BIOLOGICAL NITRIFICATION AND DENITRIFICATION IN A MODIFIED ACTIVATED SLUDGE PROCESS

by

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ABSTRACT

A 40 L/day continuous reactor, consisting of 5 basins arranged in an alternating anoxic-aerobic sequence ("modified Bardenpho process") was operated at low temperatures on municipal effluent to determine the rate and efficiency of nitrogen transformations and removal. Total nitrogen removal ranged from 95% at 18°C to 79% at 6°C. The average BOD and total phosphorus removals remained in excess of 91% and 81% respectively. The maximum unit nitrification rates were 1.76, 1.44, 0.38 and 0.42 mg oxidized N/gm MLSS/hr at 18°C, 14°C, 10°C and 6°C respectively. The maximum unit rates for endogenous denitrification and with waste-water substrate were 0.95, 0.86, 0.60, 0.31 and 1.52, 0.88, 0.71, 0.36 mg oxidized N/gm MLSS/hr at 18°C, 14°C, 10°C and 6°C. For the system studied, rates and performance appear significantly influenced by BOD, C:N ratio, sludge age, substrate concentration and possibly pH and toxicity. The necessary consensus among investigators on standardized techniques for reporting viable biomass and nitrogen concentration remains to be attained.

KEY WORDS

Activated Sludge; Advanced Waste Treatment; Denitrification; Extended Aeration; Nitrification.

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CHAPTER 1

INTRODUCTION

The uncontrolled discharge of nitrogen-containing wastewaters to the aquatic environment has significant aesthetic, economic and health consequences, and thus is a major consideration in many related decision making processes. In recent years, regulations and technology have been developed to monitor and control such discharges and when implemented they can go a long way toward preventing or reversing the continuing degradation of receiving waters. Widespread research continues, aimed at a better understanding of nitrogen's role in the life process and, among other things, improving the technology of its removal from wastewater.

1.1 Eutrophication of Lakes

Most lakes undergo a slow natural transition from a low productivity or oligotrophic state, through a mesotrophic state, to that of highly productive eutrophication. Typically, oligotrophic lakes have low nutrient to volume ratios, high dissolved oxygen (DO) levels and are deep, cold and clear with a distinctive flora and fauna. Eutrophic lakes have high nutrient to volume ratios and a different characteristic hierarchy of species. They tend to be warmer, shallow and turbid and often have areas of low DO. Mesotrophic lakes exhibit intermediate traits.

The natural transition of a lake is slow and complex; influences include the rate of nutrient supply, climate (principally light intensity and temperature), the depth and the shape of the lake. Some lakes remain oligotrophic over many millenia (Vallentyne 1974).

The two major nutrients influencing eutrophication are nitrogen and phosphorus. Fosberg (1977) indicates that nitrogen is probably growth limiting in lakes eutrophied by domestic sewage, while phosphorus is usually growth limiting in oligotrophic waters. In a few instances organic carbon may be limiting. The ability of some algae to fix nitrogen from the air gave rise to the conventional wisdom that phosphorus was most frequently limiting (Horne 1977).

1.1.1 Man's contribution to eutrophication:

Man can hasten the eutrophication of water bodies, most often by increasing the rate of nutrient input. Sources of such nutrients include:

(i) Municipal and individual (tile field) sewage discharges;

(ii) Industrial waste discharge;

(iii) Agricultural runoff from animal feed lots and from fertilizer applied to fields;

(iv) Increased siltation from forestry, mining, agricultural, construction and flood control operations.

1.1.2 Problems associated with eutrophication:

(i) With high nutrient levels, "blooms" of algae or of aquatic plants may occur;

(ii) Such blooms give rise to diurnal changes in DO, pH and alkalinity, thus stressing unadapted extant species and altering ionic concentrations;

(iii) The increased turbidity and shade associated with such blooms decreases light intensity to the lake water, further changing the habitat of existing species.

(iv) The death and decay of blooming species recycles the nutrients, causes high DO demand and local depletion, further stressing extant fauna;

(v) From an aesthetic and recreational point of view, the floating mats of weeds or algae are undesirable for swimming and boating. New and coarser fish species become dominant. Rotting plant material gives rise to colour, odour and taste problems;

(vi) Natural channels become obstructed, thus restricting drainage. Water inlet pipes may be blocked. Water treatment costs increase because of the necessity to remove colour, odour and taste, or to draw water from more expensive sources.

1.2 Additional Concerns Associated With Aqueous Nitrogen

Apart from their important role in eutrophication, nitrogen compounds in water are of concern from public health, ecological, industrial and practical points of view:

(i) Prior to development of the coliform test, a high ratio of reduced to oxidized nitrogen forms in water was taken to indicate recent pollution by sewage and thus danger of water-borne disease transmission (Sawyer 1978).

(ii) McKee (1963) indicates that nitrate concentrations over 100 mg/L-N render the coliform test unreliable.

(iii) Nitrate concentrations in excess of 50 mg/L in domestic water may give rise to methemoglobinemia (a blood oxygen deficiency) in infants (Shuval 1977). Nitrite produced by reducing conditions in the stomach forms methemoglobin which prevents oxygen transfer

in the blood, giving rise to the characteristic blue colouration of suffocation. Such a problem is of most concern where shallow wells are used to provide potable water.

(iv) The role of nitrosamines and other nitrogen compounds as carcinogens is discussed by Mirvish (1977).

(v) Free ammonia is the most toxic to aquatic fauna of the nitrogen compounds associated with domestic sewage (McKee 1963). The toxicity is strongly related to pH, temperature and DO. In high concentrations, other nitrogen forms also exhibit toxicity (Cairns 1975).

(vi) Where effluent, rich in reduced nitrogen, is discharged to receiving waters with low dilution, subsequent nitrification may cause significant oxygen depletion. This nitrogenous oxygen demand (NOD) adds to the requirement for oxygen supply in biological sewage treatment. It may also contribute to high results in the standard BOD test (Bishop 1976).

(vii) When breakpoint chlorination of drinking water or effluents is carried out, reactions occur between ammonia and hypochlorite ions, with the formation of chloramines. High concentrations of ammonia will increase the consumption of chlorine prior to the formation of the desirable chlorine residual and thus detract from the process economics.

(viii) The reduction of oxidized nitrogen to nitrogen gas in anoxic regions of sludge settling tanks may cause rising sludge, due to gas bubble entrainment in the settling floc and thus lower the efficiency of solids removal.

(ix) In several industries (eg. brewing and dyeing), nitrates and

nitrites are harmful to the process or the product, while in others they may be desirable (eg. metal corrosion protection in boilers).

1.3 Available Processes for Nitrogen Control in Water

The most generally used control is to treat the water stream carrying the nitrogen. Depending on the applicable regulations or specifications, practice may entail only oxidation of reduced nitrogen forms (nitrification) or removal of all nitrogen forms from the effluent (nitrogen removal).

The available processes may be classified as biological or physical-chemical (Table 1.1).

1.3.1 Physical-chemical processes are relatively unaffected by temperature or toxicity, two banes of biological systems. However, they often do not remove all the forms of nitrogen present, and they are mostly high technology, energy-intensive processes with individual idiosyncrasies restricting their usefulness or economic competitiveness to narrow areas of applicability.

1.3.2 Biological processes may employ plant species or mixed cultures of algae or microbes to effect nitrogen transformations and removals. The availability of several biological treatment systems, such as trickling filters, activated sludge units, rotating biological discs, oxidation ditches, etc. gives great flexibility to the design for nitrogen removal.

Careful environmental control must, however, be exercised to maintain the desired microbial populations and thus the process efficiency.

TABLE 1.1

NITROGEN REMOVAL PROCESSES (After Sutton 1974)

PROCESS	REFERENCE
1. Physical-Chemical Processes	
Ammonia Stripping	EPA (1975)
Breakpoint Chlorination	EPA (1975)
Ion Exchange Using Clinoptilalite	EPA (1975)
Electrodialysis	Sutton (1974)
Electrochemical	Poon (1975)
Reverse Osmosis	Sutton (1974)
Distillation	Sutton (1974)
2. Land Application	EPA (1977)
3. Biological Processes	
Aerobic Nitrification/Anaerobic Denitrification	EPA (1975)
Water Plant Harvesting (Hyacinth)	Dinges (1978)
Activated Algae	Regan (1977) McGriff (1972)
Lagoons and Oxidation Ponds	EPA (1973)

1.3.3 Land application of sewage relies on a combination of biological and physical-chemical processes to stabilize wastewater. Bacterial and plant life transform nitrogen species, while clays in the soil arrest the movement of ammonia. Designers of such systems must consider the possibility of public health problems, nitrate infiltration to groundwaters and the effects of seasonal climatic variations.

CHAPTER 2

RESEARCH RATIONALE: NUTRIENT REMOVAL VIA THE BARDENPHO PROCESS

2.1 Development of the Bardenpho Process

The Bardenpho Process (BARnard-DENitrification-PHOsphorus removal) utilizes biological activity alone to remove nitrogen and phosphorus from wastewater and to stabilize organic carbon in a modified, extended aeration, activated sludge operation.

The development of this process in South Africa, from the work of Ludzack (1962), is outlined by Barnard (1975b). In the "Ludzack" reactor (see Section 5.8.2), nitrified mixed liquor is recycled to an anoxic tank and mixed with incoming raw sewage. Nitrate is reduced to nitrogen by available carbon in the wastewater and leaves the system. The mixed liquor overflows to an aerobic cell where the nitrification and carbon stabilization occur. Barnard added a third basin, where under anoxic conditions, endogenous nitrate respiration removed the nitrate not eliminated in the first basin (Section 5.8.2). For nitrogen stripping, final ammonia oxidation, reaeration and sludge stabilization prior to settling, a final aerobic basin was added (Figure 2.1).

A Modified Bardenpho Process (Figure 2.2) was developed, by the addition of an initial anaerobic reactor (no oxygen or nitrate) prior to the wastewater denitrification step, to "condition" the sludge for subsequent biological phosphorus removal.

2.2 Applicability of the Bardenpho Process

Barnard (1975a) outlines the results of his work on a South African pilot plant in which up to 94% total nitrogen and 90% COD (average)

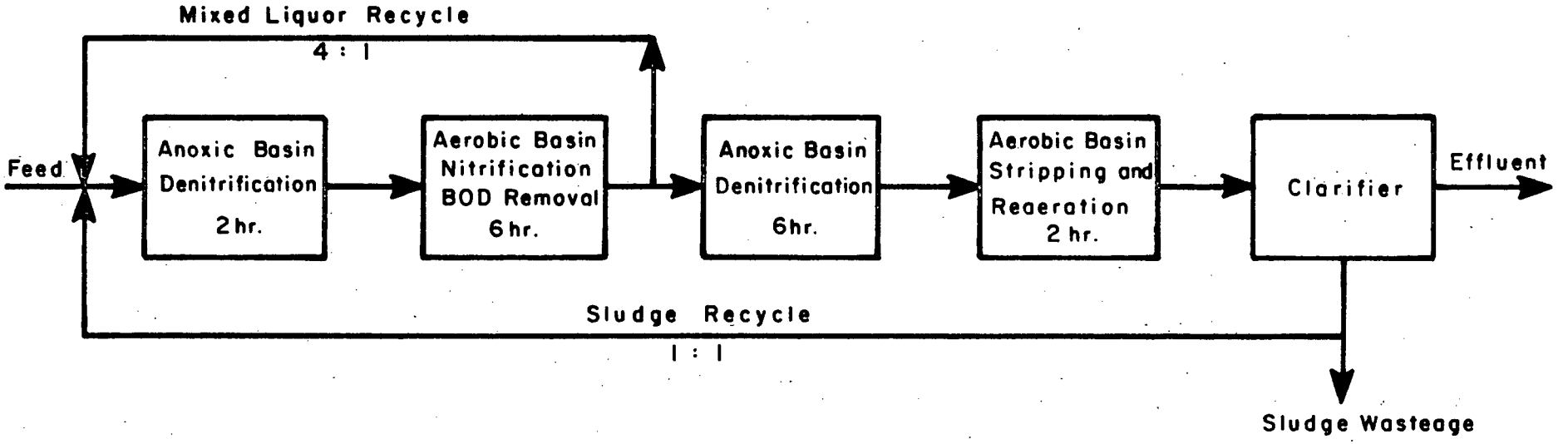


FIG.2.1 BARDENPHO PROCESS (Barnard 1975).

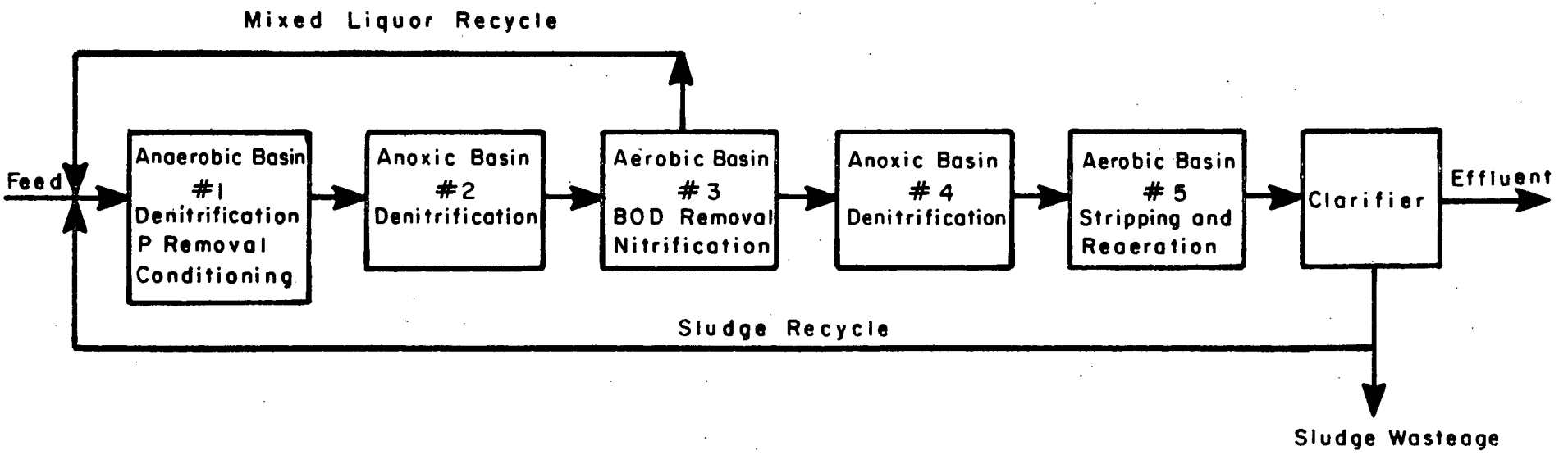


FIG.2.2 MODIFIED BARDENPHO PROCESS (Jank 1978).

removals and less than a 1 mg/L total phosphorus residual were achieved. A mixed liquor recycle of 4:1 and a sludge return of 1:1 were used. Feed COD of 340, TKN of 81 and system MLSS in the 4500 to 6000 mg/L range were reported. Operational temperatures were between 18°C and 25°C. The system nominal hydraulic retention time (HRT) was about 16 hours and the solids retention time (SRT) was generally between 18 and 25 days.

Nicholls (1975), Venter (1976), Osborn (1978) describe modifications to full scale extended aeration plants and pilot plants in the Johannesburg area, which when operated in the Bardenpho mode, regularly achieved total nitrogen removals in excess of 80%. The reported operating temperatures were generally in excess of 17°C; BOD:TKN in excess of 7:1; MLSS in the 3000-6000 mg/L range; system SRT greater than 20 days and system HRT greater than 20 hours.

McLaren (1976), in Pretoria, reported 76% total nitrogen removal from a pilot plant operated in the modified Bardenpho mode and optimized for phosphorus removal.

Barnard (1978) indicated that the endogenous basin may not be necessary, except where: (i) the raw sewage is highly nitrogenous, in which case high removal efficiencies in the first anoxic reactor would still leave high nitrate residuals; or (ii) where low BOD (eg. from weak sewage) could limit first stage denitrification rates due to carbon deficiency. Barnard indicated that cold-weather, second-stage denitrification rates could be increased by a controlled methanol or ethanol addition to this nominally endogenous reactor.

The South African experience is so encouraging that most new plants there are using the Bardenpho process (Burdick 1978). Particularly in the Johannesburg area, fresh water is scarce and receiving waters are

generally impounded and reused for potable water supply, irrigation and recreation. The city has a long established policy of nutrient reduction in sewage effluents in order to retard reservoir eutrophication. The Bardenpho process at present is the nutrient removal process of choice (Venter 1976).

Recently the city of Palmetto, Florida has chosen to install a Bardenpho plant for nitrogen and phosphorus removal. Burdick (1978) outlines the relative costs and other factors that saw this process chosen.

