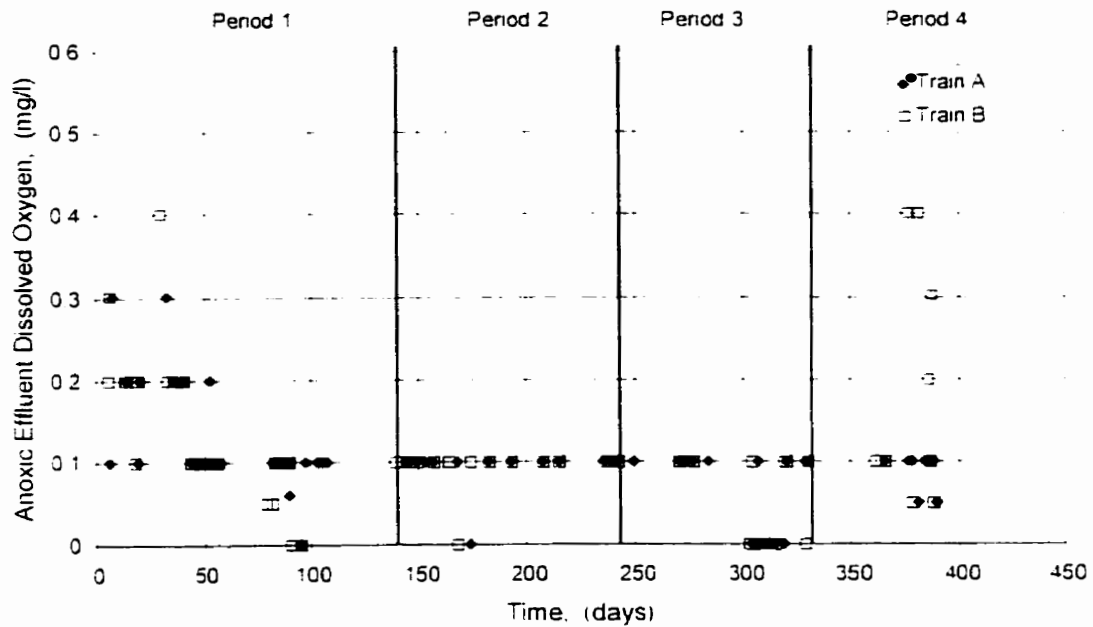


Figure 11. Anoxic effluent dissolved oxygen concentration histogram.

### Effects of $COD/NO_3-N_{eqv.}$ on Denitrification

The quantity of carbon available required for growth, reduction of nitrite, nitrate and oxygen is important such that if the system becomes limited by carbon, the denitrification will proceed at a reduced rate. Maximum denitrification rates can be observed under non-carbon limiting conditions, but will continue through endogenous respiration at a much slower rate. In systems where low influent carbon conditions persist would require an external source of carbon to ensure maximum denitrification rates. Methanol has traditionally been used as an external carbon source, but recent advances in prefermentation technology indicate that VFAs may provide a readily available and economically feasible source while eliminating the need of purchasing additional chemicals.

Results from Figure 12 and Figure 13 show that a  $COD/NO_3-N_{eq}$  ratio greater than 10 would be required for these systems. More data, especially at the higher recycle ratio, would provide a better estimate. This result corresponds to other studies where it was found that a ratio ranging from 8.5 to 15 is required to ensure non-carbon limiting conditions (Sutton et al. (1979)). The value of nitrate in this ratio includes the effects of oxygen where oxygen is expressed as nitrate equivalents.

Although the graphs indicate that lower  $COD/NO_3-N_{eq}$  ratios appear to be sufficient, it should be noted that a majority of these values constitute all values including start-up and winter conditions (period 2) where poor nitrification performance limited the amount of nitrate returned. Low nitrate and zero dissolved oxygen return ensured denitrification at ratios of less than 6, possibly due to endogenous respiration providing the necessary carbon.

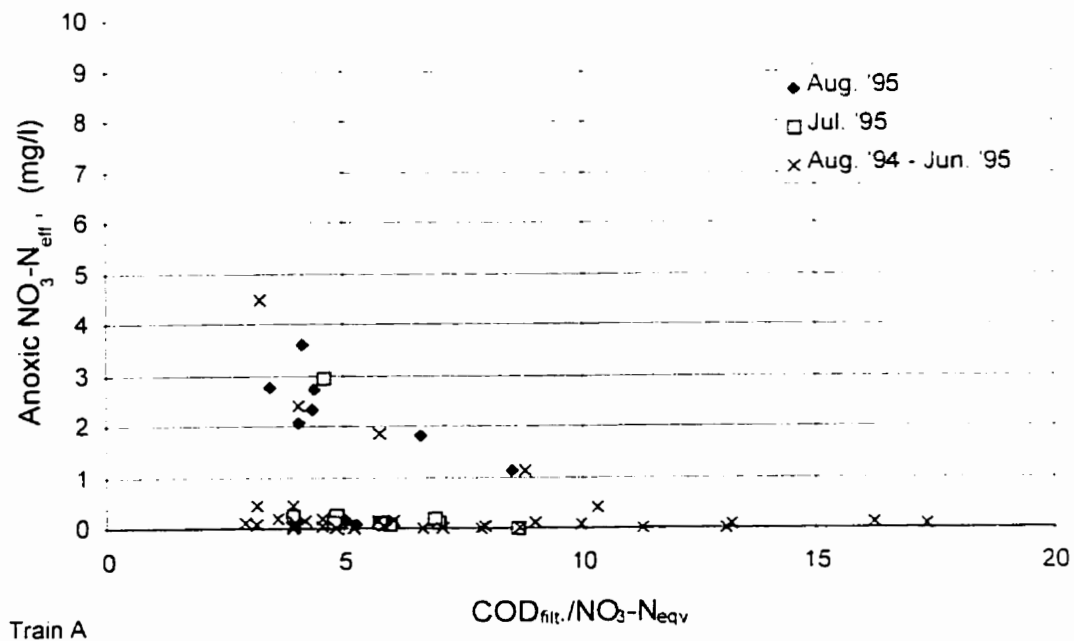
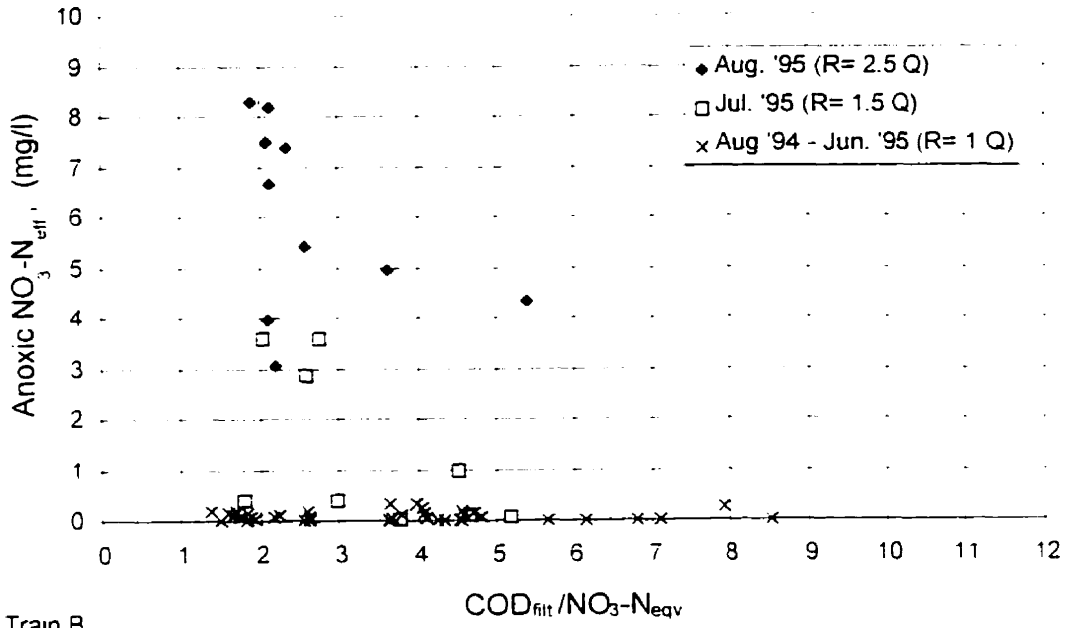


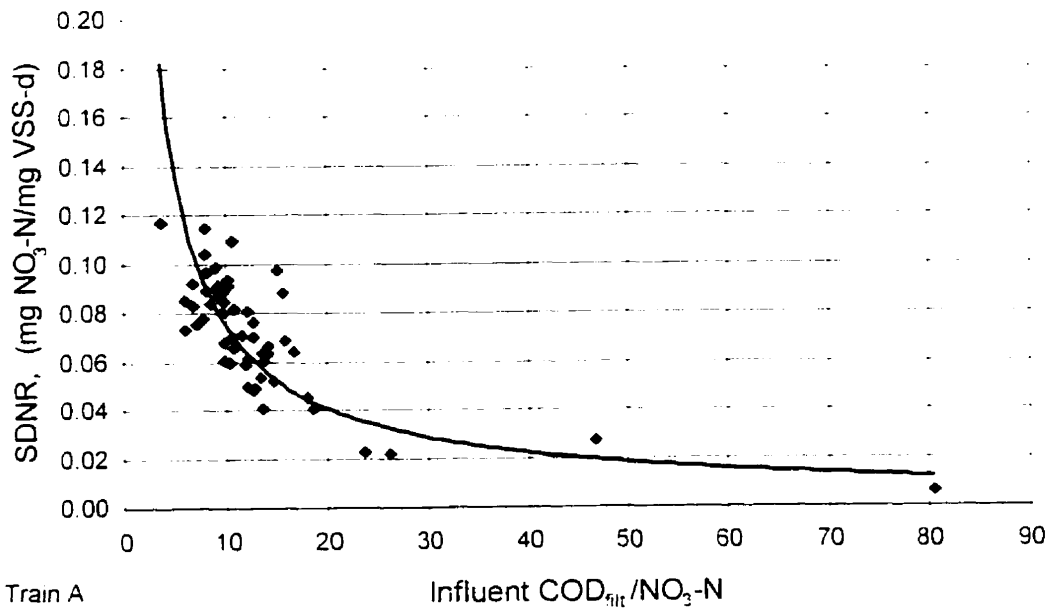
Figure 12 Train A effluent anoxic nitrate concentration as a function of  $COD/NO_3-N_{eq}$  ratio