2.3 The Bardenpho Process Under Canadian Conditions

The Provincial Government of British Columbia (B.C.) has imposed restrictions and deadlines on the levels of nutrient discharge that may be made to the Okanagan lake system by bordering municipalities. These restrictions will require the upgrading of existing waste-water treatment facilities or the cessation of effluent discharge to surface waters.

Because operating temperatures in central B.C. are lower than those encountered in South Africa, evaluation of the Bardenpho process for B.C. operation requires investigation at the lower temperatures and weaker sewage strengths more typical of Canadian conditions. Such research will be of increased value because very little published data is available on the low temperature operation of any biological nutrient removal systems.

2.4 Required Research for Canadian Applicability

Any research programme will be seeking answers to several general but basic questions.

For a given sewage with its expected range of concentrations and flow rates:

(i) What efficiency of nitrogen, phosphorus and BOD removal can be anticipated at the lowest expected operating temperature and what will be the removal rate for these constituents?

(ii) How may the rate be optimized to maintain the efficiency or quality of effluent, but to minimize the capital cost (eg. tank volume) and the operating cost (eg. power/chemical addition/ penalty charges) of the system?

(iii) How will rates and efficiencies vary with seasonal temperature cycles?

(iv) What factors will be most critical in their effects on each of nitrification, denitrification, phosphorus and BOD removal and effluent solids, and how significant will such effects be?

(v) Which of the parameters restricted by a discharge permit is the most likely to exceed this limitation and how much more likely is it than any other parameter?

(iv) How will low temperatures effect the settling and handling properties of the process mixed liquor and sludge?

2.5 Experimental Outline:

Based on the above considerations the following experimental program was undertaken:

1. A 50 litre model of the modified Bardenpho process was operated in a temperature controlled room in the Environmental Engineering Laboratory of the Department of Civil Engineering at the University of British Columbia (U.B.C.).

2. Testing was undertaken at 18°C, 14°C, 10°C and 6°C.
3. Physical and chemical data were collected in order to understand and describe the operation of the process.
4. Removal efficiencies of nitrogen, phosphorus and BOD were determined.
5. Nitrification and denitrification rates were measured.
6. Factors that limited or affected rates and efficiencies were identified.
7. Experience was gained in the design, planning and execution of an experiment using a small, complex continuous-flow biological reactor, with numerous inter-relationships among variables and many significant output parameters.

2.6 This Thesis

This work summarizes some of the available literature on biological nitrification and nitrogen removal that is relevant to waste-water treatment. That part of the outlined experimental work, relating to nitrogen transformation and removal and to the actual operation of the modelled system, is also discussed.

CHAPTER 3

BACKGROUND TO BIOLOGICAL NITROGEN REMOVAL

3.1 Microbial Growth

Under the circumstances of most relevance to biological waste treatment, an organism reproduces by binary fission into two cells, each with an equal metabolizing ability. Each such event occurs within a time interval known as the "generation time".

The life cycle of an isolated bacterial population or of an active biomass can be broken into three phases: a rapid (logarithmic) increase, a levelling off and a decline. During the log growth phase, the rate at which both the population and the biomass grow is restricted only by the rate at which substrate is metabolized and by the generation time.

With the rising population and biomass concentration, competition for the available food increases and both rates begin to decline and then to level off. The viable population begins to fall at an accelerating rate as an increasing food shortage lowers the growth rate and raises the death rate, leading ultimately to the "death" of the colony. The biomass undergoes a less spectacular decline. As the available food decreases the auto-consumption of cellular protoplasm increases (endogenous metabolism) together with consumption of the cellular contents of dead (lysed) bacteria. With prolonged maintenance of the endogenous phase, a high degree of waste stabilization is achieved.

In the design of a biological system the log growth phase appears advantageous due to the rapid waste stabilization rate. Practical difficulties occur, however, in meeting the necessary oxygen

demand and maintaining high substrate concentrations. Further problems are associated with high sludge production. Generally this phase is passed over for design and the more easily controlled declining or endogenous growth phases are chosen.

3.2 Waste Stabilization Kinetics

Two empirical relationships form the basis for an understanding of the kinetics of the biological system responsible for stabilizing an organic waste or some component of that waste.

(i) A relationship between substrate utilization and biomass growth:

$$[3.1] \qquad \frac{dX}{dt} = Y\frac{dF}{dt} - bX$$

(ii) A Monod type relationship (Schroeder, 1977) indicating the rate of substrate utilization:

$$[3.2] \qquad \frac{dF}{dt} = (kXS)/(K_s+S)$$

where:

X = biomass concentration (M/V)

$(\frac{dX}{dt})$ = net biomass growth rate (M/VT)

Y = yield (biomass per amount of substrate utilized (M/M))

$(\frac{dF}{dt})$ = rate of substrate utilization by biomass (M/VT)

b = biomass decay coefficient (T^{-1})

k = maximum rate of waste utilization per unit weight of biomass (M/MT)

K_s = waste concentration at which rate of utilization is 0.5k (M/V)

S = waste concentration surrounding biomass (M/V)

Using these two equations (or slight modifications) and a model for a complete mix reactor, a series of relationships can be derived to describe the operation and control of a continuous biological process, such as the Bardenpho operation. (See, for example, Lawrence (1970) or Metcalf and Eddy (1979) for a detailed discussion.

Two of these equations are of major concern here:

(i) Solids Retention Time (SRT) or Sludge Age:

$$[3.3] \qquad \theta_c = X'/dX' = 1/\mu$$

(ii) A relationship between SRT and the rate of waste utilization:

$$[3.4] \qquad 1/\theta_c^m = Yk - k_d$$

where

X' = Solids Inventory (M)

dX' = Solids Wastage per Unit Time (M/T)

μ = Specific growth rate (ln.2/doubling time) (T^{-1})

θ_c^m = Minimum SRT to maintain an adequate viable biomass able to perform the required biological stabilization (T).

k_d = Decay Coefficient (T^{-1})

Unless a sludge age in excess of θ_c^m is maintained, decay will exceed growth for the population in question and "washout" will occur.

3.3 Temperature Effects on Reaction Kinetics

3.3.1 Temperature:

Temperature has two significant effects on biological reactions: firstly, it affects the types of biological population present and, secondly, it influences the rate at which reactions proceed.

3.3.2 Biological Populations:

According to the temperature range in which they survive, bacteria may be classified as: (Sutton 1974)

psychrophiles	$<20^{\circ}C$
mesophiles	$20-50^{\circ}C$
thermophiles	$>50^{\circ}C$

These categories are flexible but, generally, bacteria acclimated to one temperature environment will be severely inhibited or killed by a radical thermal change.

3.3.3 Reaction Rates:

The Arrhenius equation or one of several modifications have been used to model the variation of reaction rates with temperature (Sawyer 1978):

$$k = A \exp(-E/RT)$$

or $d(\ln k)/dT = E/RT^2$ - (change in rate constant k with temperature)

integrating

$$[3.5] \qquad \ln(k_2/k_1) = \frac{E(T_2-T_1)}{RT_2T_1}$$

where:

T = Absolute Temperature ($^{\circ}K$)

k_1, k_2 = Reaction Rate Constants at T_1 and T_2 (1/time).

A = Frequency Factor (constant)

E = Activation Energy (cal/gm-mole)

R = Universal Gas Constant (cal/gm-mole/$^{\circ}K$)

Where the temperature range is small, Equation 3.5 may be written:

$$\ln(k_2/k_1) = \theta(T_2 - T_1)$$

or

$$k_2 = k_1 \exp(\theta(T_2-T_1))$$

where θ is a constant.

Further simplification (Metcalf 1979) replaces $\exp\theta$ with a constant θ' (the thermal coefficient) such that:

$$k_2 = k_1 \theta'^{(T_2-T_1)}$$

Sutton (1974) discusses the Q_{10} concept, with Q_{10} being the ratio of the rate at temperature T to the rate at $T' = T - 10^{o}C$. The van't Hoff rule (Sawyer 1978) indicates a doubling in reaction rate for a $10^{o}C$ temperature rise (ie. $Q_{10} = 2.0$).

In all instances these rate-temperature relationships are empirical and valid only for the specific system tested over relatively narrow temperature ranges.

3.4 The Nitrogen Cycle

Air by weight is 79% nitrogen and yet, paradoxically, a nitrogen shortage limits the growth of plants and, thus, the world's food supply.

Before it is available for use by most plants, nitrogen must be combined with another element (usually hydrogen or oxygen), a state referred to as "fixed nitrogen".

Nitrogen gas, particularly near "room" temperature, is remarkedly inert. This is due both to its slow reaction kinetics in otherwise thermodynamically favourable reactions (eg. nitrogen:hydrogen reactions) and to the unfavourable positive free energy of formation of, for example, its oxides (and thus their intrinsic instability with respect to nitrogen and oxygen (Mahan 1969)).

Nontheless, fixation may be achieved in the atmosphere by high energy phenomena such as lightning. However, the main source of combined nitrogen is a few dozen marine and terrestrial organisms that are

biologically able to fix nitrogen (Painter 1977, Horne 1977). The best known are those of the genus rhizobium which form symbiotic relationships with leguminous plants. Free living nitrogen fixers are found in numerous environments in the soil, the water and even the gut of certain insects. Aerobes, anaerobes and phototrophs have been documented as nitrogen fixers (Brill 1977).

Man, mostly via the high temperature and pressure HABER process, but also by extensive legume planting and industrial technology, makes a contribution of fixed nitrogen approaching the natural production prior to modern farming (Delwich 1970). He thus is making a significant intrusion into the "Nitrogen Cycle" in terms of the sum total of all the forms of nitrogen and their inter-relationships in the ecosphere (Figure 3.1).

Much of the complexity of this cycle is due to the wide range of oxidation states exhibited by nitrogen (ranging from -3 to +5), to the numerous microbial populations that utilize the energy released during transformation from one oxidation state to another, and to the essential part played by nitrogen in living matter, as a constituent of nucleic acids and cellular protein.

In plant and animal tissue nitrogen is present in its most reduced form (-3) as amino acids (protein constituents) or as the ammonium ion. In natural aerobic soils and waters it mostly occurs in the +5 state as the nitrate ion. Both these ions are suitable for assimilation (incorporation into plant tissue) although the nitrate ions usually must first be reduced. In soils, ammonium ions tend to be trapped on clay particles due to their electronic charge and thus must first be oxidized to the highly mobile nitrate form, unless they are already in close

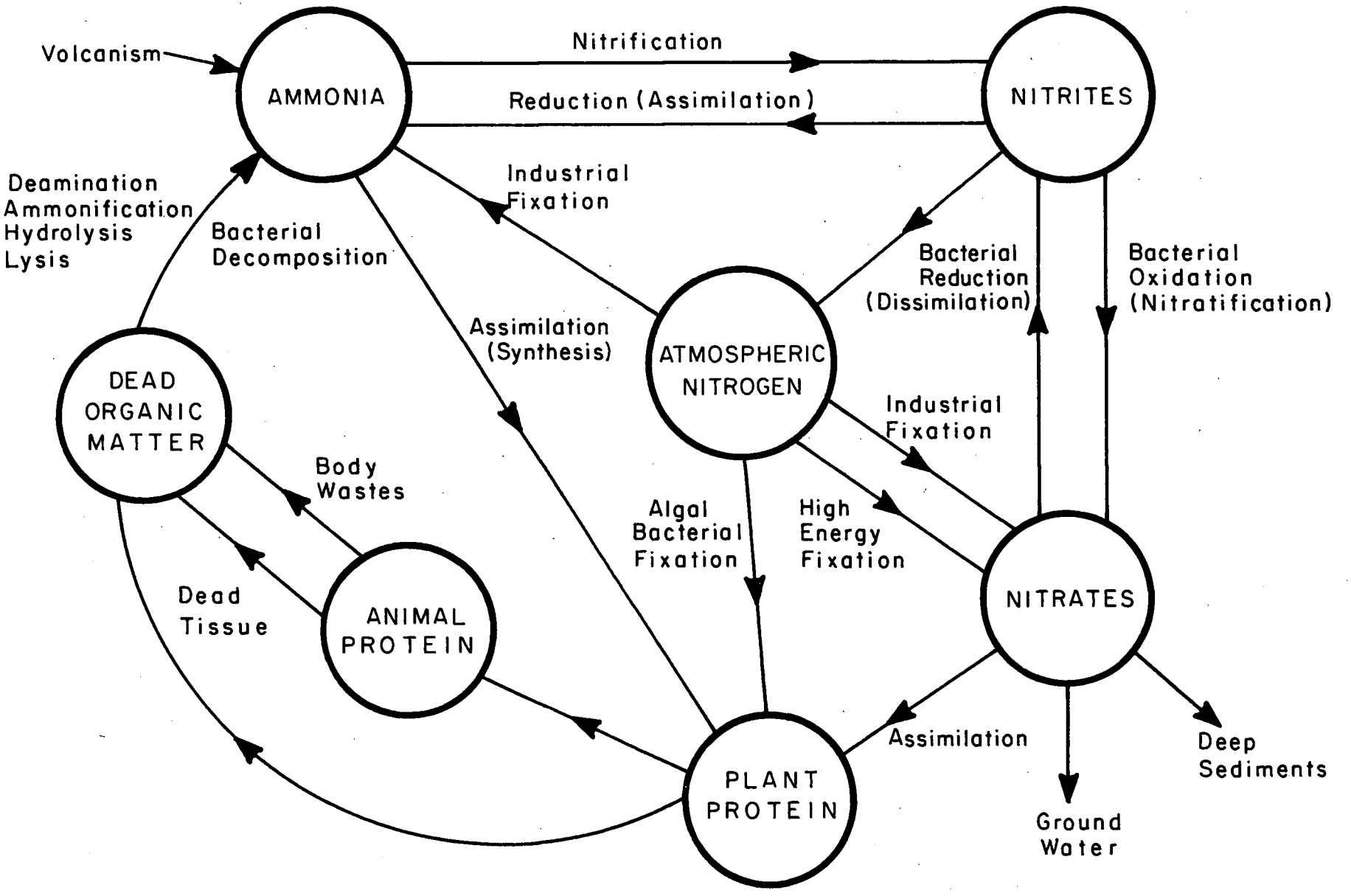


FIG.3.1 NITROGEN CYCLE (EPA, 1975).

proximity to plant roots.

Unlike plants, animals are unable to synthesize many of their essential nutrients and must rely on their diet to provide these. When plant or animal tissue is consumed by animals, much of the protein is broken down into amino acids and reassembled into new tissue forms or else metabolized for energy.

Ultimately, most of the nitrogen locked up in protein is returned to the soil or water as body waste or dead tissue and is there broken down into amino acids, urea, ammonia and organic residuals by a series of biological actions. Organisms of the genus nitrosomonas extract energy by the oxidation of ammonium to nitrite; those of the genus nitrobacter carry the oxidation through to nitrate. In areas devoid of oxygen and in the presence of suitable reduced organic substrate, further bacteria (eg. Pseudomonas Denitrificans) use these oxidized nitrogen forms as electron acceptors while extracting a high energy yield from the oxidation of the substrate. The electron acceptor is generally reduced to nitrogen gas and returned to the atmosphere. Nitrate which is not assimilated or reduced is available for carriage to ground water by infiltration because of its high mobility in soils.

Table 3.1 compares the energy yields from some of the reactions involved in the nitrogen cycle.

3.4.1 Nitrogen Balance:

Delwiche (1970) indicates that prior to industrial fixation and large scale legume cultivation, nitrogen fixation and reduction balanced out. Presently, with fixation outstripping denitrification, the principal observed effect is that of accelerated eutrophication of inland waters with cascading ecological consequences.

TABLE 3.1

ENERGY YIELDS FROM NITROGEN REACTIONS (Delwiche 1970)

	Kilocalories per mole
Denitrification	
$5C_6H_{12}O_6 + 24KNO_3 = 30CO_2 + 18H_2O + 24KOH + 12N_2$ (glucose)	570
$5S + 6KNO_3 + 2CaCO_3 = 3K_2SO_4 + 2CaSO_4 + 2CO_2 + 3N_2$	132
Respiration	
$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$	686
Ammonification	
$2CH_2NH_2COOH + 3O_2 = 2CO_2 + H_2O + NH_3$	176
Nitrification	
$2NH_3 + 3O_2 = HNO_2 + H_2O + H^+$	66
$2KNO_2 + O_2 = 2KNO_3$	17.5
Nitrogen Fixation	
$N_2 = 2N$ (Activation	-160
$2N + 3H_2 = 2NH_3$	12.8
	-147.2 *

* Requires a net energy input.

CHAPTER 4

AMMONIFICATION AND NITRIFICATION IN DOMESTIC WASTEWATER

4.1 Wastewater Composition:

Detailed analysis of municipal sewages is presented by Bond (1974), while specific consideration of nitrogen forms has been undertaken by Hanson (1971), Kahn (1964) and Hunter (1965).

Nitrogen in urine occurs mostly as urea, which is rapidly hydrolyzed to ammonia (ammonification); faecal nitrogen occurs principally as amino acid or protein, 70% being contained in bacterial cells (Krueger 1973).

Bond (1974) reports that a representative raw sewage of medium strength contains about 20 mg/L of organic - N; 30 mg/L of free ammonia - N; 0.2 mg/L of nitrate - N and 0.05 mg/L of nitrite - N.

4.1.1 Amino Acids and Proteins

Amino acids are organic molecules identified by the presence of an amino group (NH_2) and a carboxylic acid group (COOH). These are linked to a central carbon atom saturated with hydrogen or with a side chain (Krueger 1973).

Twenty different amino acids (with their individuality resulting from variations in the hydrogen and side chain configuration) are commonly present in proteins, being linked in a chain by peptide bonds formed by interaction between the carboxyl group of one and the amino group of another.

One, or numerous chains of amino acids (polypeptides) constitute a protein molecule. Each protein is distinguished by a constant ratio

of the constituent amino acids and by a unique configuration in space; the result of numerous bonding interactions between the component sub-molecules.

Proteins are relatively sensitive to variation in pH and temperature, to rupturing by applied shear forces and to attack by certain enzymes. Under such adverse conditions "denaturing" or loss of the characteristic protein configuration occurs, with an accompanying break down into smaller polypeptide chains.

4.2 Deamination and Ammonification

Painter (1970) discusses three ways of producing ammonia from organically bound nitrogen:

(i) Extra-cellular deamination, whereby exoenzymes from a cell break down organic molecules remote from the cell with the eventual formation of ammonia which may then be reassimilated;

(ii) Endogenous respiration, where stored or expendable internal components of the cell including amino acids are broken down, resulting in cell shrinkage and the release of byproduct ammonia in the form of urea (deamination);

(iii) Death or lysis, where cell contents, including unassimilated ammonia are discharged to the surrounding medium.

Prasad (1978) showed that the rate of hydrolysis of urea in wastewater varied from 3.2 mg/L/hr at $2^{o}C$ to 10.9 at $20^{o}C$. He demonstrated that 44% of the viable bacteria in a domestic wastewater and 58% in an activated sludge were ureolytic (ie. produce the enzyme urease which brings about urea hydrolysis). Wong-Chong (1975) asserts that the ammonification reaction is a first order reaction, even up to substrate concentrations exceeding 500 mg/L of convertible organic nitrogen.

4.3 Nitrification

4.3.1 Substrate Oxidation

As indicated by Painter (1970), the production of nitrate or nitrite as a product of bacterial activity may be accomplished by autotrophic organisms which extract their total energy requirement from the oxidation of ammonia to nitrite and thence to nitrate, and by heterotrophic nitrifiers that produce oxidized nitrogen forms by reactions which are not necessarily oxidations, nor the sole energy source for the organism. In wastewater treatment, nitrification by autotrophs is decidedly more important. At a typically high or low pH value, heterotrophic nitrification may be significant (Focht 1975).

Nitrification is generally represented as taking place in two separate stages (Painter 1977). First, the oxidation of ammonia to nitrite by Nitrosomonas:

[4.1] $$NH_4^+ + 1.5\,O_2 = NO_2^- + H_2O + 2H^+$$

Second, completion of the oxidation to nitrate by Nitrobacter:

[4.2] $$NO_2^- + 0.5\,O_2 = NO_3^-$$

Biochemically, however, these reactions are actually more complex than merely two sequential oxidations, there being several enzyme systems integrally involved, and in the case of ammonia oxidation, a number of intermediate steps. Inhibition of the nitrification process is, in part, due to interference in the operation of these intermediate pathways (Delwiche (1956); Painter (1970); Sharma (1977).

4.3.2 Classification of nitrobacter and nitrosomonas

Both genera are strictly aerobic and usually autotrophic, although Painter (1977) suggests nitrobacter may be a facultative autotroph. Because energy is solely derived from the chemical oxidation of ammonia or nitrite, the organisms are also classed as chemolithotrophs.

4.3.3 Energy yields and synthesis

In addition to deriving energy from the oxidation of reduced nitrogen species (Table 3.1), nitrifying bacteria synthesize new cell tissue from some of the nitrogen present. Using the empirical cell composition $C_5H_7O_2N$ (Porges 1956), and considering these reactions in aqueous solution with carbonate system alkalinity, EPA (1975) proposed the following synthesis equations:

Synthesis of Nitrosomonas:

[4.3] $$13NH_4^+ + 23HCO_3^- = 8H_2CO_3 + 10NO_2^- + 3C_5H_7O_2N + 19H_2O$$

Synthesis of Nitrobacter:

[4.4] $$NH_4^+ + 10NO_2^- + 4H_2CO_3 + HCO_3^- = 10NO_3^- + 3H_2O + C_5H_7O_2N$$

Using yield coefficients of 0.15 for nitrate nitrogen and 0.02 for nitrite nitrogen, EPA (1975) presents an overall oxidation plus synthesis equation:

[4.5] $$NH_4^+ + 1.83\,O_2 + 1.98HCO_3^- = 0.021\,C_5H_7NO_2 + 0.98NO_3^- + 1.041\,H_2O + 1.88\,H_2CO_3$$

4.3.4 Alkalinity Consumption

Combining Equations 4.1 and 4.2 in the context of the carbonate alkalinity system, the following is obtained:

[4.6] $$NH_4^+ + 2O_2 + 2HCO_3^- = NO_3^- + 2H_2CO_3 + H_2O$$

It can be calculated that the removal of 1 mg/L of ammonia will consume 7.14 mg of alkalinity (as $CaCO_3$), or using Equation 4.5, the consumption will be only 7.07 due to the incorporation of some ammonia into cell biomass. In practice EPA (1975) reports an observed range of 6.0 to 7.1 mg alkalinity per mg ammonia. Benninger (1978) determined that the consumption ratio was lower at increased SRT, probably due to changes in microbial chemical composition, shift in the predominant species or to augmentation of alkalinity by denitrification in the settler.

Sherrard (1976b) asserted that wastewater BOD:N:P ratios and sludge age influence the amount of alkalinity destroyed. Higher BOD:N ratio and longer sludge age give increased destruction.

Thus, to an extent determined mainly by the buffering capacity of the system, nitrification in an aqueous system destroys alkalinity and lowers the pH, which may in turn decrease the nitrification rate (EPA 1975).

4.3.5 Environmental factors of importance in nitrification

4.3.5.1 Dissolved Oxygen

From Equations 4.6, which neglects synthesis, and 4.5 which includes synthesis, NOD's of 4.57 mg/L and 4.33 mg/L respectively per mg/L of ammonia oxidation are calculated. This difference is reportedly due to oxygen release during carbon fixation, as part of the overall synthesis reaction (Painter, 1970). Other researchers (Sharma 1977) indicate that variations are explained by the oversimplification of the reaction chemistry implicit in Equations 4.1 through 4.6.

Additionally, in any practical biological nitrifying system, further demands for oxygen will be made by other oxidizing reactions, principally the stabilization of organic carbon.

Sharma (1977), Painter (1970) and Downing (1964a) have compiled extensive data from the literature on the effects of dissolved oxygen concentration on nitrification in both pure and mixed cultures. While there is ample evidence that low DO values inhibit nitrification, there is no precisely defined upper level at which nitrification rates become independent of oxygen concentration. Painter (1970) found evidence that nitrobacter is more sensitive to oxygen depletion than is nitrosomonas. Downing (1964a), indicates that "some of the differences in the reported effects of DO on the nitrifying ability of activated sludge may be due to the local oxygen lack because of the respiration of other (heterotrophic) organisms".

In using a Monod model for the effect of DO on nitrification rate, EPA (1975) advocates a Michaelis-Menten (half-rate) constant of 1.3 mg/L. Thus, if a DO of 2.0 mg/L is maintained in solution, the observed nitrification rate should exceed 60% of the peak rate. Further work is required to determine other factors affecting the half-rate constant and thus the most economical DO level for nitrification. McHarness (1975), in a pure oxygen, submerged filter, found no effect on nitrification at DO levels as high as 60 mg/L.

4.3.5.2 Effect of Anaerobic Storage on Nitrifying Activated Sludge

It has been established that maintaining a nitrifying sludge under anaerobic conditions for up to 4 hours does not lower its nitrifying ability as measured by nitrification rate (Downing, 1964a; Wuhrmann, 1968; Jank, 1978). A conclusive investigation of longer anaerobic periods and factors such as sludge age, sludge type and temperature remains to be carried out.

4.3.5.3 Effect of pH

Sharma (1977) indicated that pH effects on nitrification may be looked at from three angles:

(i) Effect of pH on nitrification by existing cells;

(ii) Adaption of nitrifiers to adverse pH;

(iii) Growth of nitrifiers.

A consensus is that nitrification rates follow a bell curve relationship, with pH being optimum in the slightly alkaline range (Focht 1975; Painter 1970). As shown by Painter (1970), in pure culture studies, different strains of nitrosomonas and nitrobacter exhibited various optimum pH values spanning the range 6 to 9.3. EPA (1975) presents a relationship between observed nitrification rate, peak rate and pH for use when the pH is less than 7.2:

[4.7] Nitrification Rate = Peak Rate (1 - 0.833 (7.2 - pH)

For pH between 7.2 and 8.0 the rate is assumed constant. A pH higher than 8.0 is unusual in domestic wastewater nitrification.

Painter (1970) reported that in a nitrifying activated sludge treating a poorly buffered domestic waste, nitrification had ceased before the pH decreased to 6.3. Prakasam (1972) indicated that nitrification rates were unaffected up to pH 11.0, provided un-ionized ammonia concentrations were held below 0.02 mg/L. Generally, the upper optimum pH is less than 9.0 (Focht, 1975), due to inhibition by un-ionized ammonia.

EPA (1975) reports on work that showed a rapid increase in effluent ammonia when the pH was quickly changed from 7.2 to 5.8. When the initial pH was abruptly restored, a rapid improvement ensued, indicating that the low pH was only inhibitory and not toxic.

Haug, as reported by EPA (1975), was able to acclimate nitrifiers to pH 5.5 in a submerged filter.

4.3.5.4 Temperature:

Painter (1977) indicates that nitrification proceeds in the temperature range $4^{o}C$ - $45^{o}C$. The optimum for nitrosomonas is about $35^{o}C$; that for nitrobacter 35 - $42^{o}C$. Thus, from a temperature point of view, wastewater nitrification is usually operated under sub-optimal conditions. Sharma (1977) reports thermal death of a pure nitrosomonas culture between $54^{o}C$ and $58^{o}C$. Haug (1972) was able to maintain nitrification in a pure oxygen submerged filter down to $1^{o}C$. Rimer (1972) reported difficulty in establishing a nitrifying flora in activated sludge at $10^{o}C$, but no difficulty in maintaining an existing culture. At $5^{o}C$ Painter (1970) noted that nitrification could continue, but that there was minimal growth of new bacteria.

4.3.5.5 Effect of Light:

Sharma (1977) and Painter (1970) indicate that light inhibits the activity of nitrifiers in pure culture, but do not explain the mechanism.

4.3.5.6 Effect of Solid Surfaces and Turbulence

Painter (1970) supports the idea that particles or surfaces are not necessary for nitrifier growth. Sharma (1977) contends that the effect of surfaces, of surface type and of turbulence is not yet clear, and thus cannot be discounted. Kholdebarin (1977) shows an increase in nitrification rate with increased suspended solids concentration in surface waters. In natural systems, nitrifiers appear to be concentrated in sediments or at interfaces with respect to surface waters (Sharma 1977). Sharma reports on the enhancement of nitrification in an aeration unit with the addition of zeolite particles. Besik (1977) describes a modified activated sludge process in which reaction rates are enhanced by powdered and granulated activated carbon additions. (See Section 5.8.4)

4.3.5.7 Micronutrients:

Apart from a carbon source (carbonate system), substrate or electron donor (ammonium for nitrosomonas, nitrite for nitrobacter) and an electron acceptor (dissolved oxygen), small quantities of other elements are essential nutrients for nitrifier growth. While the requirements may differ for genera or species, Painter (1970) shows the following elements to be beneficial in various pure cultures:

P; Ca; K; Mg; Cu; S; Fe; Mo; Na.

Usually in domestic sewage, such nutrients are present in adequate quantities (Bond 1974).

Sharma (1977) presents detailed tabulations of stimulatory and inhibitory substances and suggests that some of the inconsistencies in nitrification work may be related to the presence or absence of adequate micro-nutrient concentrations.

4.4 Inhibition of Nitrification

In an activated sludge process, nitrification can be severely curtailed or halted by the introduction of inhibitory or toxic materials or conditions. Downing (1964b) indicates three general manifestations of toxicity:

(i) Death of the nitrifying bacteria (Toxicity)

(ii) Decreased organism growth rate (Inhibition)

(iii) Temporary inhibition of respiration (nitrification) with a return to near normal rates after removal of the inhibitory conditions.

Inhibitors act either on the general cell metabolism or on one of the primary oxidation reactions (Painter 1977).

The most commonly reported data are from short term screening tests

that compare nitrification rates with and without the addition of test inhibitory materials (Hockenbury, 1977b; Stensel, 1976; Loveless, 1968). Numerous factors affect the extent to which nitrification is inhibited, including pH, temperature, DO, acclimation, MLSS, culture type (pure or mixed), nature of the toxicant/inhibitor, method of addition (slug or continuous), other ionic species present and their concentrations, synergistic and antagonistic reactions, and hydraulic regime (Downing 1964b; Hockenbury 1977b). Wide variations in reported inhibition data are caused by these factors and make it impossible to develop specific quantitative relationships between toxic materials and the behaviour of nitrifying bacteria (Loveless 1968; Stensel 1976).

Autotrophs are much more susceptible to inhibition than heterotrophs. The ammonia oxidizers are more susceptible than the nitrite oxidizers (Painter 1977). Pure cultures are affected by lower concentrations than are mixed (activated sludge) cultures which, in turn, are more sensitive than acclimated sludges (Tomlinson 1966; Painter 1977).

The most potent inhibitors are a family of nitrogenous organosulphur compounds including thiourea and thioacetamide. In pure culture, thiourea is 75% inhibitory at 0.08 mg/L but in the same sludge after acclimation, 3.5 mg/L had no effect. Cyanide is a strong toxicant at less than 1 ppm (Barth 1965). In pure culture, Skinner (1961) reports Ni and Cr inhibitory at 0.25 mg/L and Cu at 0.5 ppm. Loveless (1968) reports Zn and Co inhibitory at 0.5 mg/L. Tomlinson (1966) demonstrated that the same degree of inhibition in acclimated sludge, as in a pure culture, needed a concentration of inhibitant two or three logarithmic units greater. Downing (1964b) showed that sludges acclimated to low levels of continuous heavy metal exposure may become inhibited due to metal accumulation in the sludge.

4.4.1 Acclimation

Two major mechanisms allow a nitrifying sludge to build up a resistance to inhibition:

(i) Adaptation with time of the nitrifier population to the agent.

(ii) Development of an associated heterotrophic population capable of metabolizing the toxicant.

4.4.2 Chlorination

Strom (1977) demonstrated that chlorine doses up to 50 mg/L in recycled sludge did not affect the rate of nitrification or the BOD removal in an activated sludge. Nitrifiers were more resistant to chlorination than were E. Coli or fecal streptococci.

4.4.3 Substrate and Product Inhibition

Painter (1970) indicated that both nitrosomonas and nitrobacter are inhibited by their own nitrogen substrates and more so by the substrate of the other. The reported concentrations at which inhibition occurred were one or two orders of magnitude greater than those normally found in municipal wastewater treatment. The degree of inhibition was affected by the environmental conditions including pH, temperature and acclimation (Sharma 1977). The work of Prakasam (1972), Anthonisen (1976) and Verstraete (1977) demonstrated that free ammonia and free nitrous acid concentrations, rather than ammonium or nitrite ion concentrations, inhibit nitrification. Anthonisen (1976) developed an operating chart relating pH, nitrite ion - nitrous acid equilibrium and total ammonia - free ammonia equilibrium. Inhibitory concentrations were dependent on the pH, which, as it increased, displaced the ammonia equilibrium toward free ammonia, and, at lower pH, the nitrite equilibrium toward nitrous acid. Free ammonia was inhibitory toward nitrobacter beginning at 0.1 mg/L

to 1.0 mg/L and toward nitrosomonas beginning between 10 and 150 mg/L. Free nitrous acid inhibition toward nitrifiers began at concentrations between 0.2 and 2.8 mg/L.