Train B

Figure 13 Train B effluent anoxic nitrate concentration as a function of COD/NO<sub>3</sub>-N<sub>eqv</sub> ratio



Train A

Figure 14 Train A specific denitrification rate as a function of influent COD/NO<sub>3</sub>-N ratio

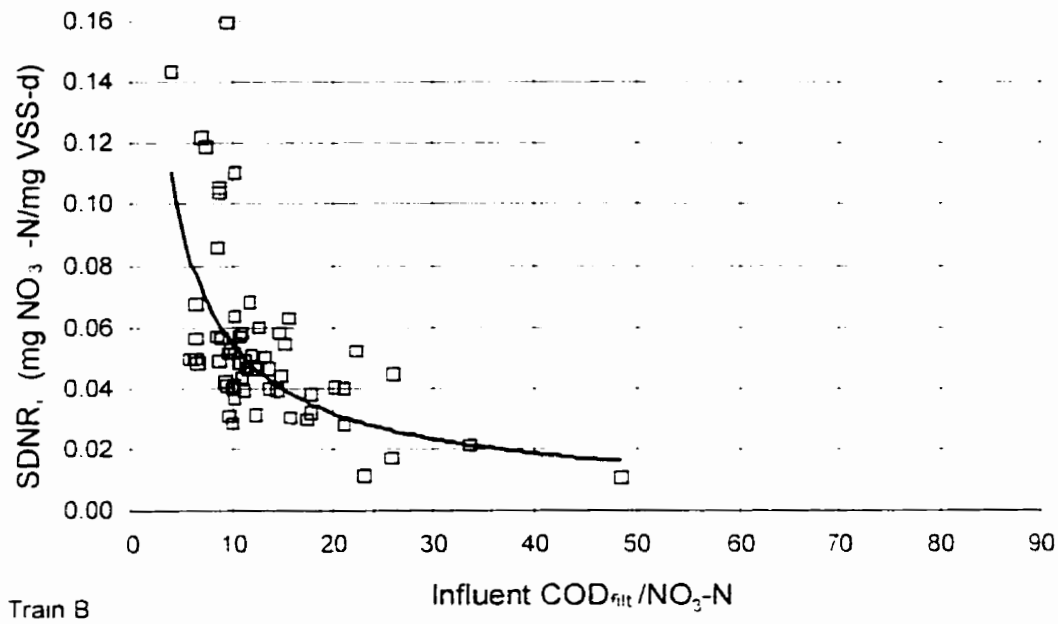


Figure 15 Train B specific denitrification rate as a function of influent COD/NO<sub>3</sub>-N ratio

Intuitively, one would expect the SDNR to increase as the COD/NO<sub>3</sub>-N ratio increased which would be the case for a system where the nitrification efficiency was greater than 90% (Figure 14 and Figure 15). This would also be the case in a system where carbon was obtained from endogenous respiration, but neither of these conditions were met in these systems for an extended period of time. Another factor to consider is that nitrate must be present in the anoxic reactor effluent in order to determine the maximum denitrification rate. Most results from this study indicate nearly zero nitrate or nitrite in the anoxic reactor effluent, hence the maximum denitrification rate could not be determined for most conditions. As a result, the graph indicates the relationship between the SDNR and the nitrate return to the anoxic zone. As was discussed previously, the system exhibited complete denitrification

throughout the study and where the COD/NO<sub>3</sub>-N was low, the required carbon was apparently obtained from endogenous respiration in the anoxic zone.

Considering non-carbon limiting conditions, Figure 14 and Figure 15 reflect that the SDNR depends on the nitrate returned to the anoxic reactor. Further studies with an external carbon source and higher recycle rates normally used in single-sludge systems 3 to 4 based on  $Q_{R(N)}$  are required to produce the desired graph.

Figure 16 shows that denitrification efficiency which increases as the COD NO<sub>3</sub>-N ratio increases. This result conforms to theory and shows the dependency of denitrification on carbon. The lower points reflect conditions in period 4 where weak wastewater conditions existed. If period 4 were removed, the graph would exhibit a linear trend. A COD NO<sub>3</sub>-N ratio of greater than 10 for denitrification efficiencies greater than 70% is needed as was discussed earlier.

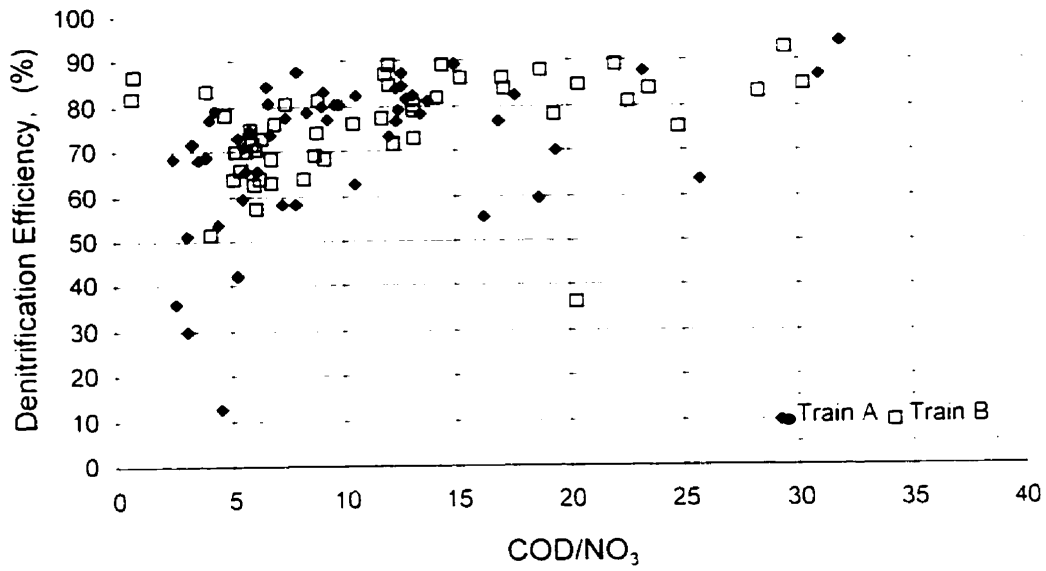


Figure 16 Denitrification efficiency as a function of COD/NO<sub>3</sub> ratio

### Effects of Recycle on Denitrification

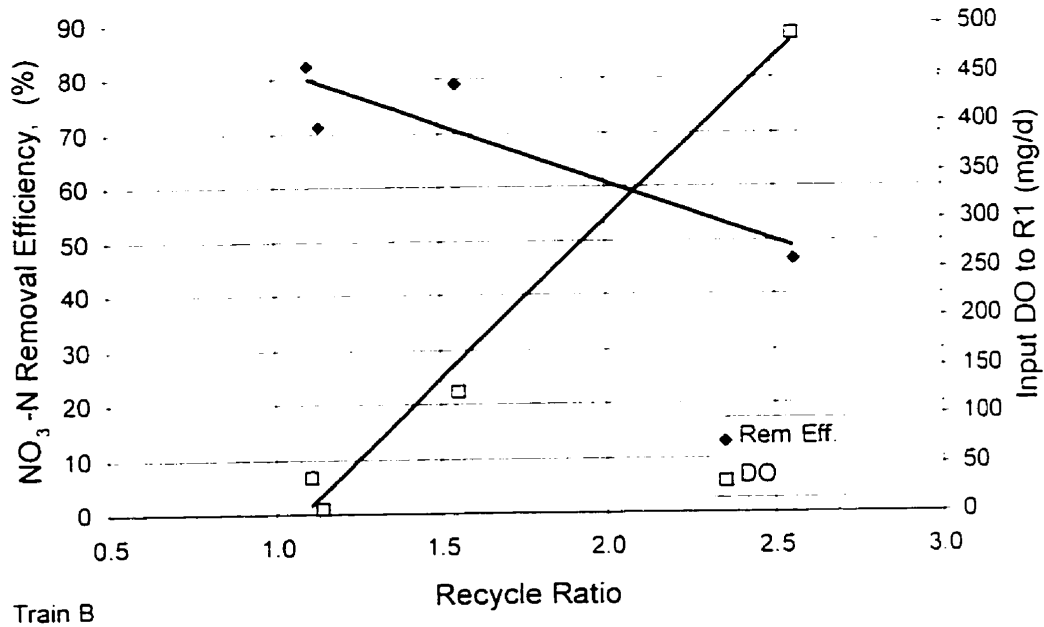


Figure 17 Effect of increased recycle ratio on nitrate removal efficiency in the anoxic reactor and returned dissolved oxygen.

As discussed previously, dissolved oxygen is detrimental to the denitrification process. The main benefit of pure-oxygen systems is the higher driving force for the dissolution of oxygen into the bulk solution as well as into the floc. It is suspected that in pure-oxygen systems, a greater portion of the floc maintains aerobic conditions, which is not present in conventionally aerated system.

Process configuration determines the maximum attainable total nitrogen removal. In separate-stage systems such as that used in Tampa, total nitrogen removals approaching 100% are possible. In a predenitrification system, total nitrogen removal is limited by the amount of nitrate which can be recycled to the anoxic reactor. Theoretically and economically, the maximum removal approaches 80% at a recycle ratio of  $+Q_{\text{max}}$  assuming sufficient carbon is present.

Nitrate removals in the anoxic reactor decrease dramatically as the recycle ratio increases (Figure 17) and appear to be directly related to the returned dissolved oxygen. This graph exemplifies the fact that denitrification micro-organisms will preferentially select oxygen as the terminal electron acceptor in an anoxic environment, reducing the overall nitrate removals with a corresponding increase in returned dissolved oxygen. The clumping of the first three points indicates that approximately 72-83% nitrate removal occurred even though it appeared that carbon availability played a significant role in denitrification.

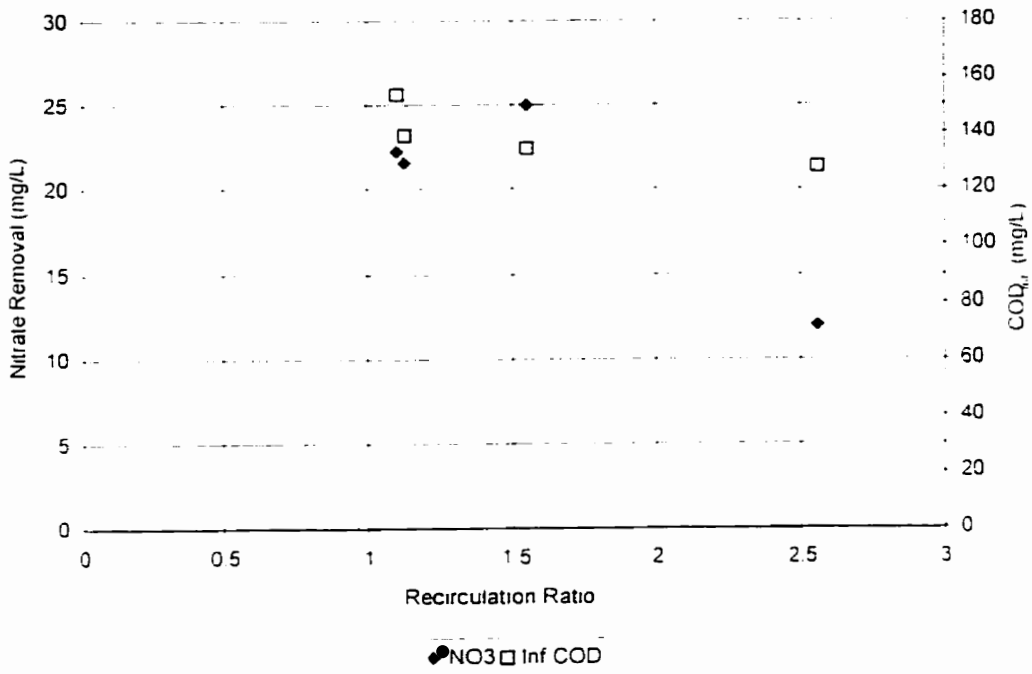


Figure 18: Train B nitrate removal: Recycle ratio vs. influent COD concentration.

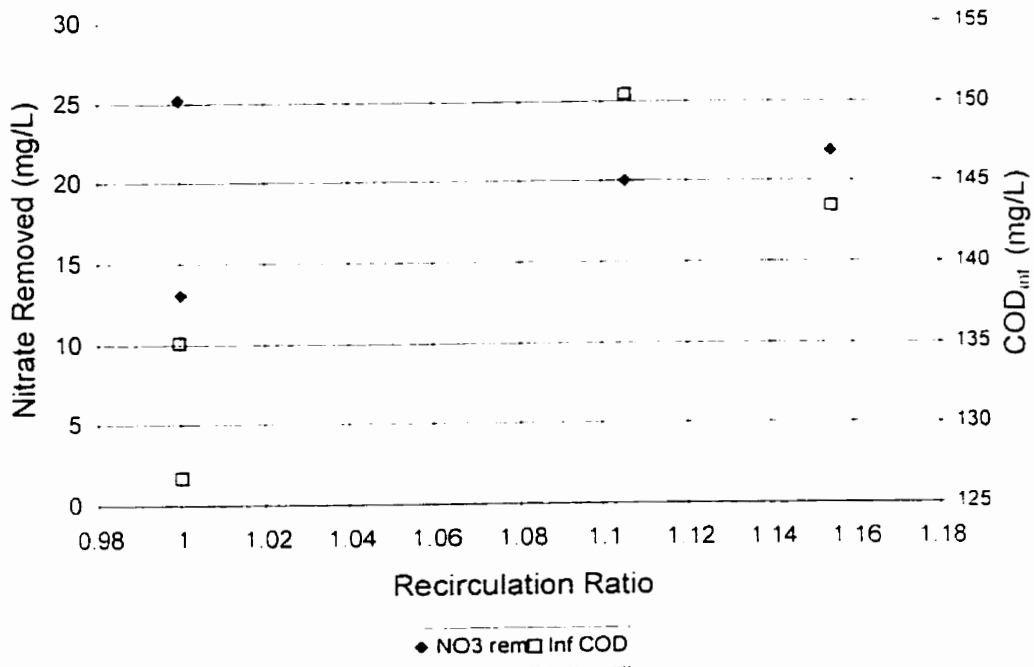


Figure 19: Nitrate removal in Train A vs. recycle ratio and influent COD concentration.

This is further exemplified in Figure 18 and Figure 19 where nitrate removals are compared to recycle ratio and influent COD (soluble). Here one can see that as the recycle ratio increases, nitrate removal decreases. If carbon was the limiting factor, one expects that the decrease in nitrate removal would correspond fairly closely with the influent COD concentration. The effect of higher returned dissolved oxygen loading can be clearly seen in the increased reduction of nitrate removal in Train B where higher recycle ratios had been employed. Train A did not increase the recycle and the nitrate removal as a function of influent COD concentration can be seen. This figure shows that nitrate removal toward the end of the study decreased due to carbon limitation.

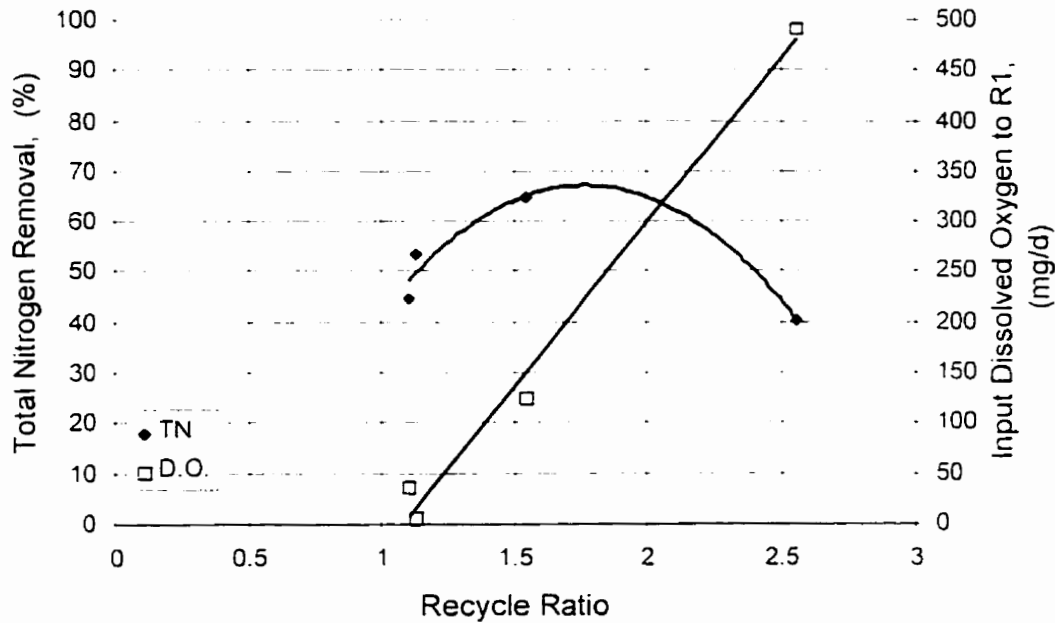


Figure 20 Effect of recycle ratio on total nitrogen removal and returned dissolved oxygen

Figure 20 shows that total nitrogen removals reach an optimum level at a recycle ratio of approximately  $1.8 \cdot Q_{RAW}$ . Again, oxygen appears to have a direct affect on total

nitrogen removals. These graphs are important because they indicate that the particular wastewater entering the NEWPCC contains enough carbon to sustain a recycle ratio of  $1.8 \cdot Q_{RAW}$ . Higher removals should be possible with an external source of carbon while minimising the volume of the anoxic reactor provided a readily available carbon source such as VFA's or methanol is used.

## **NITRIFICATION**

### **Effect of COD/TKN on Nitrogen Removal**

Carbon, while required for denitrification, is not desired for nitrification. Literature indicates that heterotrophic organisms, carbon oxidisers, have growth rates up to twenty times that of nitrifying organisms. It is therefore essential to remove as much carbon as possible in order to minimise the competition between the heterotrophic and autotrophic organisms. Failing to remove carbon, the operator would have to increase the system SRT or HRT in order to ensure sufficient aerobic residence time is provided to the nitrification organisms.

The influent COD/TKN ratio is a particularly important parameter to observe when considering single-sludge systems. While a low ratio indicates good nitrification potential and is preferred for a nitrifying system, it could inhibit denitrification in a single-sludge predenitrification system. A high ratio, on the other hand benefits denitrification, but hinders nitrification performance if excessive carbon bleeding occurs. A proper ratio must be maintained in order to optimise the performance of a single-sludge predenitrification system.



The effects of COD/TKN on nitrification can be seen in Figure 21 and Figure 22 where effluent total nitrogen increases as COD/TKN ratio decreases. The decreasing trend in these two graphs indicates that as the influent carbon loading decreases, a corresponding decrease in denitrification would also take place resulting in a higher effluent total nitrogen concentration.