Cairns (1975) showed that, for a temperature increase from 10°C to 20°C, the percentage of un-ionized ammonia increased by a factor of 1.3 to 1.6 depending on the pH.

Poduska (1975) cites evidence that ammonium ion, nitrite and nitrate are not inhibitory at concentrations normally encountered in domestic wastewater treatment. Problems may occur, however, with high strength industrial or agricultural wastes.

4.4.4 Organic Matter

Organic matter per se is not inhibitory. However, in the presence of high organic concentrations, the heterotrophs may slow down nitrification by reducing the available DO to a suboptimal concentration (Painter 1977).

4.5 Kinetics of Nitrification

EPA (1975) and Wong-Chong (1975) modelled nitrification reactions using a Monod-type relationship. Generally, because the required kinetic data (Table 4.1) is gathered from pure cultures or from controlled laboratory experiments, the model accuracy is limited in predicting full scale nitrification performance (Beer 1978; EPA 1975).

A consensus has the overall wastewater nitrification rate being limited by the rate of ammonia oxidation to nitrite (Gujer 1975; Poduska 1975). Where the ammonia concentration exceeds 2-3 mg/L, the rate is frequently accepted as being "zero order" or independent of the ammonia concentration (Wild 1971, Sutton 1974). As the concentration falls, an accelerating reduction in the ammonia utilization rate is observed (Heide 1977; EPA 1975).

TABLE 4.1

TYPICAL VALUES OF KINETIC CONSTANTS FOR NITRIFIERS

(After Sharma 1977* and Painter 1977)

Constant	Nitrosomonas	Nitrobacter	Heterotrophs
Cell Yield Y (wt cells/wt energy substrate)	0.03 - 0.13*	0.02 - 0.08*	0.37 - 0.79*
Max Specific Growth Rate μ. (day^{-1})	2.2 ($30^{o}C$) 0.46 - 2.2*	1.39 ($32^{o}C$) 0.28 - 1.44*	7.2 - 17.0*
Michaelis-Menten Constants (mg/L)			
Energy Substrate	0.06 - 5.6* 10 ($30^{o}C$) 3.5 ($25^{o}C$) 1.2 ($20^{o}C$)	0.06 - 8.4* 8 ($32^{o}C$) 5 ($25^{o}C$)	<1 - 181*
Electron Acceptor (oxygen) mg/L	0.3 - 1.3* 0.5 ($30^{o}C$) 0.3 ($20^{o}C$)	0.25 - 1.3* 1.0 ($30^{o}C$) 0.25 ($18^{o}C$)	<0.1*

Painter (1970) and EPA (1975) indicate that the maximum specific growth rates in activated sludges are from 60% to 85% less than those observed in pure culture, due principally to the less favourable and uncontrolled environment.

4.5.1 Reported Nitrification Rate Parameters

The lack of generally accepted procedures and consistent nomenclature for determining and reporting nitrification rates frequently precludes comparison of data from different investigators. Biomass is variously reported as MLSS, MLVSS, cellular TKN and "nitrifiers" or else left ill-defined. Rates are expressed either as "substrate utilization" or "product increase" with such parameters as TKN (total and soluble), ammonia, oxygen uptake rate, nitrite and nitrate being monitored by one investigator or another.

Further complication is introduced by such factors as ammonia assimilation, stripping, endogenous oxidation, nitrite build up and other environmental or process considerations which may influence results, but are seldom documented.

4.5.2 Variation of Nitrification Rate with Temperature

Few useful studies of temperature effects on the nitrification rate of domestic wastewater have been reported in the literature.

Lawrence (1970) and Sutton (1977b) have found nitrification to be more sensitive than denitrification or carbon oxidation. (Sayigh (1978) showed a heterotrophic BOD stabilizing population with a three day sludge age to be substantially temperature independent in the $4^{o}C$ to $31^{o}C$ range.)

Focht (1975) and EPA (1975) discuss the strong temperature dependence of specific growth rates and half-rate constants for nitrifiers. As a general rule, an Arrhenius type of relationship adequately models

most of the observed variations in rates (Sutton 1977a; Wild 1971; Mulbager 1971). In Table 4.2 values of some experimentally determined temperature coefficients are listed together with source references. The wide variation in data is generally attributable to different experimental techniques and variations in environmental conditions other than temperature. (See Section 4.5.1.)

TABLE 4.2

ARRHENIUS CONSTANTS FOR NITRIFICATION

Temperature (^{o}C)	Q_{10}	θ'	Arrhenius E (cal/mole)	Reference
10-20	2.2			Wild (1971)
20-30	3.3			Painter (1970)
		0.075	12,730*	Sutton (1978a)
	2.1		12,000*	Sutton (1978b)
10-20	3.3		20,570[a]	Ibid
10-20	2.1		12,000[a]	Ibid
10-20	2.4		15,400[a]	Ibid
10-20	2.6		16,300[t]	Ibid

Notes:

Nomenclature: See Chapter 3.2.3.

* Combined nitrification-denitrification (7-25^{o}C)

[t] Separate nitrification (8-23^{o}C)

[a] Combined nitrification-carbon oxidation (5-30^{o}C)

Other References (Data not included): Wong-Chong (1975); Sharma (1977); Mulbager (1971); Sutton (1975b), (1977b).

Focht (1975) indicated that at temperatures below 10° or $15^{\circ}C$, other physical factors such as reduced solubility and lower diffusion rates exert an increasing influence, thus raising Q_{10} values. Particularly at low substrate levels, Q_{10} values were directly proportional to substrate concentration.

Sutton (1975b) showed that the TKN removal rate became less sensitive to temperature at higher sludge ages. In a series of experiments with a combined sludge system using sludge ages of 4, 7 and 10 days and varying the temperature from $5^{\circ}C$ to $20^{\circ}C$ a linear (and not Arrhenius) dependency of nitrification rate on temperature was observed by Sutton (1975b).

4.5.3 Nitrification in Wastewater

Both reduced nitrogen (TKN) and reduced carbon (BOD) exist together in normal domestic wastewater. The oxidation of carbon by heterotrophs is more rapid than autotrophic nitrification and the yield coefficient is also higher (see Table 4.1). Unless certain conditions are met, the heterotroph population will increase at the expense of the nitrifiers and nitrification will not occur.

In order to maintain nitrification it is necessary that the actual growth rate of nitrifiers, μ_N, under the environmental conditions of the system, be equal to or greater than that of the associated heterotrophs, μ_H (Lawrence 1970).

Recalling that growth rate = 1/sludge age (Equation 3.3), the minimum sludge age to maintain nitrification θ_c^m can be established by calculation or by experiment and a design sludge age θ (design) can be used in the system such that:

[4.8] $$\theta_{(design)} \geq \theta_c^m$$

From Equation 3.4

[4.9] $$\frac{1}{\theta_{(design)}} = \mu_H = Y_H q_H - b_H$$

(where the subscript H refers to the heterotrophic carbon oxidizers). As both Y_H and b_H are nominally constant, control of the heterotroph growth rate can be achieved by control of the removal rate q_H of organic substrate, where q_H may be expressed as:

[4.10] $$q_H = \frac{S_o - S_e}{X \cdot (HRT)}$$

(S_o and S_e are the influent and effluent organic carbon substrate concentrations associated with the nitrification reactor, X is the biomass concentration (MLVSS) and HRT the reactor hydraulic retention time.) By increasing the MLVSS or the HRT or by lowering the influent substrate concentration, the requisite sludge age to hold down the heterotrophic growth rate and thus maintain nitrification can be obtained. The use of a prior organic carbon removal step is one procedure used to lower the organic influent concentration (Wild 1971).

4.5.3.1 Safety Factor in Design:

As discussed by Lawrence (1970), a safety factor (SF) for nitrification may be defined as:

[4.11] $$SF = \frac{\text{Design solids retention time}}{\text{Minimum SRT for nitrification}} = \frac{\theta_{(design)}}{\theta_c^m}$$

Such a factor allows a temporary inhibition of nitrifier growth rate to occur without causing washout of the nitrifying organisms. In addition, an operating plant undergoes a diurnal variation in flow rates and thus in

HRT and frequently in the BOD/TKN ratio (EPA 1975). Where an adequate safety factor is provided, significant ammonia breakthrough from the nitrification stage will not occur. As a general rule EPA (1975) recommends the safety factor be the ratio of peak TKN concentration to mean TKN concentration.

4.5.4 Fraction of Nitrifiers in Activated Sludge

In a nitrifying activated sludge only a fraction, f, of the biomass (MLSS) or (MLVSS) are nitrifiers, the rest mostly heterotrophs. Thus the observed nitrification rate of a sludge, r (pounds ammonia oxidized per pound MLVSS per day), can be related to q (lb NH_4 oxidized per pound of nitrifiers in the sludge per day) as follows:

$$r = q \cdot f$$

Normally, although q may be calculated theoretically for a pure or mixed culture, the actual rate 'r' is determined experimentally. EPA (1975) indicates that f may be approximated by using:

$$f = \frac{M}{M+m}$$

where M is the mass of nitrifiers grown through ammonia oxidation $= Y_N(N_o - N_e)$

m is the mass of heterotrophs grown through carbon oxidation $= Y_H(S_o - S_e)$

where the effluent TKN and BOD are small:

$$[4.12] \qquad f = 1 \Big/ \left(\frac{BOD}{TKN} \cdot \frac{Y_H}{Y_N} + 1\right)$$

Using Equation 4.12 with yield coefficients of 0.15 and 0.55 for TKN and BOD_5 respectively, EPA (1975) estimates the following nitrifier fractions:

BOD/TKN	f	BOD/TKN	f
0.5	0.35	4.0	0.064
1.0	0.21	6.0	0.043
2.0	0.12	8.0	0.033

It is apparent that the nitrification rate of activated sludge is strongly dependent on the BOD:TKN ratio of the feed.

Srinath (1976) proposed that the nitrifier population could be estimated by using cellular TKN instead of MLVSS as a measure of active biomass. The nitrifying ability of a test sample can be compared to that of a pure standard sample on a unit biomass basis and the fraction of nitrifiers thus determined. Painter (1970) and Sharma (1977) indicate however that numerous factors dictate lower nitrification rates per unit of nitrifier biomass in activated sludge compared to pure culture, and not just the percentage of biomass that is comprised of nitrifiers.

4.6 Design Approaches to Nitrification:

EPA (1975) and Sutton (1977a) indicate two approaches for designing activated sludge nitrification systems:

(a) Solids Retention Time approach.

(b) Nitrification Rate approach.

4.6.1 Solids Retention Time Approach:

By experiment (Sutton 1978a, Lawrence 1976), or by calculation, using the estimated environmental conditions (EPA 1975, Downing 1964a), the minimum SRT necessary for nitrification is determined. The application of a suitable safety factor determines the design SRT. The use of equation 4.9 relates this SRT to the carbonaceous substrate concentration and its removal rate, allowing a suitable process MLSS and HRT to be determined.

TABLE 4.3

RANGE OF AEROBIC SRT
REPORTED FOR NITRIFICATION

Temperature	SRT Range (Minimum)
5°C	10-20 days
7-8°C	4-9.5 days
10°C	10 days
14-16°C	6-10 days
20°C	1.3-4 days
23°C	3-4 days
24-26°C	1.6-4.5 days

References:

Balakrishnan (1969a)
Horstkotte (1974)
Lawrence (1970, 1976)
Wilson (1977)
Rebbun (1978)
Sherrard (1977)
Sutton (1975b, 1978a)
Stover (1976)

Table 4.3 summarizes some of the SRT data reported in the literature. In single sludge nitrification-denitrification systems the SRT used for nitrification is equal to the system SRT times the fraction of MLSS under aerobic conditions (Sutton 1978a). EPA (1975) indicates that the retention time approach is most commonly used for combined sludge systems. Jank (1978) suggests it is the preferred approach of the two design methods.

4.6.2 Nitrification Rate Approach:

By experiment, ideally in a pilot plant operation, the unit nitrification rate of a sludge is measured. By using an appropriate safety factor, suitable MLSS and HRT data, the use of Equation 4.9 will provide a design SRT. However, as previously demonstrated, the unit rate depends on the SRT and on the fraction of nitrifiers present, which is determined by the BOD:TKN ratio. Sutton (1977a) asserts that the wide variation in unit rates as observed in his work and by others (reported by EPA 1975) is attributable mostly to C:N variations (Figure 4.1). Sutton (1977a) also found in a combined sludge system that the nitrification rates at a given SRT decreased as the MLVSS increased. Lawrence (1976) discounts the nitrification rate approach by asserting that "specific oxidation rate of ammonia is meaningless because the predominant fraction of VSS consists of carbonaceous heterotrophs".

4.7 Processes Available for Biological Nitrification

A wide range of biological processes are available for nitrification of wastewaters containing reduced nitrogen. Only those systems using some modification of the activated sludge process are elaborated upon here. Some other systems are referenced in Chapter 1.

4.7.1 Suspended Growth Systems

Sherrard (1976b) characterizes activated sludge operations by SRT:

SRT	Activated Sludge Variation
<3 days	High Rate
5-10 days	Conventional
>20 days	Extended Aeration

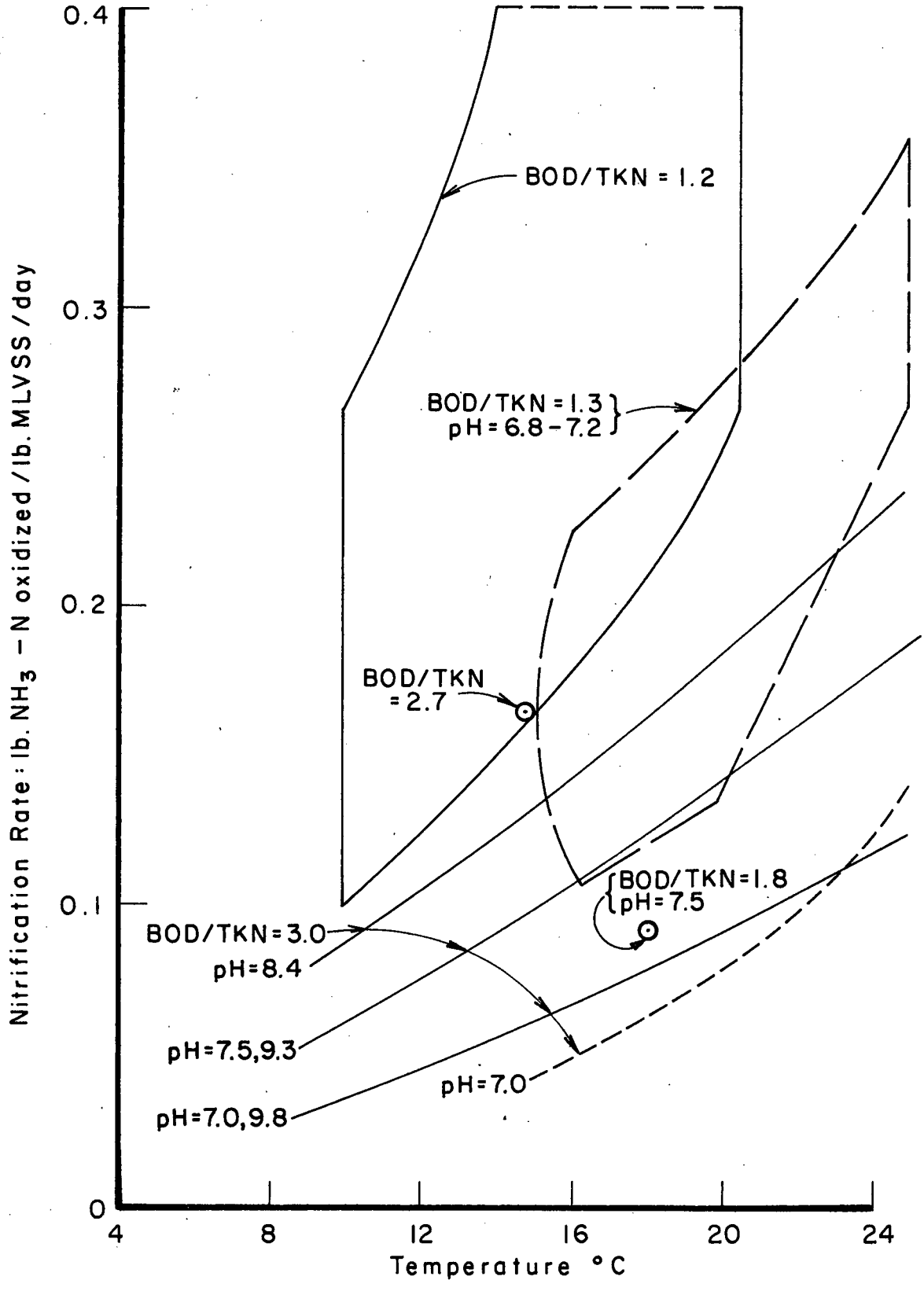


FIG. 4.1 NITRIFICATION RATES (EPA, 1975).

As a general rule, EPA (1975) indicates that extended aeration plants, including oxidation ditches, are capable of nitrification even at cold temperatures. Conventional plants including complete mix, plug flow, step aeration and high purity oxygen modifications may nitrify at warm temperatures but usually not at cold (Lawrence 1976; Khararjian 1978). High rate plants, including contact stabilization (C.S.) and modified activated sludge variations, are generally poor nitrifiers (EPA 1975; Zoltek 1976).

4.7.2 Combined and Separate Sludge Systems

Suspended sludge nitrification systems are subclassified as combined systems when the same sludge carries out both nitrification and BOD removal. Separate sludge systems use a different (specialized) sludge for each operation.

Further diversification occurs when combined sludges carry out BOD removal and then nitrification in sequential tanks, or when the sludge undergoes a period of anaerobiasis for denitrification purposes (Barnard 1975a).

Separate systems may use a fixed biomass (trickling filter or rotating biological contactor) for one or several of the operating stages (Balakrishnan 1969b).

Increasing diversity is added by the use of primary chemical treatment for BOD or phosphorus removal (Rebbun 1978; Horskotte 1974) by modification of environmental conditions to enhance biological phosphorus removal, or by the use of oxidation ditch systems which often bypass primary treatment and simultaneously carry out BOD removal, nitrification and denitrification (Matsche 1977a).

4.7.3 Pros and Cons of Combined and Separate Sludge Systems

The early development of nitrification sludge theory by Downing (1964a) used a combined system. European engineers persevered with this system while the North American thrust tended toward two sludge systems, principally to overcome the problems caused by loss of nitrification during low temperature winter operations (Wild 1971, Mulbager 1971).

4.7.3.1 Advantages of Two-Stage (Separate Sludge) Systems

(i) Optimization and easier control of the separated carbon oxidation and nitrification functions;

(ii) Lower BOD:TKN ratios in the nitrifier tank allow the build up of larger nitrifier population and thus higher conversion rates;

(iii) Lower overall SRT and HRT in the system;

(iv) Ability to nitrify in all seasons;

(v) The prior carbon oxidation stage provides a buffer against toxic agents that may affect the sensitive nitrifiers. Some organic toxicants may be bioxidized and thus allow nitrification of an effluent that could not otherwise be treated.

4.7.3.2 Disadvantages of the Separate Sludge Operation

(i) A greater capital, operating and maintenance expenditure with dual tanks and clarifiers.

(ii) A higher total sludge production due to lower SRT and thus lessened endogenous biomass decay.

(iii) Duplication of the major operating problem - the clarifier.

(iv) If the BOD:TKN ratio is too low, the daily loss of biomass in the clarifier overflow may surpass the total daily biomass production in the nitrifying reactor, leading to nitrifier washout.

(v) The use of a high rate first stage in order to keep an adequate BOD:TKN ratio in the second stage can lead to poor first stage settling characteristics.

Lawrence (1976) discounts many of the advantages of the two stage system. Most recently published work on activated sludge nitrification and denitrification systems indicates a movement away from these multi-sludge systems toward combined systems (Barnard 1975a;Jank 1978; Besik 1977). In part, this must be due to the development of improved knowledge about, and an adequate data base for, single sludge design at all temperatures. Increased capital, labour and energy costs and a consequent trend toward simpler systems probably also play a role.

Lawrence (1976) and Sutton (1975b) observed no apparent differences in the efficiency or the performance of one and two stage nitrifying systems operated under the same growth and temperature conditions. Jank (1978) found similar nitrification performances for both systems in nitrification reactors using a combined sludge that was also performing denitrification and phosphorus removal functions under different environmental conditions. The comparison was based on similar aerobic SRT's.

CHAPTER 5

NITROGEN REMOVAL OR DENITRIFICATION

5.0 Biological Nitrogen Utilization

Micro-organisms active in wastewater use nitrate either by assimilation or by dissimilation (Painter 1977).

Assimilation processes reduce nitrate to ammonia and then incorporate it into cellular organic nitrogen. Dissimilation or "nitrate respiration" utilizes the oxygen of the nitrate as a final electron acceptor, during the oxidation of organic substrate by heterotrophic microbes in an oxygen free (anoxic) environment.

From an engineering point of view, dissimilation is the more important because most of the influent nitrogen may be entirely removed from the system by this route.

5.1 Dissimilation

Dissimilation is generally represented as a two stage process (Table 5.1): firstly, nitrate reduction to nitrite and secondly, reduction to nitrogen gas. However, as discussed by Delwiche (1956) and Painter (1970), the reduction involves various other intermediates and the final product depends on the bacteria and environmental conditions. Moore (1970) indicates that a greater variety of microbes are available in sewage to reduce nitrate to nitrite than to reduce nitrite to (di)nitrogen. Some species are capable of reducing both nitrate and nitrite; others are more selective.

The term "Denitrification" is used to describe a process which provides final products of nitric oxide, nitrous oxide or dinitrogen (Painter 1977).

Unlike nitrifying organisms, most other bacteria in sewage or activated sludge are capable of nitrate dissimilation (Christensen 1977a). The bulk of these denitrifying species are facultative chemo-organoheterotrophs, deriving both energy and carbon from reduced organic substrate but being capable of using oxygen, nitrate, nitrite or, in some cases, sulphate ions as a final electron acceptor. In any denitrifying system, the variety and numbers of species present are determined by environmental conditions and by changes in these conditions (Davies 1971). The plethora of potential denitrifiers in a sewage treatment plant and the ability of populations to change with environmental conditions is a major reason for the wide range of observed denitrifying responses to factors such as pH and temperature (Dodd 1975).

5.1.1 Respiration Modes:

Respiration is classified as aerobic or anoxic according to whether oxygen or nitrate is the final electron receiver. The biochemical pathways are identical except for one enzyme at the final electron transfer interface (Painter 1970). The facultative organisms are thus able to switch rapidly between the two respiration modes. However, because the energy yield from aerobic respiration is greater, (Table 3.1) nitrate respiration is severely curtailed in the presence of oxygen. Dodd (1975) indicates that the oxygen inhibits the synthesis of enzymes capable of catalyzing the denitrification reaction (ie. nitrate respiration).

5.2 Energy, Synthesis and Stoichiometry

In a practical denitrifying system, there are several reactions that influence nitrogen removal: biomass (new cell) synthesis,

nitrate respiration with an extra-cellular carbon source, endogenous nitrate respiration, and aerobic respiration, (which will occur until the DO levels are very low) (Painter 1970).

From Table 5.1, Equations 5.1 to 5.4 represent "half-cell" reactions for oxygen and nitrate respiration. Half-cell reactions for methanol and domestic sewage oxidation, using the $C_{10}H_{19}O_3N$ wastewater description of Christensen and McCarty (1975), are shown by Equations 5.5 and 5.6. Overall energy equations for methanol, wastewater and endogenous (cell tissue) substrates with oxygen or nitrate electron acceptors are represented by Equations 5.7 to 5.12. It is noted that where the substrate contains nitrogen, ammonia is released. This will be discharged in the system effluent unless assimilated into biomass or else oxidized in a subsequent aerobic step.

Except in the case of endogenous respiration where biomass is being oxidized, the synthesis of new biomass occurs simultaneously with energy production. Synthesis is represented by Equations 5.13 for a methanol substrate (McCarty 1969) and 5.14 for wastewater substrate (Beer 1978).

Equations of greater accuracy and complexity, which include phosphorus and consider variations in the cell composition with sludge age, are available in the literature (Sherrard 1976a).

The complete picture of substrate utilization must combine equations for synthesis and for respiration. For this, the relative proportions of substrate used in energy production and in biomass synthesis must be known. Beer (1978) derived an energy:synthesis ratio of 35:65 for aerobic and 65:35 for anoxic synthesis using the results of McCarty (1969), Barnard (1975a) and Porges (1956) for

TABLE 5.1

STOICHIOMETRIC REPRESENTATIONS OF DENITRIFICATION REACTIONS
(After Beer 1978, McCarty 1969)

HALF CELL REDUCTION REACTIONS

Nitrate Respiration

$$\tfrac{1}{2}NO_3^- + H^+ + e^- = \tfrac{1}{2}H_2O + \tfrac{1}{2}NO_2^- \quad - (5.1)$$

$$\tfrac{1}{3}NO_2^- + H^+ + e^- = \tfrac{1}{3}H_2O + \tfrac{1}{6}N_2 + \tfrac{1}{3}OH^- \quad - (5.2)$$

Overall

$$\tfrac{1}{5}NO_3^- + H^+ + e^- = \tfrac{2}{5}H_2O + \tfrac{1}{10}N_2 + \tfrac{1}{5}OH^- \quad - (5.3)$$

Oxygen Respiration

$$\tfrac{1}{4}O_2 + H^+ + e^- = \tfrac{1}{2}H_2O \quad - (5.4)$$

HALF CELL SUBSTRATE OXIDATION

Methanol

$$\tfrac{1}{6}CH_3OH + \tfrac{1}{6}H_2O = \tfrac{1}{6}CO_2 + H^+ + e^- \quad - (5.5)$$

Domestic Wastewater

$$\tfrac{1}{50}C_{10}H_{19}O_3N + \tfrac{9}{25}H_2O = \tfrac{9}{50}CO_2 + \tfrac{1}{50}NH_4^+ + \tfrac{1}{50}HCO_3^- + H^+ + e^- \quad (5.6)$$

OVERALL ENERGY EQUATIONS

Methanol Substrate - Oxygen Electron Receiver

$$2CH_3OH + 3O_2 = 4H_2O + 2CO_2 \quad - (5.7)$$

Methanol Substrate - Nitrate Electron Receiver

$$5CH_3OH + 6NO_3^- = 3N_2 + 5CO_2 + 7H_2O + 6OH^- \quad - (5.8)$$

Wastewater Organic Substrate - Oxygen Electron Receiver

$$C_{10}H_{19}O_3N + 12.5\,O_2 = 10CO_2 + 8H_2O + NH_3 \quad - (5.9)$$

Wastewater Organic Substrate - Nitrate Electron Receiver

$$C_{10}H_{19}O_3N + 10NO_3^- = 10CO_2 + 3H_2O + NH_3 + OH^- + 5N_2 \quad - (5.10)$$

Endogenous Oxygen Respiration

$$C_5H_7O_2N + 5\,O_2 = 5CO_2 + NH_3 + 2H_2O \quad - (5.11)$$

Endogenous Nitrate Respiration

$$C_5H_7O_2N + 4NO_3^- = 5CO_2 + NH_3 + 2N_2 + 4OH^- \quad - (5.12)$$

BIOMASS SYNTHESIS REACTIONS

Methanol Substrate

$$14CH_3OH + CO_2 + 3NO_3^- + 3H^+ = 3C_5H_7O_2N + 19H_2O \quad - (5.13)$$

Wastewater Substrate

$$C_{10}H_{19}O_3N + 1.5NH_3 + 2.5CO_2 = 2.5C_5H_7O_2N = 3H_2O \quad - (5.14)$$

OVERALL SUBSTRATE REMOVALS

Aerobic Respiration - Methanol Substrate

$$0.93CH_3OH + 0.056NO_3^- + O_2 = 0.056C_5H_7NO_2 + 1.04H_2O + 0.59H_2CO_3 + 0.056HCO_3^- \quad - (5.15)$$

Nitrate Respiration - Methanol Substrate

$$1.08CH_3OH + NO_3^- + H^+ = 0.065C_5H_7O_2N + 0.47N_2 + 0.76CO_2 + 2.44H_2O \quad - (5.16)$$

Aerobic Respiration - Wastewater Substrate

$$C_{10}H_{19}O_3N + 4.375\,O_2 + 0.625NH_3 = 1.625C_5H_7O_2N + 1.875CO_2 + 4.75H_2O \quad - (5.17)$$

Nitrate Respiration - Wastewater Substrate

$$C_{10}H_{19}O_3N + 6.5NO_3^- = 0.875C_5H_7O_2N + 0.125NH_3 + 3H_2O + 3.25N_2 + 6.5OH^- + 5.625CO_2 \quad - (5.18)$$

wastewater carbon removal. Equations 5.17 and 5.18 use these ratios for aerobic and nitrate respiration respectively. Beer advocates further work to improve the reliability of these ratios and of the assumed wastewater composition ($C_{10}H_{19}O_3N$). Equations 5.15 and 5.16, using methanol as the carbon substrate, are based on the work of McCarty (1969).

5.2.1 Alkalinity Production

These biochemical reactions take place in aqueous solution and the equations could be modified to reflect the effect of changes in alkalinity. From Equation 5.16, 3.57 mg of alkalinity (as $CaCO_3$) are produced per mg of NO_3^- reduced to dinitrogen. In practice, the actual production is less than this, due to oversimplification of the equation and neglect of assimilation. EPA (1975) suggests the use of 3.0 mg/mg in design. Jeris (1977) observed 2.95 in a fluid bed reactor and suggested the use of alkalinity as a control parameter, where an acceptable NO_3^-: alkalinity correlation is available. Beer (1978) indicates that for endogenous nitrate respiration (Equation 5.12), a total of 4.46 mg of alkalinity is produced per mg NO_3^- reduced because of the additional nitrogen in the biomass.

5.3 Factors Affecting Denitrification

5.3.1 Dissolved Oxygen

Christensen (1977a) indicates that dissimilation is inhibited by oxygen; assimilation is not. Painter (1970) points out that a few organisms in pure culture have been shown to denitrify under highly aerobic conditions. Where denitrification occurs under nominally aerobic conditions (Mulbager 1971), it is most probably due to an oxygen gradient, whereby some part of the system is actually at zero DO (Painter 1977; Dawson 1973). Wuhrmann (1968) asserts that oxygen is a powerful inhibitor

to nitrate or nitrite respiration at pH 6.5 to 7.0, but at lower pH, inhibition is diminished. Christensen (1977a) suggests that for denitrification, DO should be less than 0.5 mg/L in suspended cultures. Painter (1977) showed that the denitrification rate dropped by 50% as conditions were changed from anoxic to 0.2 mg/L DO.

5.3.2 pH:

Delwiche (1956) reports that denitrifying systems generally function best in a near neutral pH range. The actual optimum range is dependent on the culture and system under test. Generally, denitrification is supported in the 5.8 to 9.2 pH range with a peak rate between 7.0 and 8.2 (Delwiche 1956). EPA (1975) suggests that operation of denitrification processes is optimum from pH 7.0 to 7.5. Dodd (1975) suggests that the sensitivity of a denitrifying biomass to environmental conditions is increased as the pH is raised above 7.0.

5.3.3 Temperature:

Because of the diversity of species present in a mixed culture, denitrification is generally less sensitive to the mixed liquor temperature than is nitrification, but is more sensitive than carbon oxidation (Sutton 1977b; Focht 1975). Focht (1975) indicates that denitrification is optimal between 65°C - 75°C and ceases at 85°C. Christensen (1977a) suggests an optimum near 40°C and a maximum near 50°C.

Painter (1977) summarizes work indicating that active denitrification occurs at temperatures as low as 4°C, and suggests that it should occur near 0°C but at reduced rates. Dawson (1972) found rates at 5°C to be only 10% of those at 27°C in pure culture, with denitrification ceasing at 3°C.

5.3.4 Micronutrients

Painter (1970, 1977) itemizes both macro- and micronutrient requirements for heterotrophic dissimilation (denitrification). Apart from an organic substrate, the absence of oxygen and presence of nitrate, the macronutrients S, P, Cl, Na, K, Mg and Ca and traces of Mo, Fe, Cu and Mn are required. Some species require ammonia or amino acids for cell synthesis.

5.3.5 Inhibition of Denitrification

Compared to nitrification, there is limited data in the literature on inhibition of denitrification. As indicated by Painter (1970), the more diversified heterotroph population has a greater resistance to inhibition than is the case with nitrifiers. Christensen (1977a) and Moore (1971) show that ammonia, nitrite, methanol, pH and oxygen can be toxic. Oxygen and pH are discussed in Section 5.3.1 and 5.3.2. Nitrite may inhibit above 30 mg/L as nitrogen. Dawson (1972) observed that nitrite may accumulate during adaptation of denitrifiers to new conditions. A study of salinity additions up to 0.63% was reported by Christensen (1977a) to indicate no inhibitory effects. Painter (1970) itemizes inhibition of pure cultures by such agents as:

metal chelating agents (cyanide and "dithiol"); chlorate;
Cu II (16% inhibitory at 3 mg/L); pyruvic acid and hydroxylamine.