The specific effects of carbon can be seen in Figure 23 and Figure 24 where higher influent COD concentration decreases nitrification capacity and increases effluent ammonia values. The spread in the data points reflects a problem associated with sampling procedure. The influent container contained enough feed to supply the system for approximately 1.5 days. The container was mixed continuously maintaining uniform COD concentrations throughout the day. Effluent samples were taken from the clarifier and depended entirely on the performance of the system for the previous two-hour interval only. Although strict control of operational parameters was practised, variations in nitrification performance occurred.

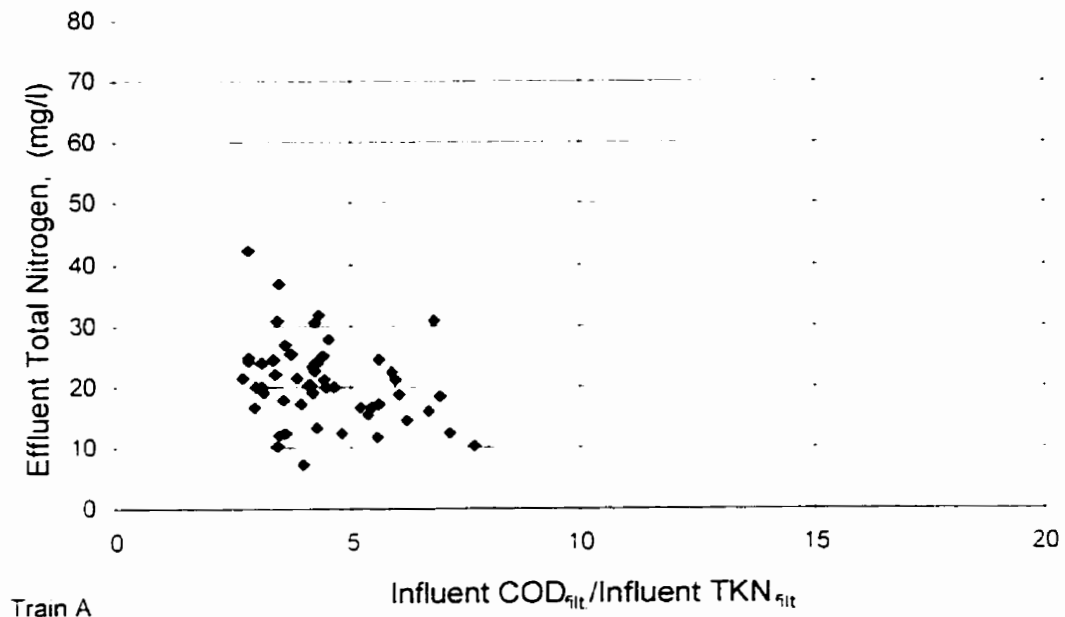


Figure 21 Train A effluent total nitrogen concentration as a function of influent COD:TKN ratio.

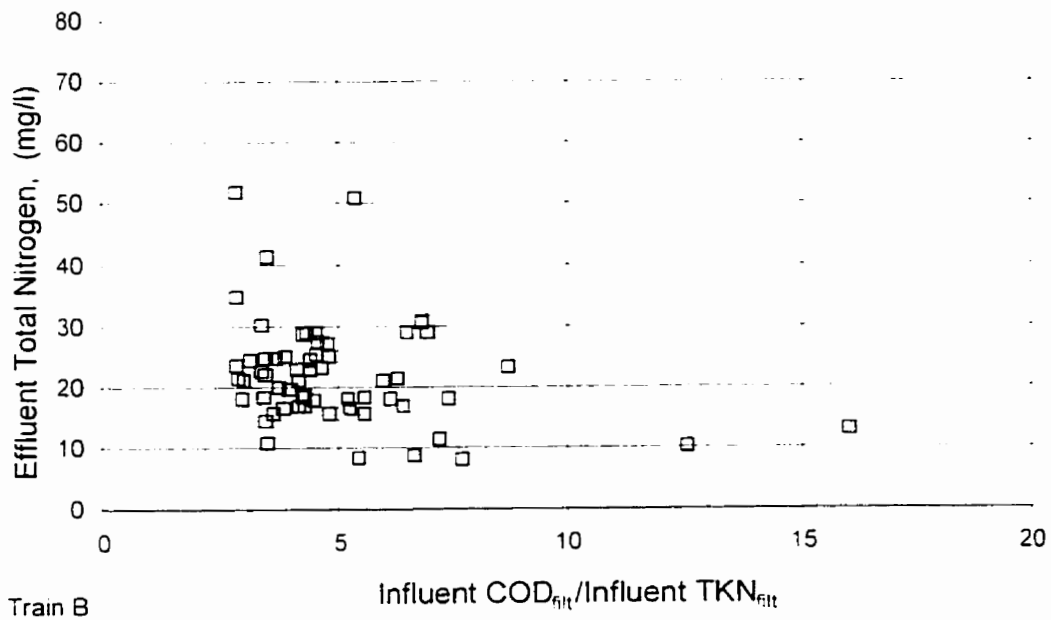
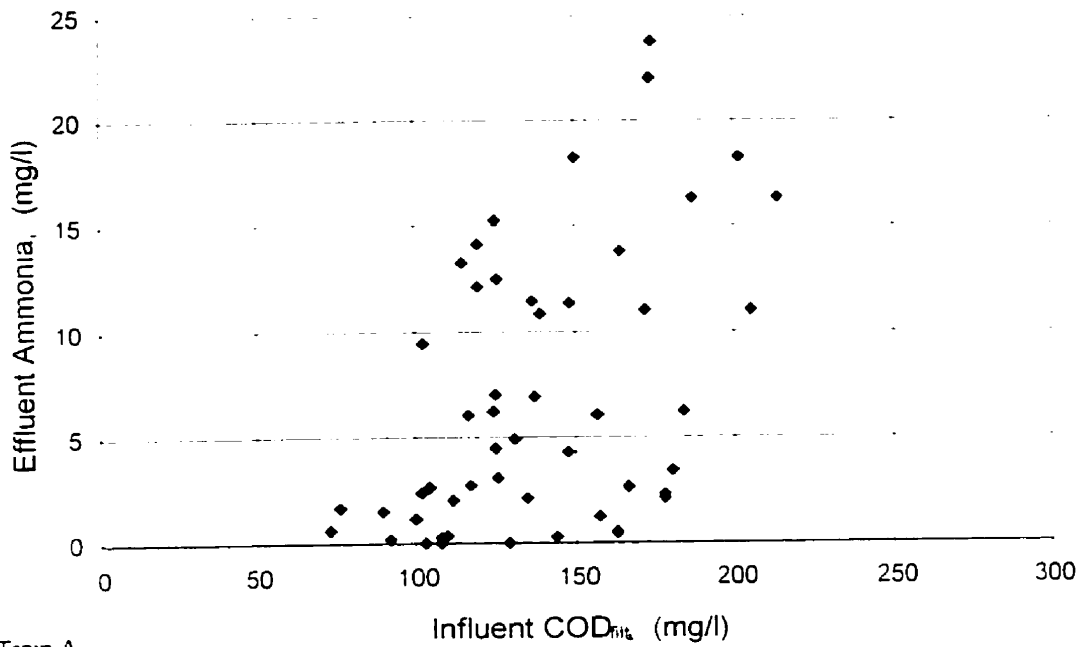
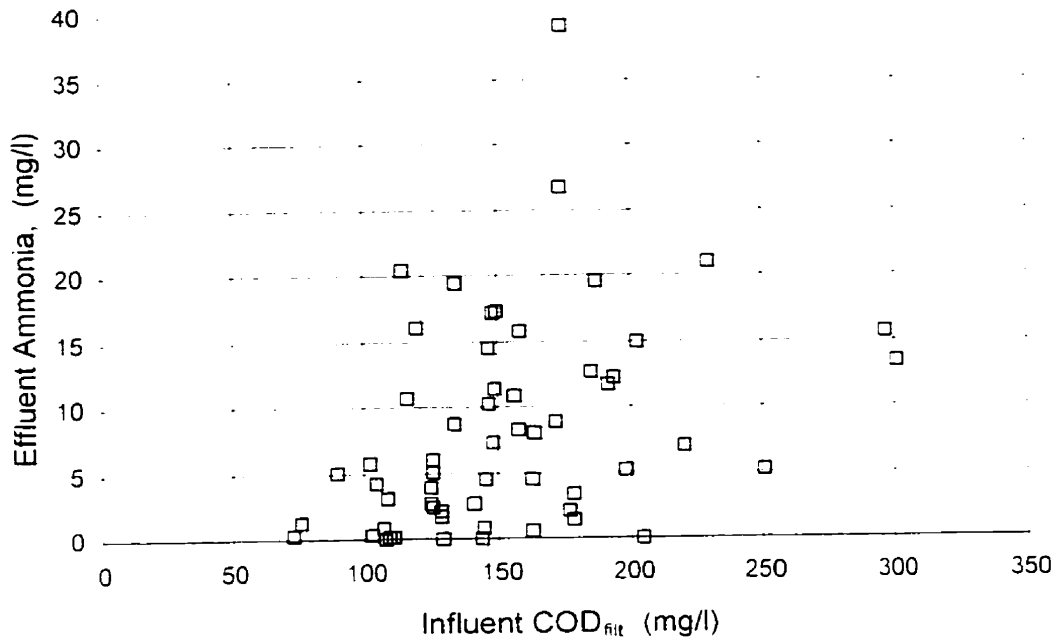


Figure 22 Train B effluent total nitrogen as a function of influent COD:TKN ratio



Train A

Figure 23 Train A effluent ammonia concentration as a function of influent COD concentration



Train B

Figure 24 Train B effluent ammonia concentration as a function of influent COD concentration.