Focht (1975) suggests that nitrate, or end product inhibition is of minimal consequence in denitrification.

There are indications that denitrifying sludges require a finite conditioning period after aerobiasis before the respiration rate reaches a maximum. Painter (1977) suggests 30 to 60 minutes.

5.4 Kinetics of Denitrification

The work of Moore (1970) and Stensel (1973) (which shows that nitrite does not normally build up in a denitrifying system) has allowed the process to be modelled as a one step operation - nitrate directly to nitrogen gas.

Monod type relationships have been used by EPA (1975), Paskins (1977), and Engberg (1975) to describe the dependence of denitrification rates on both nitrate and on organic substrate concentrations. Little work directed at determining half-rate constants has been reported. Moore (1970, 1971) and EPA (1975) indicate values less than 1 mg/L for both nitrate and methanol. Paskins (1978) found a half-rate constant of 10.6 mg/L for methanol. As a general rule, provided both nitrate and methanol are present in excess of 1 to 2 mg/L, the denitrification rate is independent of either concentration (EPA 1975), (Painter 1977). Dawson (1972) suggests carbon is limiting unless it is present in excess of the "theoretical need" for cell growth and energy. Murphy (1975) advocates a C:N ratio in excess of unity and a nitrate plus nitrite concentration greater than 1 mg/L for zero order kinetics.

In practice, where the aim is to reduce nitrate levels below 1 mg/L, nitrate is usually limiting (Sutton 1975a, Engberg 1975). In other systems where a carbon source (eg. methanol) is not used, the energy substrate may be limiting (Sutton 1977b; Stensel 1973).

Focht (1975) points out that denitrification kinetics are far more complex than nitrification and are not well developed.

5.4.1 Denitrification Rates

Denitrification rates are dependent on numerous factors including substrate composition and concentration, temperature, SRT, pH,

sludge density, proportion of denitrifiers in the biomass, toxicity, DO, etc. Because of this, the most common design approach is via experimentally rather than theoretically determined rates.

The wide variation in reported denitrification rates at any temperature is indicated in Figures 5.1 and 5.2 for endogenous and wastewater carbon sources respectively. Sutton (1978b, 1977b) demonstrated that rates with combined sludge systems were approximately 40% of those with separate sludges. This was explained by a lower fraction of denitrifiers in the combined sludge due to the relatively lower proportion of time available for denitrifier growth under anoxic conditions.

5.4.1.1 Solids Retention Time:

Engberg (1975) and Davies (1971) point out that denitrification rates and reaction stoichiometry vary with the SRT because different sludge ages alter the environment and thus change the dominant bacterial species. Sutton (1974) indicated that the unit denitrification rate was 1.3 times greater when the SRT was reduced from 6 days to 3 days. It was suggested that a 6 day minimum SRT at $5^{o}C$ and 3 day minimum at $20^{o}C$ was needed to ensure denitrification. Stensel (1973) found a doubling in rate as the SRT was lowered from 7 to 2 days and Moore (1971) a similar increase with an SRT reduction from 6 to 3 days.

5.4.1.2 Solids Concentration:

Christensen (1977a) presents data showing a decrease in unit denitrification rate with an increase in solids concentration. Suggested reasons included lower active biomass and increased diffusion resistance.

5.4.1.3 Temperature:

Sufficient evidence exists to indicate that the denitrification rate dependence on temperature may be represented by an Arrhenius type

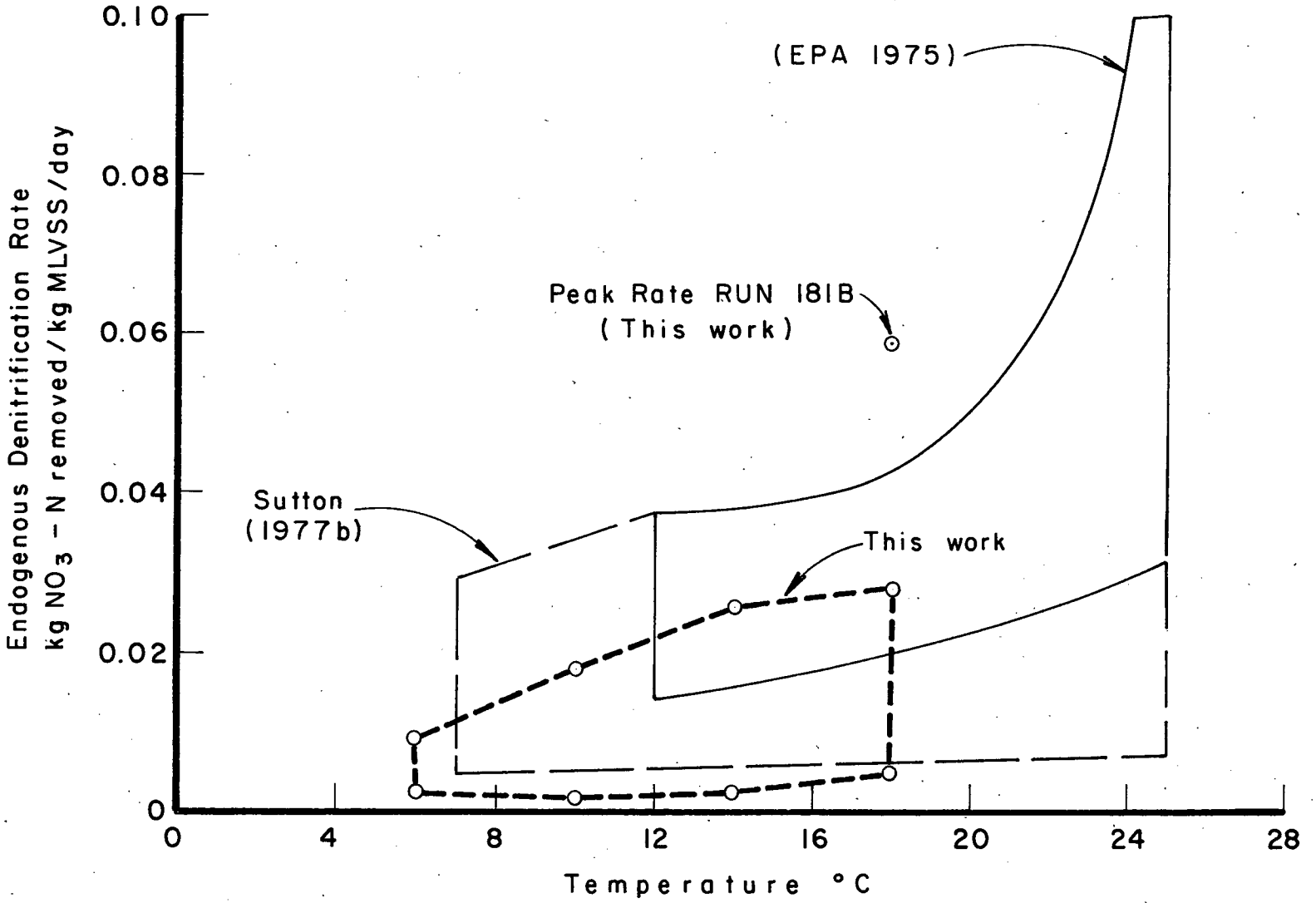


FIG.5.1 ENDOGENOUS DENITRIFICATION RATES: THIS WORK AND OTHERS.

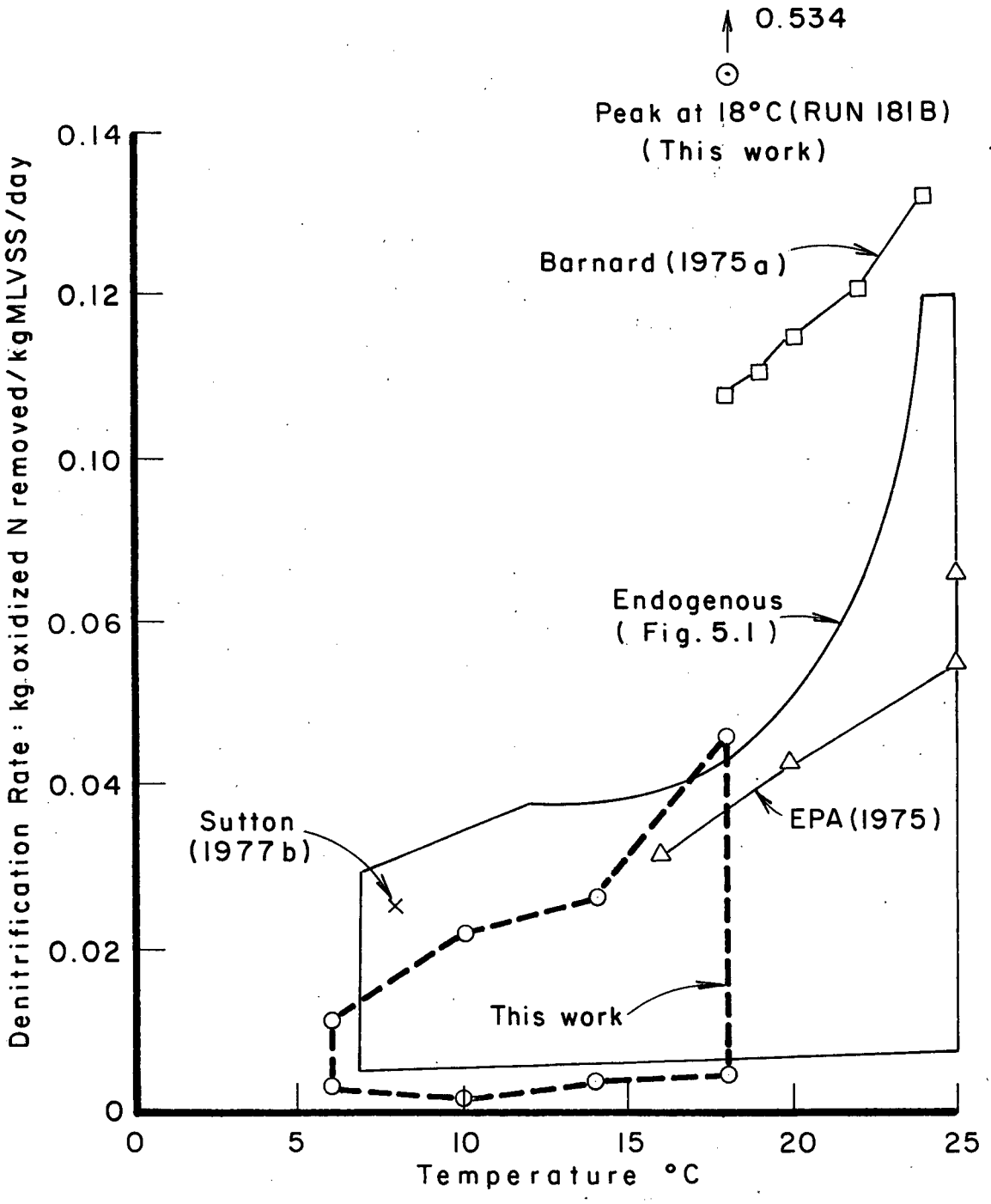


FIG. 5.2 DENITRIFICATION RATES WITH WASTEWATER CARBON SOURCE.

curve. Dawson (1972) demonstrated this dependence between 3°C and 27°C. Sutton (1974, 1975a, 1977b, 1978a) presents tables of Arrhenius relationship constants for denitrification (see Table 5.2). Sutton (1978a) showed that the temperature sensitivity of both combined and separate sludge systems was similar. The response appeared independent of sludge age (Sutton 1977b). Focht (1975) suggests the Q_{10} values are larger below 15°C than above. Reported rates are dependent on the methods used for determining the progress of denitrification (ie. gaseous product appearance or substrate disappearance).

Apart from the work of Sutton, Murphy, Jank, Dawson and others at Burlington, Ontario, very little comprehensive work has been published on the relationships between temperature and denitrification rates. The ample variation reported by these authors suggests the existence of no simple general relationship, but rather one particular to the situation under test.

TABLE 5.2

ARRHENIUS CONSTANTS FOR DENITRIFICATION

Temperature (°C)	Arrhenius E (cal/mole)	θ	Q_{10}	*k	Reference
6-19				0.02	Christensen
10-20				0.05-0.07	(1977a)
15-24				0.07	Ibid
10-40				0.05	Ibid
18-24		1.094		0.04	Barnard (1975a)
6-25	15,900	1.09	2.5		Murphy (1975)
3-27	16,800	1.12			Dawson (1972)
10-20	19,500	1.13	3.3		Stensel (1973)
10-20	19,000	1.15	3.3		Mulbager (1971)
7.26	12,730	1.075			Sutton (1978a)
7-25	15,900				Sutton (1977b)

Notes: Nomenclature: see Chapter 3.2.3.

*Rate at T_1 = Rate at $T_2 \cdot 10^{k(T_1-T_2)}$.

5.5 Substrate

As indicated in Section 5.1, denitrifying bacteria require a source of reduced carbon for energy production and cell synthesis. In wastewater treatment, the carbon/energy source is usually one of the following: (Painter 1977)

(i) Raw Sewage

(ii) Cell Tissue (for endogenous nitrate respiration)

(iii) External chemical or organic carbon addition.

Table 5.3 summarizes the advantages and disadvantages of the various substrates.

The work of numerous investigators such as Dawson (1972), Dodd (1975), Stensel (1973), Christensen (1977a) and McCarty (1969) indicates that both denitrification rates and the percentage of nitrogen removed increase proportionally with carbon substrate additions until a certain ratio of carbon to nitrogen is reached, at which point the values level off. This plateau approximates the stoichiometrically-determinable level at which sufficient organic carbon is available to satisfy the system needs for growth, energy production and oxygen consumption (Barnard 1977).

Of these substrates, methanol has been the most widely studied in North America, while raw sewage and biomass have received the major European attention (Christensen 1978a).

5.5.1 Wastewater as a Substrate

The increased cost of methanol, the cheapness and availability of raw sewage, together with a greater understanding of the denitrification process has increased the interest in domestic wastewater as a carbon source.

Denitrification with wastewater is generally regarded as being slower than with methanol addition (EPA 1975, Christensen 1977a).

TABLE 5.3

WASTEWATER DENITRIFICATION SUBSTRATES

Substrate	Advantages	Disadvantages	Reference
Cell Biomass	Readily available Reduces biomass Temperature insensitive	Low rate Ammonia release	Sutton (1978b) Christensen (1977a)
Raw Sewage	Cheap Readily Available	Ammonia, organic N release Lower rate than methanol Uncontrolled variations in strength composition & flow Mix of refractory and biodegradable	Christensen (1977a)
Methanol	Chemically simple & pure Easily degraded, nitrogen free Easy monitoring and control Cheap and available Small sludge production	Toxic to Nitrifiers Escalating price Excess adds BOD to effluent	EPA (1975) Christensen (1977a)
Molasses	Cheap and available in some areas	Slow Rate, Bulking Sludge	EPA (1975)
Methane	Cheap & available (Digester)	Explosive, few bacteria can use.	Rhee (1978)
Volatile Acids	Cheap and available (Digester)	Variable contaminants including NH_3	McCarty (1969)
Brewery Waste	Local Availability High Rate	High Solids Production	Wilson (1973)
Ethanol	Less toxic than Methanol	More expensive	McCarty (1969)
Other	-	-	Christensen (1977a)

Paskins (1978) indicates that raw sewage with its numerous different organic constituents (few of them in high concentrations) is most probably a carbon limiting substrate.

Sutton (1978a) determined that organic carbon would be limiting unless "3 mg of filtered COD are available for each mg of nitrogen according to stoichiometric calculations". (Based on the equation: mg/L methanol = 1.91 NO_3-N + 1.14 NO_2-N + 0.67 DO and a conversion factor from methanol to COD of 1.5).

Christensen (1977b) suggests a BOD_5:NO_3-N ratio from 3 to 6 is desirable; Bishop (1976) a COD:TKN greater than 10:1. Barnard (1977) indicates 11.5 COD mass units to one nitrogen unit is desirable. Recent publications by Sutton (1978a) and Barnard (1977) have highlighted the value of raw sewage as a denitrification substrate. Sutton demonstrated that denitrification rates, under parallel batch conditions were equal for methanol and raw sewage. Barnard (1977) analyzed the three separate zero order denitrification rates observed in his batch denitrification tests using raw sewage additions:

A rapid initial (5-15 minutes) rate of 60 mg/gm MLSS/hr;

An intermediate rate of 16 mg/gm MLSS/hr;

A slow, long term rate of 5.4 mg/gm MLSS/hr.

The initial rapid rate was brought about by the oxidation of highly reduced organic compounds in the wastewater. (The extent of such material in raw sewage depends on the particular system under examination.) This rapid rate continued until the difference in redox potentials between the mixed liquor and raw sewage was removed.

The intermediate rate was that commonly observed under steady state conditions with wastewater substrate and lasted until all the

available carbon was depleted, at which time the slow or endogenous rate was abruptly apparent. Barnard (1977) indicated that methanol addition was equivalent to the intermediate rate. At the highest rate, denitrification could normally be completed extremely rapidly - say five minutes. In his endogenous denitrification studies, Barnard (1977) observed only the two slower rates.

The existence of this rapid initial rate of denitrification (or oxygen uptake) could possibly be utilized to economic advantage when designing nitrogen removal systems to treat highly septic wastewater.

5.5.2 Methanol as a Substrate

Methanol has been used extensively in North America to provide a readily available carbon source in denitrification systems with low carbon availability in the nitrate respiration reactor (EPA 1975; Sutton 1974; Mulbager 1971; McHarness 1973).

McCarty (1969) defined a Consumption Ratio as:

$$\frac{\text{Quantity of Organics Consumed During Denitrification}}{\text{Stoichiometric Organic Requirement for Nitrate, Nitrite, and Oxygen Removal}}$$

Experimentally, this ratio was determined as 1.3 for methanol by McCarty (1969) and 1.26 by Stensel (1973). Using this ratio and a knowledge of the biomass synthesis, McCarty (1969) determined the required methanol addition as: (All data in mg/L)

$$\text{Methanol} = 2.47\,(NO_3\text{-}N) + 1.53\,(NO_2\text{-}N) + 0.87\,(DO)$$

Biomass production can also be calculated:

$$\text{Biomass} = 0.53\,(NO_3\text{-}N) + 0.32\,(NO_2\text{-}N) + 0.19\,(DO)$$

EPA (1975) suggests that 3.0 mg methanol added per mg nitrate is sufficient in practice. Stensel (1973) suggests that an excess of 1 mg/L in the effluent allows denitrification without carbon limitation. Horskotte

(1974) indicates difficulty in controlling methanol levels in a full scale operation. Numerous authors point out that excess methanol addition may add BOD to the effluent unless subsequent removal is practised (Wuhrmann 1973; Murphy 1975; Barnard 1975a; Sutton 1977b).

5.5.3 Endogenous Nitrate Respiration

Wuhrmann (1968) indicated that the endogenous carbon reserves in bacteria are sufficient to maintain nitrate respiration until all the oxidized nitrogen is reduced in normal domestic wastewater treatment. The nitrogen removal rate is limited only by the endogenous decay rate.

Beer (1978) pointed out that endogenous nitrate respiration is slower than oxygen respiration. The reaction rate is zero order with respect to substrate, electron acceptor and biomass. From Equation 5.12, a biomass destruction of 2 mg is indicated for each mg of nitrate removed, with a total alkalinity production of 4.4 mg ; 3.57 from nitrate reduction, the rest from biomass conversion to nitrate and subsequent reduction.

Sutton (1978a) points out the wide variation in reported endogenous denitrification rates (Figure 5.1). There is no good agreement among investigators on the extent to which temperature affects rates (Table 5.4). Sutton (1978a, 1978b) found that temperature had a minor effect on rate in the 7°C to 26°C range at similar SRT. Changing SRT's had a significant effect, with the endogenous denitrification rate decreasing by 80% as the SRT was raised from 2 to 32 days. This was explained by the dependence of the denitrification rate on the release of organic carbon from lysing cells. The number of viable cells decreases with increasing SRT and thus the rate of carbon release diminishes.

On the other hand, Marais (1975) concluded that the unit rate of endogenous denitrification was constant at any temperature for all SRT's.

TABLE 5.4

DEPENDENCE OF ENDOGENOUS NITRATE RESPIRATION ON TEMPERATURE

Temperature:Rate relationship $R_T = R_{20}\,\theta^{T-20}$

R_{20}	θ	Reference
0.045*	1.2	Barnard (1974)
0.04	1.06	Beer (1978)
0.007-0.01*		Christensen (1977a)
0.006-0.04	(Substantially independent of temperature)	Sutton (1978a)

Notes: R_T = removal rate (lb NO_3-N/lb MLVSS/day) at T^oC.

* assumes MLVSS = 70% MLSS.

5.6.1 Post Denitrification Aeration:

The imposition of a short period of aerobic treatment between denitrification and settling has several process advantages (EPA 1975; Barnard 1975a; Horstkotte 1974).

(i) Nitrogen gas is stripped from the biomass allowing a lower SS in the discharged effluent and improved sludge settling.

(ii) The ammonia released during endogenous respiration and any excess carbon source additions are oxidized.

(iii) Denitrification is halted and the residual DO prevents nitrogen formation in the clarifier, with its consequent rising sludge problems.

(iv) Sludge stabilization is increased by endogenous oxygen respiration, thus lowering the BOD per unit of biomass in the effluent. However such stabilization also lowers the denitrifying ability

of the sludge by reducing the heterotroph population, thus requiring a larger anoxic reactor or longer HRT to effect denitrification.

Retention times studied and reported in the literature range from 10 to 120 minutes (Christensen 1977a). Horstkotte (1974) indicates that one hour is generally adequate.

EPA (1975) suggests that a short period of mild turbulence between this aeration and clarification will improve settling by allowing flocculation to occur.

5.7 Nitritification and Denitritification

As outlined by Prakasam (1972) these terms are used to describe ammonia oxidation to nitrite only and direct reduction of nitrite to gaseous products. Prakasam, in treating highly nitrogenous poultry waste, experienced a nitrite buildup during a nitrification process, due to nitrobacter being inhibited by the high ammonia concentrations. By denitritifying the partially nitrified liquor, he was able, in a subsequent step to completely convert the remaining ammonia to nitrate. The demonstration that the nitritified liquor could be completely denitrified offered several advantages:

(i) Nitrobacter inhibition by ammonia was no longer a problem.

(ii) Higher loading rates and simple flow sheets were possible as complete conversion to nitrate was not necessary.

(iii) Denitritification was more rapid than nitrate reduction (denitrification).

(iv) Less energy and substrate were needed (oxygen and methanol).

(v) High strength wastes could be simply treated.

Voets (1975) determined that denitritification occurred under both aerobic and anaerobic conditions. The nitrite can also be chemically removed by

acidification, plus urea or sulfamic acid addition.

5.8 Flow Sheets for Biological Nitrogen Removal

Numerous process configurations have been proposed or used for the biological denitrification of municipal sewage (see Sutton 1974; EPA 1975; Christensen 1977a; Beer 1978; Sharma 1977; Jank 1978 for summaries).

The distinguishing characteristics of the various systems include the following:

(i) Attached or suspended biomass;

(ii) Combined or separate sludges;

(iii) The number of distinguishable process basins;

(iv) Extent and nature of denitrification substrate addition (if any);

(v) Sequence of operations and recycle (if any);

(vi) Other associated chemical and biological operations.

For the purpose of this review, only suspended biomass, combined sludge systems with wastewater or cell biomass carbon sources are relevant.

The basic principles on which many of these systems are based arise from the work of either Wuhrmann (see Christensen 1977a) or Ludzack (1962).

5.8.1 Wuhrmann Denitrification System (Post-denitrification)

Wuhrmann made use of a two reactor system with BOD removal and nitrification carried out simultaneously in the first and endogenous denitrification in the second. Mixed liquor was apparently not recycled. Using a MLVSS of approximately 5.3 gm/L and an anoxic HRT varying between 2.2 and 2.8 hours, the calculated endogenous denitrification rates were

1.7 mg -N/gm MLVSS/hour at 17°C and 0.7 at 13.6°C. Up to 90% total nitrogen removal was achieved.

Subsequent researchers cited in Christensen (1977a) were generally unable to duplicate these results due, primarily to poor nitrification or to an insufficient anoxic HRT to allow adequate denitrification.

Christensen (1977b) was able to match Wuhrmann's results in a system with a BOD:total nitrogen ratio of between 4 and 6 in the anoxic reactor.

Beer (1978) and Christensen (1977a,b) discuss factors that influence endogenous denitrification and present design considerations for "Wuhrmann" systems.

5.8.2 Ludzack Denitrification System (Pre-denitrification)

Ludzack (1962) utilized the organic carbon in wastewater as an electron donor for biological denitrification. In a single reactor, anoxic, aerobic and settling zones were established by the use of baffles. Wastewater and recycled sludge, together with nitrified mixed liquor, were fed to the anoxic zone where up to 60% total nitrogen removal was achieved. The rate of nitrate removal increased as the mixed liquor recycle increased.

Barnard (1975b) was able to achieve up to 80% nitrogen removal by increasing the underflow sludge recycle or by mixed liquor recycle from the aerobic to the anoxic stage. The important influence of recycle ratio on denitrification efficiency is discussed further by Beer (1978) and Faup (1978).

Design considerations for "Ludzack" reactors are discussed by Beer (1978), Faup (1978), Marais (1975) and Christensen (1977a). In its most general form, the denitrifying reactor detention time is

determined by:

$$\text{Detention Time} = \frac{\text{Nitrate from Aerobic Reactor x Recycle Ratio}}{\text{Unit Denitrification Rate x MLSS}}$$

5.8.3 Bardenpho Process

The Bardenpho Process, which uses both wastewater and biomass as carbon sources for denitrification in separate parts of the operation, is discussed in Chapter 2.

Heide (1977) describes a process similar to the Bardenpho process in which nitrogen is removed by denitrification and phosphorus by lime addition. 93% COD and 85% total nitrogen removals were achieved at 10°C using a MLSS recycle of between 2 and 4 and a sludge recycle of 1:1 (based on incoming feed). The nominal system HRT was 40 hours.

Design procedures of relevance to the Bardenpho process are discussed by Barnard (1974), Beer (1978), Christensen (1977b) and Marais (1975).

5.8.4 Adsorption-Bio-oxidation (A.B.) Process

Besik (1977) describes a high-rate, single stage, activated sludge process capable of 90% soluble nitrogen removal. It utilizes a mixed liquor consisting of granular and powdered charcoal with both attached and freely suspended biomass, in a non-aerated reactor. Airlifts continually recycle mixed liquor from the reactor bottom to the top, where contact is made with incoming raw feed. Organics are adsorbed to the biomass and charcoal, then oxidized as the MLSS moves downward. The required oxygen is obtained in the airlift and from oxidized nitrogen. Processed wastewater is drawn from the base of the reactor into a clarifier where solids are separated and recycled to the reactor top after undergoing reaeration.

The system MLSS, including charcoal, ranged between 4.5 and 9.0 gm/L with loading rate and HRT ranging from 0.14 to 0.16 lb BOD/lb MLSS/day and 4 to 9 hours respectively. Recycle ratios varied from 3 to 5.

5.8.5 Alternating Contact Process

This process, as described by M.H. Christensen (1975), has been successfully tested in Denmark under both pilot plant and full-scale conditions up to 1.5 mgd (0.067 m^3/sec). Two reactors in series and a clarifier are utilized and operated in a sequence that alternates the tanks between aerobic and anoxic environments. Raw sewage, together with return sludge, is added to the anoxic tank, with the clarifier being fed from the aerobic tank, thus maintaining an anoxic-aerobic-settling flow sequence. For a short period between changeover, both tanks are operated aerobically. This alternating mode simulates a high degree of MLSS recirculation. The author's paper presents a detailed design model.

5.8.6 Alternating Anoxic-Aerobic System

Bishop (1976) describes this process at Blue Plains (Washington, D.C.) where a 150 m^3/day pilot plant was used. Two identical basins, provided with non-aerating mixers are operated in series with air being supplied alternately in thirty minute sequences. Feed is to the head of one basin while overflow from the other basin passes to a clarifier after a brief period of reaeration. Recycled sludge enters with the feed. No mixed liquor is recycled. Nitrogen removals of 84% were achieved under summer operating conditions.

5.8.7 "Bio-denitro" Process

Tholander (1977) and Bundgaard (1978) reported on a 21,000 cubic meter daily extended aeration plant used in Denmark. This denitrification

process consists of four complete mix ditches, the first being a preaeration unit with a 1.25 hour HRT; the other three being units with 5.5 hour HRT's and variable operating characteristics. Wastewater is fed without primary settling. The MLSS is about 4.1 gm/L and a SRT of 12 days is used.

The three ditches are operated in series with ability to alternate the flow directions and to maintain aerobic, anoxic or non-stirred conditions to achieve nitrification, carbon oxidation, denitrification or settling as required. Automatic DO control is practised. Simultaneous phosphorus precipitation is carried out using ferric chloride. Cycle time is about eight hours. Tholander (1977) reports 90% removal of nitrogen.

5.8.8 Oxidation Ditches

The oxidation ditch was developed by Pasveer (see Matsche 1977b) for BOD removal and subsequently modified to carry out denitrification (EPA 1975, Heide 1977). Variations of the system are known by several names: Pasveer ditch; Orbal, Carousel or Bio-denitro plants. Generally, all are characterized by continuous endless channels, high recycle rates and a long SRT. The major differences include the size and arrangement of ditches, the type, location and number of the aerators and of the mixing equipment.

As indicated by Matsche (1977a,b) denitrification in large carousel type plants is achieved by controlling the level of oxygen input at each aerator, thus allowing alternate aerobic and anoxic zones to develop between aerators. A series of simultaneous carbon oxidation, nitrification and denitrification reactions thus occurs along the reactor length, using initially raw sewage and latterly endogenous (cell tissue)

carbon sources for denitrification.

In operation, oxidation ditches usually have adequate MLSS and SRT levels to effect good cold weather denitrification. Beer (1978) suggests efficiency could be improved by step-feeding raw sewage along the reactor length, thus making better use of the carbon for denitrification.

As discussed by Beer (1978), V.d. Geest (1977) and Drews (1973), advantages of oxidation ditch systems include:

(i) Lower capital costs than both 2 and 3 sludge denitrification systems due to simplicity of construction;

(ii) Ability to bypass primary treatment or to include chemical precipitation.

(iii) Higher BOD and TKN removals than conventional extended aeration due to high MLSS recycle.

(iv) Low sludge yield and production of a stabilized sludge.

Similarly, disadvantages include:

(i) Difficulty in separating and controlling the mixing and aeration operations and thus difficulty in handling peak flows or variations in concentration;

(ii) A larger clarifier capacity is needed, due to the high MLSS;

(iii) Bulking and floating sludge can occur;

(iv) Inefficient use of raw sewage as a carbon source unless step feeding is used.

(v) Relatively low oxygen transfer efficiency and therefore higher power costs, and volume needs.

(vi) Total nitrogen removal efficiencies are lower than modified activated sludge processes.

CHAPTER 6

EXPERIMENTAL APPARATUS AND PROCEDURES

6.1 Model Design

The reactor model consisted of five rectangular tanks and a cylindrical clarifier arranged in the Modified Bardenpho Configuration (see Figure 2.2). Construction was of clear 0.25 inch perspex, with a maximum system volume of 50 litres. (See Table 6.1 for tank and clarifier dimensions.)

Flow was by gravity from tank #1 through to tank #5 and then to the clarifier. Each tank was fitted with a fixed baffle 2 cm from the discharge end and extending vertically from the surface to 12 cm from the tank floor. Discharge was through a single pipe in the end wall.

The clarifier consisted of a vertical cylinder with an inverted conical base. Inflow was downward through a narrow vertical central cylinder extending to the line of intersection of the cone and major cylinder. Effluent discharge was at the surface through a single 1 cm diameter discharge pipe in the outer wall. Sludge was removed through a single 0.5 cm outlet at the apex of the cone.

Tank #1 was fitted with a fixed cover, while tanks #2 and #4 were fitted with close fitting, floating polyurethane covers to minimize the transfer of atmospheric oxygen to the mixed liquor.

The mixing and aeration regimes are outlined in Table 6.1.

6.1.1 Aeration

Air injection into tanks #3 and #5 was via Fisher 12C Fritted Glass Air Filters, with the flow rate being manually controlled via a needle valve and pressure regulator linked into the building compressed air supply.

TABLE 6.1

MODEL DIMENSIONS

Basin	Basin Dimensions			Available Experimental Volumes (Litres)			Mixing Regime	Oxygen Status
	Length (cm)	Width (cm)	Height (cm)	Minimum		maximum		
#1	15.9	9.8	31.8	2.0	3.0	4.0	intermittent	Anaerobic
#2	32.1	9.8	31.8	4.0	6.0	8.0	continuous	Anoxic
#3	55.9	9.8	31.8	7.2	11.0	14.0	continuous	Aerobic
#4	55.9	9.8	31.8	7.0	10.5	14.0	intermittent	Anoxic
#5	24.1	9.8	31.8	3.0	4.5	6.0	intermittent	Aerobic

CLARIFIER DATA

Volume (litre)	Diameter		Surface Area (cm^2)	Hydraulic Residence Time (hours)	Upflow Rate (meters/day)
	(outside) (cm)	(inside) (cm)			
4.5	12.7	3.2	118.8	2.25	4.0

Note: Clarifier Residence Time and Upflow Rates are based on 2 litre per hour nominal flow.