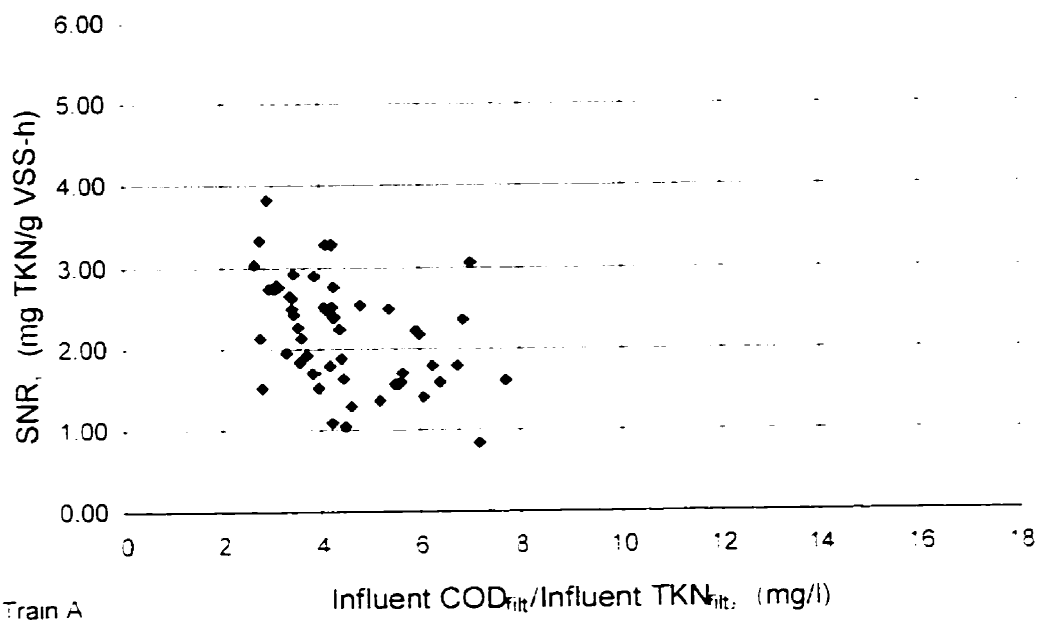


Figure 25 Train A SNR as a function of influent COD/TKN ratio

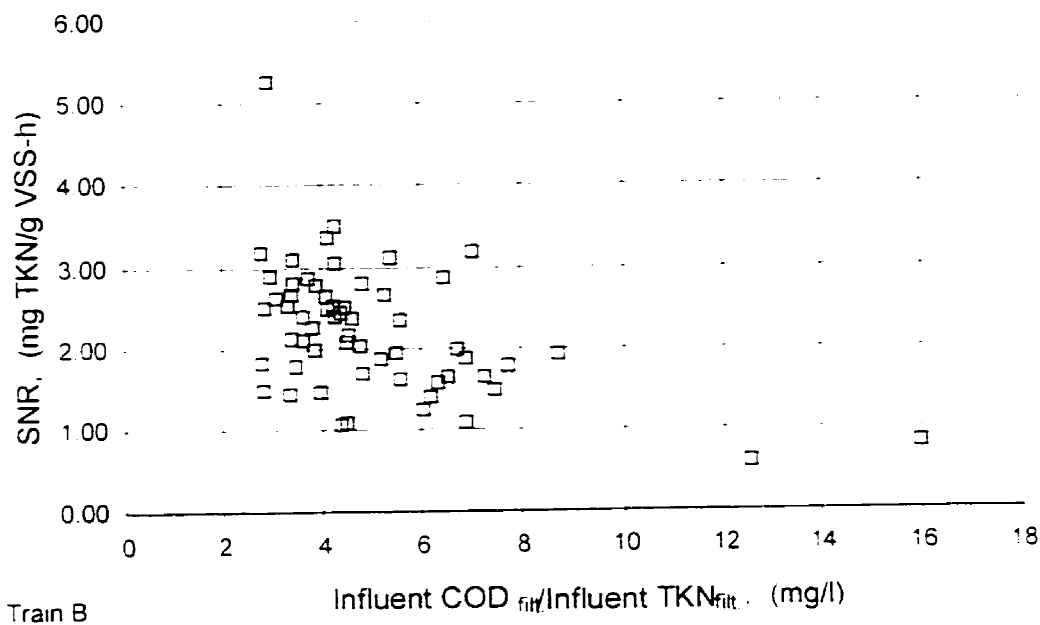


Figure 26 Train B SNR as a function of influent COD/TKN ratio

The specific nitrification rate is a function of several variables including the influent COD/TKN ratio, the D.O. levels in the aerobic zone and the quantity of biomass present relative to the nitrification achieved. Figure 25 and Figure 26 illustrate the effect of the influent COD/TKN ratio on the specific nitrification rate of the aerobic zone. Higher influent carbon loading have been shown to inhibit nitrification through an increased competition between the autotrophic nitrifiers and the heterotrophic organisms Hanaki et al. 1990a. The above graphs indicate that the specific nitrification rate decreases from a value of 2.50 mgTKN/gVSS-d down to 1.25 mgTKN/gVSS-d for the corresponding influent COD/TKN ratios of 3 and 7.

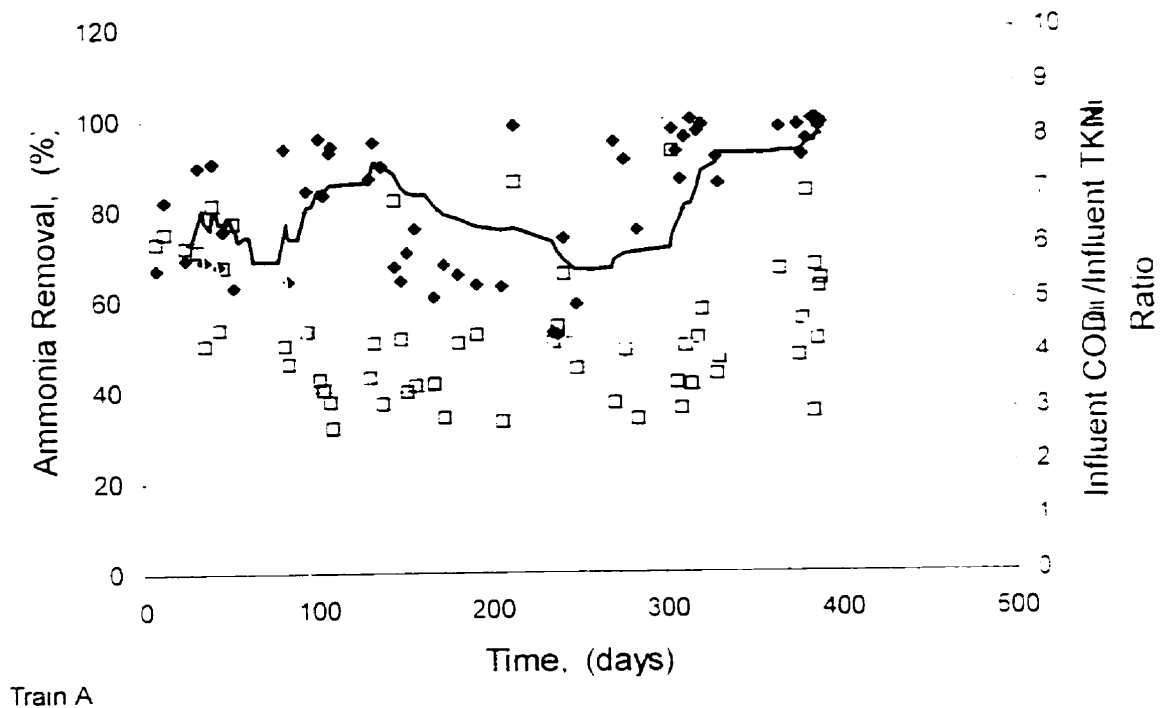


Figure 27 Train A Ammonia Removal as a function of influent COD/TKN

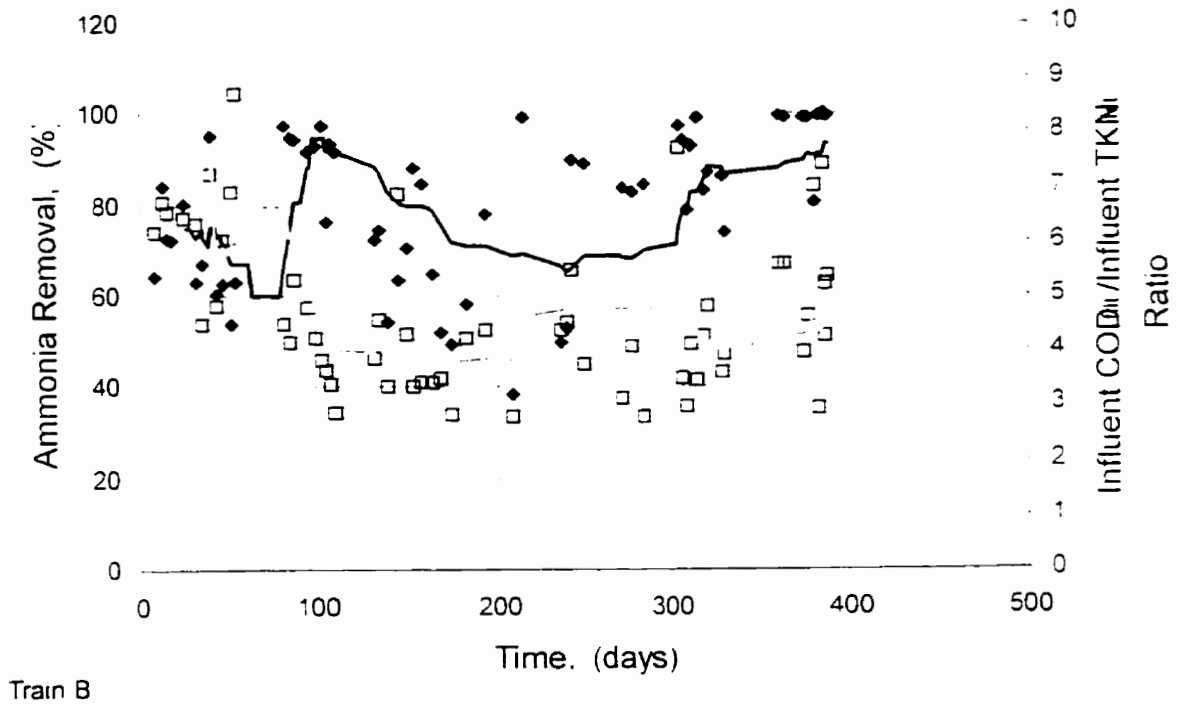


Figure 28. Train B Ammonia Removal as a function of influent COD/TKN ratio

Figure 27 and Figure 28 illustrate the effect of the influent C/N ratio on nitrification performance. The influence of the influent C/N ratio has been suggested to inhibit nitrification through the increased competition for available oxygen with heterotrophic organisms. Due to a significantly higher growth rate for heterotrophic organisms, higher influent C/N ratios have been shown to result in decreased nitrification rates in single sludge systems (George, 1996). It is evident from these graphs that an inverse relationship exists between the ammonia removal efficiency and the influent C/N ratio.

### **Effect of Influent TKN on Nitrification**

Intuitively, one would suspect that an increase in nitrogen loading to a system would result in an increase in the specific nitrification rate of the system until the nitrification rate reaches a maximum that can be provided by the biomass under the given operating conditions. This will be true provided no other factors are found to be inhibiting. A graphical representation of this consists of a straight line from the origin indicating the maximum specific nitrification rate attainable for a specific influent TKN loading rate. Figure 29 and Figure 30 use this representation to illustrate the maximum nitrification rate attainable for this system as a function of influent TKN loading. The figures show that the maximum SNR for Train A ranges from 1.25 mgTKN gVSS-d to 3.00 mgTKN gVSS-d at influent TKN concentrations of 19 and 47 mg/L, respectively. In comparison, R. George 1996 found nitrification values of 0.87 - 2.83 mgNH<sub>4</sub><sup>+</sup>-N gVSS-h at 12°C.

The graphs indicate that there is a similar maximum specific nitrification rate between Train A and Train B. Data points to the right of the line indicate periods of incomplete nitrification and inhibition that occurred during period 2 of the study.

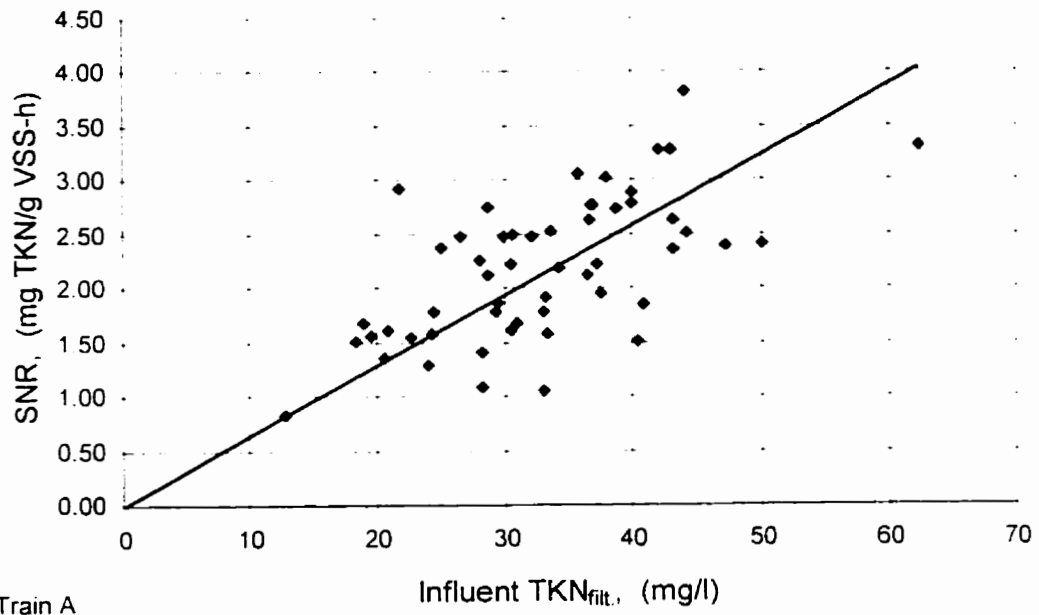


Figure 29 Specific nitrification rate indicated as a function of the influent TKN loading for Train A.

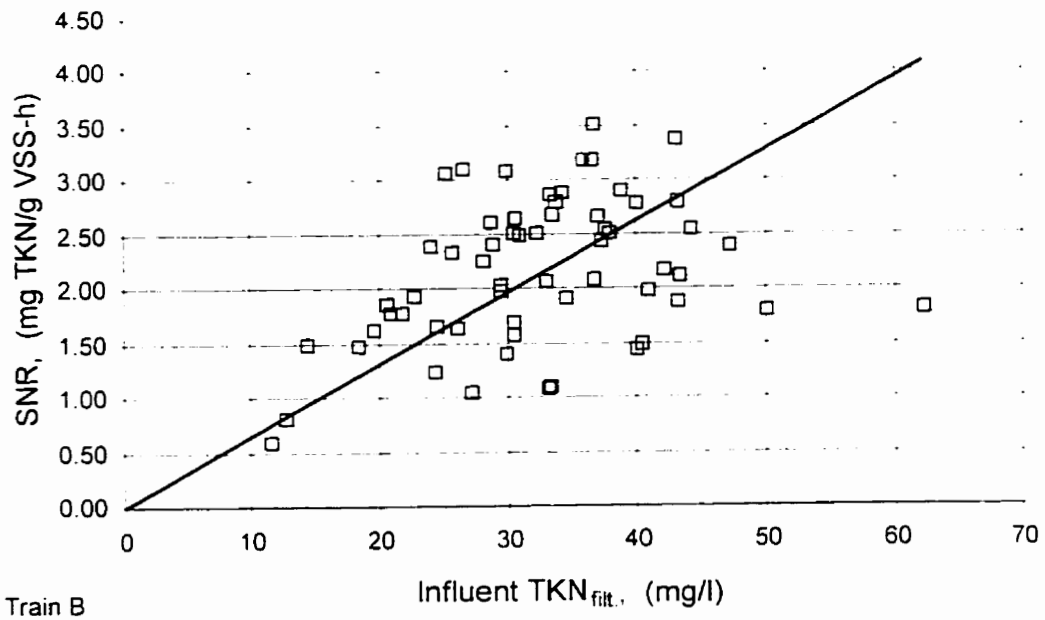


Figure 30 Specific nitrification rate indicated as a function of the influent TKN loading for Train B.



## **BENEFITS OF PREDENITRIFICATION CONFIGURATION ON ALKALINITY DESTRUCTION AND pH DEPRESSION**

Sears (1995) studied the effects of pH and alkalinity on nitrification in a pure-oxygen activated sludge system. The study was conducted at a temperature of 20-24°C. The study indicated that a 4h HRT was required to achieve stable nitrification performance, but found that pH suppression due to alkalinity destruction could hinder the process stability. Both this study and that of Sears (1995) used similar influent.

Sears (1995) found that nitrification was feasible in a pure-oxygen activated sludge system, but operational stability could become compromised by pH suppression. Because of the dependence of the nitrifier growth rate to pH, a 4 hr total HRT was required to achieve nitrification at a pH as low as 5.5. In the predenitrification configuration, pH suppression was alleviated allowing for consistent nitrification throughout the study except for period 2 when a period of inhibition to nitrification was observed. This inhibition was also observed in a parallel study by George (1996). The cause for the inhibition could not be determined, but it is suspected that a change in influent wastewater characteristics at the NEWPCC was the cause. NEWPCC staff indicated that an annual degradation in the dewaterability of their digested sludge resulting in an need for increased polymer addition. Some sources indicate that certain polymers may be inhibitory to the nitrification process, but this can not be determined from this study and should be investigated in future studies.

A comparison between the nitrification and predenitrification systems is shown in Figure 31. It can be seen that as ammonia removal increases, a corresponding decrease in effluent alkalinity occurs as a result of alkalinity destruction during the nitrification

process. Operation in a predenitrification configuration would recover approximately 3.59 mg of alkalinity per mg of nitrate reduced resulting in increased effluent alkalinity. The effluent alkalinity in the predenitrification configuration is maintained at approximately 200 mg/L as CaCO<sub>3</sub> through the recovery of alkalinity.

Figure 32 illustrates the effect of pH suppression due to alkalinity consumption in nitrification and predenitrification configurations. For nitrification alone, the pH reached a lower limit of approximately 5.5 as the nitrification efficiency approached 100%. Approximately 7.1 mg of alkalinity is required for each mg of ammonia removed. The predenitrification configuration alleviates pH suppression by increasing the buffering capacity of the system through the production of alkalinity in the denitrification reaction, thereby ensuring a more stable operation at the noted operating conditions.

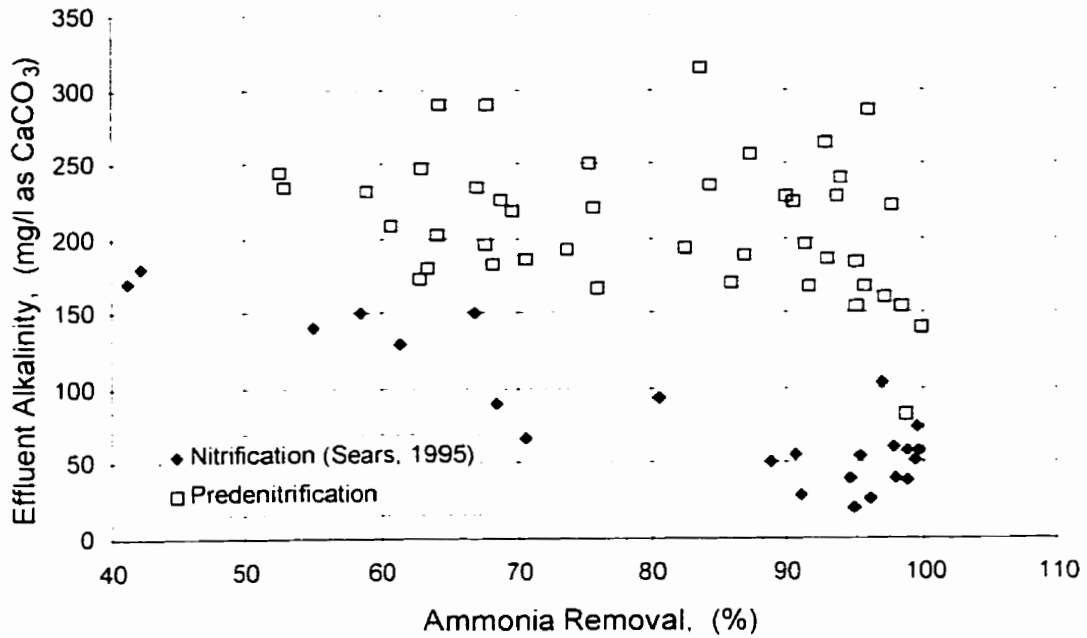


Figure 31 Effluent alkalinity concentrations as compared with ammonia removal in a nitrification and predenitrification configuration.

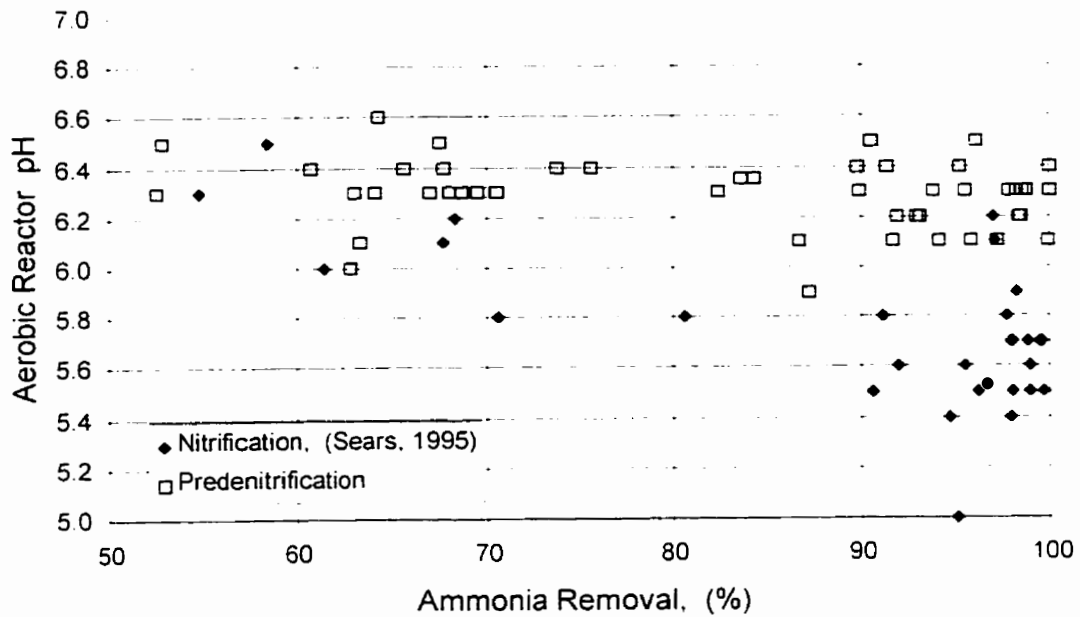


Figure 32 pH suppression as a result of alkalinity consumption in nitrification and predenitrification configuration.

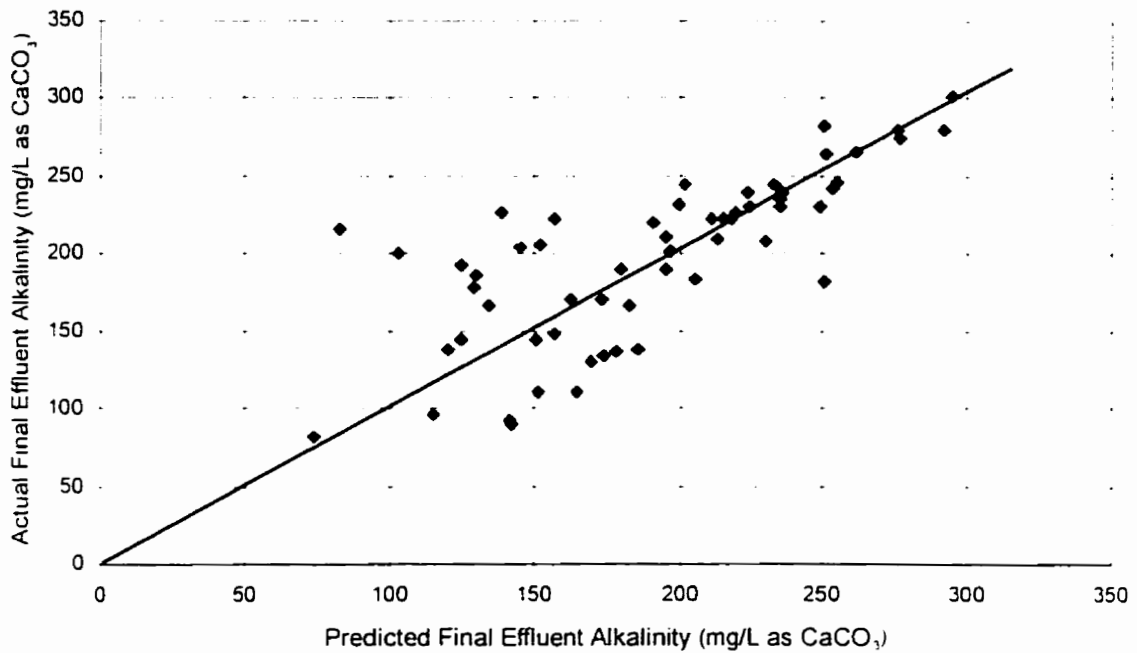


Figure 33 Predicted alkalinity of the final effluent in Train B vs. actual final effluent alkalinity

Figure 33 illustrates the predicted final effluent alkalinity of Train B. The predicted final effluent alkalinity was calculated assuming an alkalinity production of 3.59 mg alkalinity per mg of nitrate nitrogen reduced and 7.24 mg alkalinity consumption per mg ammonia nitrogen oxidised. The actual effluent alkalinity corresponds to the predicted effluent alkalinity verifying the overall alkalinity destruction and production within the system. This indicates that the overall stability of the process in terms of effect of alkalinity and pH on nitrification will be greater in a predenitrification configuration.

## SUMMARY AND CONCLUSIONS

A study was conducted to evaluate the feasibility of total nitrogen removal in a pure-oxygen, single-sludge, predenitrification system. The study was conducted at the University of Manitoba Environmental Engineering Laboratory and is a culmination of several studies investigating the use of biological nitrification and nitrogen removal previously conducted by Capponetto (1993), Hagar (1995) and Sears (1995).

The study consisted of two parallel trains in a modified Lutzack-Ettinger process. The study was conducted in four phases. The first phase consisted of the start-up phase where both trains were allowed to achieve steady state conditions. The second phase corresponded to an inhibitory phase where 50% nitrification and a corresponding decrease in denitrification was observed. The source of inhibition could not be determined during the course of this study. The third and fourth phases observed complete nitrification and corresponding increases in denitrification. However, a slight decrease in the influent COD concentration lead to difficulty in maintaining denitrification even though complete nitrification was observed in both trains. It is assumed that the composition of the influent COD changed during this period such that the fraction of refractory organics increased.

The main findings of this study indicate that utilising a pre-denitrification configuration for total nitrogen removal in a pure-oxygen activated sludge system is feasible, provided that sufficient carbon is contained in the influent wastewater stream.

The pre-denitrification configuration had the effect of increasing process stability through the production of alkalinity in the anoxic zone. Comparisons with previous studies indicate that pH in the aerobic zone was maintained above 6.0 while a single sludge nitrification configuration resulted in a pH suppression down to 5.5 and the inhibition of nitrification due to inhibition resulting from free nitrous acid formation.

Total nitrogen removals approached the theoretical value of 73% with a recycle ratio of 2.5  $Q_{RAW}$ . Total nitrogen removals depended upon several factors including ammonia removal in the aerobic zone, recycle ratio and influent carbon availability. Total nitrogen removal was severely limited due to an unknown inhibiting factor causing nitrification to drop to 50% throughout the winter months.

Optimisation of the system was achieved by decreasing the anoxic HRT from 2h to 1.5h and also by increasing the recycle ratio. Complete denitrification was observed at a 1.5 h HRT. Nitrate breakthrough from the anoxic zone was observed at higher recycle ratios. The return of nitrate along with dissolved oxygen and limited carbon availability resulted in a decrease in the nitrate removal efficiency in the anoxic zone. Recycle ratios in this study ranged from 1 to 2.5  $Q_{RAW}$ , but a recycle ratio of 1.8  $Q_{RAW}$  was found to be the optimum to ensure complete denitrification under non-carbon limiting conditions.

The conclusions to this study are summarised in the following:

1. Consistent denitrification was maintained at a short anoxic hydraulic retention time of 1.5 h. Nitrate removal efficiency was found to be 79.1% and 48.5% for recycle ratios of 1.5 and 2.5 respectively. Total nitrogen removals of 65% were observed during phase three of the study.
2. Complete nitrification was observed at an aerobic hydraulic retention time of 2 h. Ammonia removals during period 2 and 3 were observed to be 94% to 98% for Train A and 88% to 98% for Train B. An unexplained period of inhibition decreased the nitrification efficiency to 50% during period 2 of the study.
3. pH suppression due to alkalinity destruction during nitrification was alleviated and a stable effluent pH was observed throughout the study. pH in the anoxic zone, aerobic zone and final effluent was found to be 6.6, 6.3, and 6.5 respectively during periods of complete nitrification.
4. Effluent alkalinity remained stable throughout the study at an average effluent concentration of 195 mg/l and 200 mg/l for Trains A and B respectively, illustrating the ability of the anoxic zone to provide buffering capacity to the system.
5. System configuration, influent wastewater characteristics and nitrification performance determine the extent of the maximum denitrification attainable in a predenitrification configuration. A specific denitrification rate of 4.3 mgN<sub>i</sub>/gVSS-h was observed for Train B during period three of the study.
6. Total nitrogen removals approaching the theoretical limit of 65% were observed at a recycle ratio of 1.5  $Q_{R,FA}$ .

7. Influent carbon composition and concentration played a significant role in denitrification at higher recycle ratios. Available carbon in the influent wastewater limited the maximum practical recycle ratio to  $1.8 Q_{2:1}$  to ensure complete denitrification under non-carbon limiting conditions.
8. A COD  $\text{NO}_3^- \text{N}_{\text{max}}$  ratio of at least 10 is required to sustain complete denitrification under non-carbon limiting conditions.



NOMENCLATURE

ALK	Alkalinity (mg/L as CaCO <sub>3</sub> )
BOD	Biochemical Oxygen Demand (mg/L)
COD	Chemical Oxygen Demand (mg/L)
D.O.	Dissolved Oxygen (mg/L)
HRT	Hydraulic Retention Time (h)
MLSS	Mixed Liquor Suspended Solids (mg/L)
MLVSS	Mixed Liquor Volatile Suspended Solids (mg/L)
NH <sub>3</sub>	Ammonia Nitrogen (mg/L)
NO <sub>3</sub>	Nitrate (mg/L)
NO <sub>3</sub> -N <sub>ox</sub>	Nitrate Equivalent as O <sub>2</sub>
Q <sub>raw</sub>	Raw Influent Flow (L/d)
SNR	Specific Nitrification Rate (mg N/g VSS-h)
SDNR	Specific Denitrification Rate (mg N/g VSS-h)
SOC	Soluble Organic Carbon (mg/L)
SRT	Solids Retention Time (d)
SVI	Sludge Volume Index (mL/g)
TKN	Total Kjeldahl Nitrogen (as N)
TOC	Total Organic Carbon (mg/L)
TSS	Total Suspended Solids (mg/L)
VSS	Volatile Suspended Solids (mg/L)

## SUGGESTIONS FOR FUTURE STUDY

Although this study provided indicated the potential of using a pure-oxygen activated sludge system in a predenitrification configuration for total nitrogen removal, additional study is required in order to establish a complete picture of the potential capital and operational cost savings which could be provided by this system. Suggestions for future study utilising pure-oxygen activated sludge systems are as follow:

1. The scale of the project should be increased to a pilot scale. This would serve to confirm results obtained in this and previous studies conducted at the University of Manitoba.
2. Study different SRT's to determine the kinetic coefficients in the predenitrification configuration. The study should also consider a combination of HRT's to determine the minimum total HRT required to achieve total nitrogen removal.
3. Future studies are required to evaluate the need of a supplemental carbon source for complete denitrification at increased recycle ratios. Although carbon could not be readily shown to inhibit nitrification in this study, it became apparent that denitrification efficiency was hindered.
4. A problem arose in the winter months where nitrification efficiency dropped to approximately 50%. This occurred in this study, as well as a parallel study being

conducted by R. George (1996). The cause is suspected to be a change in the characteristics of the influent wastewater such that removals were being inhibited.

5. Future studies need to look at headspace gas composition and the effect that entrapped gases may have on the carbonic acid equilibrium in the bulk solution. Studies should look at various alternatives such as predenitrification with a sealed headspace, and also at nitrification and predenitrification with the headspace open to atmosphere.

## ENGINEERING SIGNIFICANCE

This study provided a brief look into the feasibility and limitations of total nitrogen removal in a pure-oxygen, activated sludge system in a predenitrification configuration. Understanding the role that oxygen and oxygenated compounds play in denitrification will lead to an overall understanding of the process and can lead to process modification that will allow full use of the advantages provided by a pure-oxygen system.

This study indicated that a total HRT of 4 hours is sufficient to achieve greater than 90% ammonia removal and to approach the theoretical limit for total nitrogen removal based on sludge and internal recycle streams. The predenitrification configuration requires a smaller aerobic zone which could lead to lower initial capital costs when considering greenfield or retrofit applications.

Lower aeration requirements can also be realised due to the consumption of readily available carbonaceous compounds in the anoxic zone and the subsequent decrease in organic loading to the aerobic zone. Although this study did not investigate the potential cost savings, based on theoretical oxygen requirements, a saving in aeration requirements of approximately 24% could be realistically achieved.

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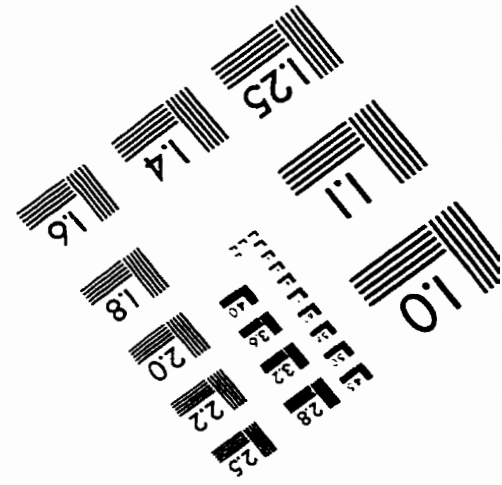
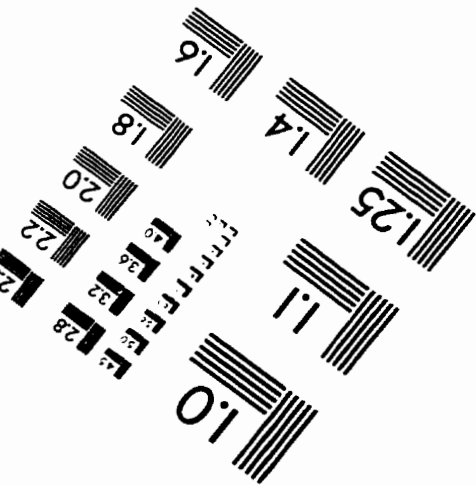
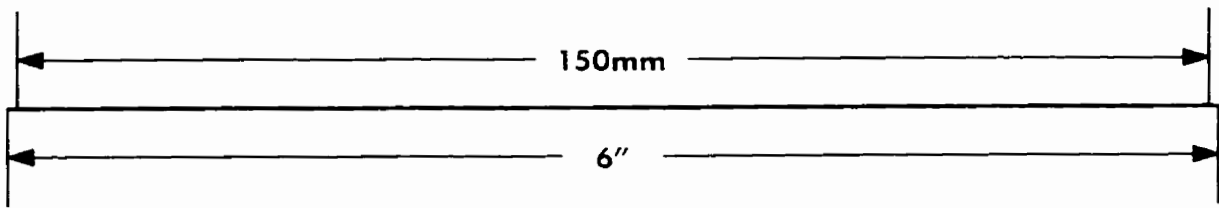
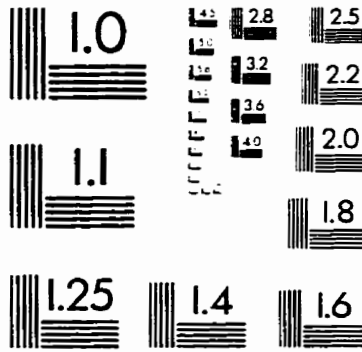
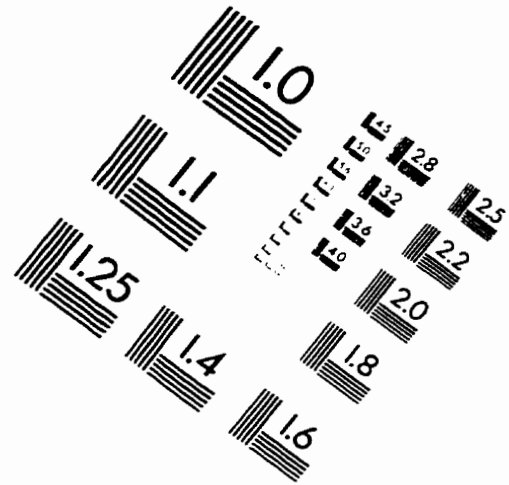
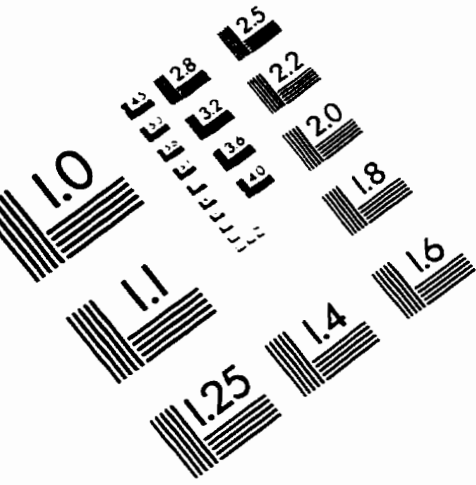
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