6.1.2 Mixing:

Each tank was equipped with a Sargent-Welch cone-drive stirrer and a single stainless steel or plastic mixing propellor. Tanks #2 and #3 were stirred continuously, the others intermittently on a regular cycle. Air injection alone was unable to prevent settling in the aerobic tanks.

6.1.3 Pumping:

All pumping was via Cole-Parmer variable speed peristaltic pumps using Cole-Parmer silicone tubing, type 6411. The pump speeds were controlled by Cole-Parmer Masterflex Controllers.

6.1.4 Flow Control:

Pump ON:OFF cycles were controlled by Eagle Signal Flexopause Timers. Each timer activated two electrical circuits allowing the simultaneous operation of both a pump and a mixer.

6.1.5 Feed Pump:

This pump transferred raw sewage from the refrigerated feed storage tanks to #1 basin. Simultaneously with pump operation these storage tanks and #1 basin were stirred.

6.1.6 Mixed Liquor Recycle Pump:

Recycle took place from the bottom corner at the discharge end of basin #3 to basin #2.

6.1.7 Sludge Recycle:

Sludge was recycled from the clarifier to the #1 basin. Solely as a convenience, #5 basin was stirred only during the active phase of this pumping cycle.

In order to minimize surges, the pumps were generally run between 10 and 20 times per hour.

6.2 Batch Reactors

Batch tests were conducted in separate 12 litre perspex cylinders with magnetic stirrers. A floating cover was used in denitrification experiments. DO, temperature and pH were continuously monitored.

6.3 Feed

At two week intervals, fresh unsettled sewage was obtained from the Lulu Island treatment plant of the Greater Vancouver Regional District and stored in two stainless steel, 50 gallon drums at $3^{o}C$. The drum contents were stirred only during the time that feed was pumped to the model. This feed was passed through a 1/16 inch square mesh as it left the storage drums. On two occasions when BOD levels were below 80 mg/L the feed was spiked with synthetic sewage. Appendix 1 summarizes typical analyses for the raw sewage and for the synthetic sewage.

This particular source of sewage was chosen because:

(i) Relatively little industrial waste entered the sewage stream.

(ii) The sewerage system is separate from the stormwater system, and is relatively new.

(iii) Phosphorus and nitrogen concentrations were higher than in sewage from other available sources.

(iv) The mechanics of sewage collection were relatively simple.

6.4 Sampling and Sample Treatment

All samples were grab samples, taken from reactor basin overflow lines or from pump discharge outlets (feed and sludge recycle). Where required for the particular analysis, samples were immediately filtered through a Whatman #4 paper. Analysis was carried out within two hours,

otherwise samples were stored at 3°C. With the exception of heavy metal determinations, preservatives were not used. As a general rule analyses were made within eight hours, with all samples and reagents being at room temperature.

In order to minimize suspended solids interferences, all oxidized nitrogen determinations were made on samples filtered through a Whatman #4 paper, in order to eliminate problems associated with poor clarifier performance.

When large sample quantities were used, a significant proportion of the solids retained during filtering was returned to the reactor.

6.5 Analytical and Monitoring Techniques

6.5.1 Alkalinity:

The alkalinity was measured on unfiltered and unsettled samples, stirred magnetically, and with 0.02N sulphuric acid to an end point at pH 4.3. Results were reported as mg/L of $CaCO_3$. Preliminary investigation indicated a wide variation between filtered and unfiltered samples of both mixed liquor and recycled sludge probably because of biological activity. Such variation was not apparent with feed and effluent samples (Appendix 2).

6.5.2 pH:

All pH determinations were made using available glass electrodes (eg. VANLAB 34106-022) referenced to a saturated calomel electrode (Fisher Calomel Reference Electrode 13-639-51), with readings being made on a Fisher Accumet Model 210 pH meter. Calibration, before use, was made with buffer solutions of pH 7.0 and pH 4.0.

6.5.3 Dissolved Oxygen (DO)

DO was monitored with a Yellow Springs Instrument Company Model 54A meter and a submersible probe. The probe calibration was checked weekly by using a water sample of known DO as determined by the Azide modification of the Iodometric Method (APHA 1976).

6.5.4 Five Day Biochemical Oxygen Demand (BOD)

BOD was determined according to "Standard Methods" (APHA 1976). DO was determined using a BOD probe with an attached stirrer boot. Samples were unseeded with preliminary tests indicating seeding to be unnecessary. Nitrogenous oxygen demand was not suppressed.

6.5.5 Ammonia

Ammonia was determined using the "Preliminary Distillation Step" and "Acidimetric Titration" of Standard Methods (APHA 1976). No dechlorinating agent was used.

6.5.6 Total Kjeldahl Nitrogen (TKN)

The TKN (organic nitrogen plus ammonia) was determined using Standard Methods for digestion, and for acidimetric titration using boric acid (APHA 1976).

6.5.7 Nitrite (NO_2^-)

Nitrite was determined using a Technicon Auto Analyzer II according to the methodology of Technicon Industrial Method 100-70w. Samples were microfiltered through a 45 micron element, diluted to the <2 mg/L range and determined in duplicate with each pair separated by a distilled water blank.

6.5.8 Nitrate (NO_3^-)

Three methods were used for nitrate analysis:

(i) Specific Ion Electrode

(ii) Ultraviolet Spectrophotometry

(iii) Cadmium Reduction

(i) Specific Ion Electrode

An Orion Model 92-07 electrode was investigated with the idea of insitu monitoring of basin nitrate levels. Extensive initial experimentation with raw sewage and with mixed liquor (filtered and unfiltered) proved unsatisfactory because of a steady drift and the inability to obtain reproducible results, even with spiked and filtered samples. Use of the specific ion electrode was abandoned.

(ii) Ultraviolet Spectrophotometry

A Pye Unicam SP8-100 Ultraviolet Spectrophotometer was used according to Standard Methods (APHA 1976). After filtration through a 45 micron element, samples were analyzed as is, or when necessary, diluted to less than 3 mg/L. The only correction made was for dissolved organics.

(iii) Cadmium Reduction

The instrumentation and methodology are described in Section 6.5.7. The chemistry is outlined in Standard Methods (APHA 1976). Peak stability was enhanced by adding 10 drops of EDTA to the ammonium chloride solution which was neutralized to pH 7.0 by NaOH addition. The cadmium column reduces nitrate to nitrite and thus gives a total oxidized nitrogen result. Nitrate nitrogen was determined by difference between total and nitrite nitrogen.

A brief outline of problems associated with nitrogen analysis is included in Section 7.12.

6.5.9 Suspended Solids

Mixed Liquor Suspended Solids (MLSS), feed suspended solids and effluent suspended solids were determined as for "Total Nonfiltrable Residue" in Standard Methods (APHA 1976), while Mixed Liquor Volatile Suspended Solids (MLVSS) were determined as for "Total Volatile Residue".

6.5.10 Temperature

A mercury in glass thermometer and a thermocouple built into the DO probe (q.v.) were used to monitor temperature. The reactor was located in a temperature controlled room.

6.5.11 Flow Rates

Flow rates were determined using a graduated cylinder and stop-watch to determine the volume of liquid delivered per pumping cycle, and thus per unit time.

6.5.12 Light

As a general rule the reactor was operated in near darkness.

6.5.13 Solids Retention Time

The total system MLSS inventory was based on the MLSS Concentration in basin #3 (assumed to represent the average system value) and the known total volume of tankage, ignoring the clarifier. Corroborative test work indicated that up to ±15% variation normally occurred between basins.

Daily solids wastage consisted of the effluent suspended solids plus an extra averaged volume to account for spillage, sampling, deliberate wastage, losses to scum and any sludge returned to the system after analysis. Because only the effluent solids were actively monitored, the reported SRT's for the system are best estimates.

6.6 Modified Bardenpho Model Operation

The model was operated at four temperatures (18, 14, 10 and 6°C) over a 15 month period, which included a four month phase necessary to establish an adequate SRT to allow the development of a nitrifying sludge (Table 6.2).

Hydraulic data including sludge and liquid retention times, feed and recycle rates are summarized in Table 6.3. The SRT was not actively controlled at a specific value, except as necessary to ensure an adequate level for nitrification and denitrification. The reported SRT values are estimates only (Section 6.5.13).

A comprehensive monitoring, sampling and analysis programme (Table 6.4) allowed overall system performance, nitrification and denitrification rates to be determined. Removal efficiencies were determined by comparing unfiltered feed with filtered effluent because of the variable clarifier efficiency. Nitrification and denitrification rates were determined by calculation using a "nitrate" (total oxidized nitrogen) balance in the relevant basin over a finite time interval:

$$[6.1] \quad \text{Rate (mg'N'/gm MLSS/hr)} = \frac{\text{Nitrate In - Nitrate Out}}{\text{Basin Volume x Basin MLSS}} \quad \left(\frac{mg.hr^{-1}}{L.gm.L^{-1}}\right)$$

For the purposes of these calculations, and also those for batch rate determinations, nitrite concentrations were assumed constant and thus acted as neither a sink for, nor a source of oxidized nitrogen.

Dissolved oxygen levels in basins #3 and #5 were maintained at between 1.5 and 4 mg/L except during periods of process failure or adjustment. In basins #1, #2 and #4 the DO was less than 0.2 mg/L, except during unexpected process upsets. To maintain an adequate pH buffering capacity in the system, the feed storage drum was spiked with

TABLE 6.2

CHRONOLOGY OF MODEL TEMPERATURE REGIMES

Run	^{o}C	Phase End	Elapsed Time (Days)	Remarks
181 A[t]	18	Sept. 12, 1977	120	Start up
181 B	18	Dec. 1	80	Stabilization of N removal
181 C	18	Feb. 3	60	Steady State
141 A	14	March 24*	49	Stable 14°C run
141 B	14	April 20	27	Partial recovery after overheating
141 C	14	May 22	30	Nitrification returning
101 A	10	June 16	25	System still recovering
182 A	18	July 14	25	Second 18°C Run (Recovery Completed)
142 A	14	July 24	9	Second 14°C Run - non steady-state
061 A	6	Aug. 10, 1978	18	6°C Run

Notes:

[t] The letters A, B, C divide each run into significant phases

* On March 24, much of the biomass was apparently destroyed when the reactor liquid temperature was accidently raised to 60°C for three hours.

TABLE 6.3

MODEL HYDRAULIC DATA AND ESTIMATED SLUDGE AGE

Run	Days	Flow Rates (L/hr)			Hours Days	Model Reaction Basin (Fig. 2.2)						
		Feed	MLSS Recycle	Sludge Recycle		System	1	2	3	4	5	CLA
181A	100	1-2	6-12	1-3	HRT	20-30	2-3	4-6	5-8	5-8	3-4	N.D.
					SRT	Highly Variable						
181B	140	1.5	6.5	2.1	HRT	23	3	4	7	7	3	3
					SRT	15-60	2-7	3-10	5-18	5-18	2-8	N.D.
181C					HRT	24	3	5	7	7	3	3
					SRT	50-70	2-7	4-14	6-19	6-18	5-8	N.D.
182A	0-11	1.7	6.7	2.2	HRT	24	2	5	8	6	3	2
					SRT	38	4	7	12	12	4	N.D.
	11-25	2.0	11.7	2.2	HRT	18-22	2	4	6-7	5-7	1	2
					SRT	37	4	7	11	11	4	N.D.
141A B	0-98	1.7	6.2	2.7	HRT	23	2	5	7	6	3	2
					SRT	18-68	2-7	4-15	5-20	5-19	2-8	N.D.
C	98-108				HRT	25	2	5	9	6	3	2
					SRT	29	3	6	10	8	3	N.D.
142A	0-5	2.0 1.7	11.4	3.2	HRT	18-23	2	3-5	5-7	5-6	2-3	2
					SRT	47	5	10	14	13	6	N.D.
	5-8	1.7	9.5	2.3	HRT	24	2	5	7	6-8	3	2
					SRT	73	7	14	19	25	8	N.D.
101A	0-10	1.7	7.3	2.3	HRT	25	2	5	8	6	3	2
					SRT	33	3	6	11	8	4	N.D.
	0-25				HRT	25	2	5	8	6	3	2
					SRT	40	4	8	13	11	4	N.D.
061A	0-13	1.0	5.7	1.1	HRT	46	4	8	15	15	5	4
					SRT	98	9	18	31	31	10	N.D.
	13-18	1.9	10.7	3.4	HRT	24	2	4	7	7	2	2
					SRT	64	5	10	18	18	6	N.D.

Notes: CLA: Clarifier N.D.: Not Determined

HRT: Nominal Hydraulic Retention Time (Based on feed only)

$$\text{Actual HRT} = \text{Nominal HRT} \times \frac{\text{Feed [L/hr]}}{\text{Feed + Sludge (+ MLSS)}}$$

SRT: Solids Retention Time (days) - estimate only

TABLE 6.4

FREQUENCY OF ANALYSIS

PARAMETER	FREQUENCY (Times Weekly)	SAMPLING POINTS
Alkalinity	1 - 3	most
pH	1 - 3	most
Oxygen		
BOD	1	feed, effluent
BOD	irregular	all
DO	3 - 4	most
COD	infrequent	feed
Suspended Solids		
MLSS	2 - 3	#3, effluent
MLSS	irregular	all
MLVSS	infrequent	most
Nitrogen		
TKN	1 - 2	feed, effluent
TKN	variable	all
Ammonia	infrequent	most
Nitrate	1 - 3	all
Nitrite	variable	most
Phosphorus		
Total	1	feed, effluent
Soluble	1	most
Temperature	continuous	air temperature
Flow Rates	1 - 2	all pumps

Note: Total available sampling points were:
feed, 5 reaction basins, effluent, sludge return.

sodium carbonate when the effluent alkalinity fell below 70 mg/L.

BOD levels in the feed were maintained at 150 mg/L or over by stirring the feed drums to increase the feed suspended solids, or in other instances by spiking the storage drums with an artificial sewage (Appendix 1).

For this work, the MLSS level in #3 basin was used to represent the average system MLSS.

6.7 Batch Tests

Batch nitrification and denitrification tests were made on 6 to 9 litres of mixed liquor to verify the results of flow-through mass balance calculations, and to ascertain the extent, if any, of unused capacity or of substrate deficiency. Spikes of KNO_3 were made to the batches from #2 and #4 basins, raising the nitrate level to between 15 and 30 mg/L of N. Small amounts of raw sewage were added to #2 aliquots, to provide sufficient external carbon source during denitrification. No sewage was added to #4. The TKN level in #3 (nitrification) was raised by spiking with ammonium chloride. In several instances, the #3 alkalinity was raised by spiking with sodium carbonate.

Usually between 15 and 30 minutes after the mixed liquor transfer to the batch reactor, a zero time sample was withdrawn for analysis, followed by further samples at regular intervals. Batch reactors were monitored for between one and eight hours.

In all cases the pH and alkalinity were determined at zero time and at the end of a run. Nitrate levels were determined at measured time intervals. MLSS was determined in triplicate at completion. During batch testing of the contents of #3 basin, one or both of TKN and ammonia were determined at the start and finish of each run.

The total oxidized nitrogen (nitrate + nitrite) was plotted against time; by the method of least squares, the line of best fit was determined, as was the relevant average nitrification or denitrification rate (Figure 6.1). Because of the random variation in rates during most batch tests, a maximum rate was also determined by using that pair of adjacent data points with the greatest variation in concentration per unit time. For this purpose, data from the first hour was not used, due to its widely scattered nature.

As can be seen from Figure 6.1 the slope of the NO_3-N removal line is greater than that of the total oxidized nitrogen line due to the build up of nitrite. In this instance, and in all other instances where both nitrate and nitrite analyses were available, it was apparent that the use of nitrate data alone would give a greater denitrification rate than use of nitrate plus nitrite data. Because the purpose of denitrification is the total removal of oxidized nitrogen, the rates reported are those for nitrate plus nitrite. In the case of nitrification, the nitrite plus nitrate line is steeper than that for nitrate alone. In this instance, the steeper line was used because the subsequent denitrification process does not require the nitrogen to be totally oxidized to nitrate.

Where total oxidized nitrogen data were available from both spectrophotometric and cadmium reduction analyses, the calculated rates varied by up to 15% depending on the source of nitrogen data used for calculation. In denitrification work, the spectrophotometrically determined concentration decreased more rapidly and thus the rate reported would be higher (Figure 6.1). The converse applied in nitrification work. These observations were not unexpected because the autoanalyzer reduces all nitrate to nitrite and reports the total NO_2+NO_3 as N, whereas the spectrophotometer

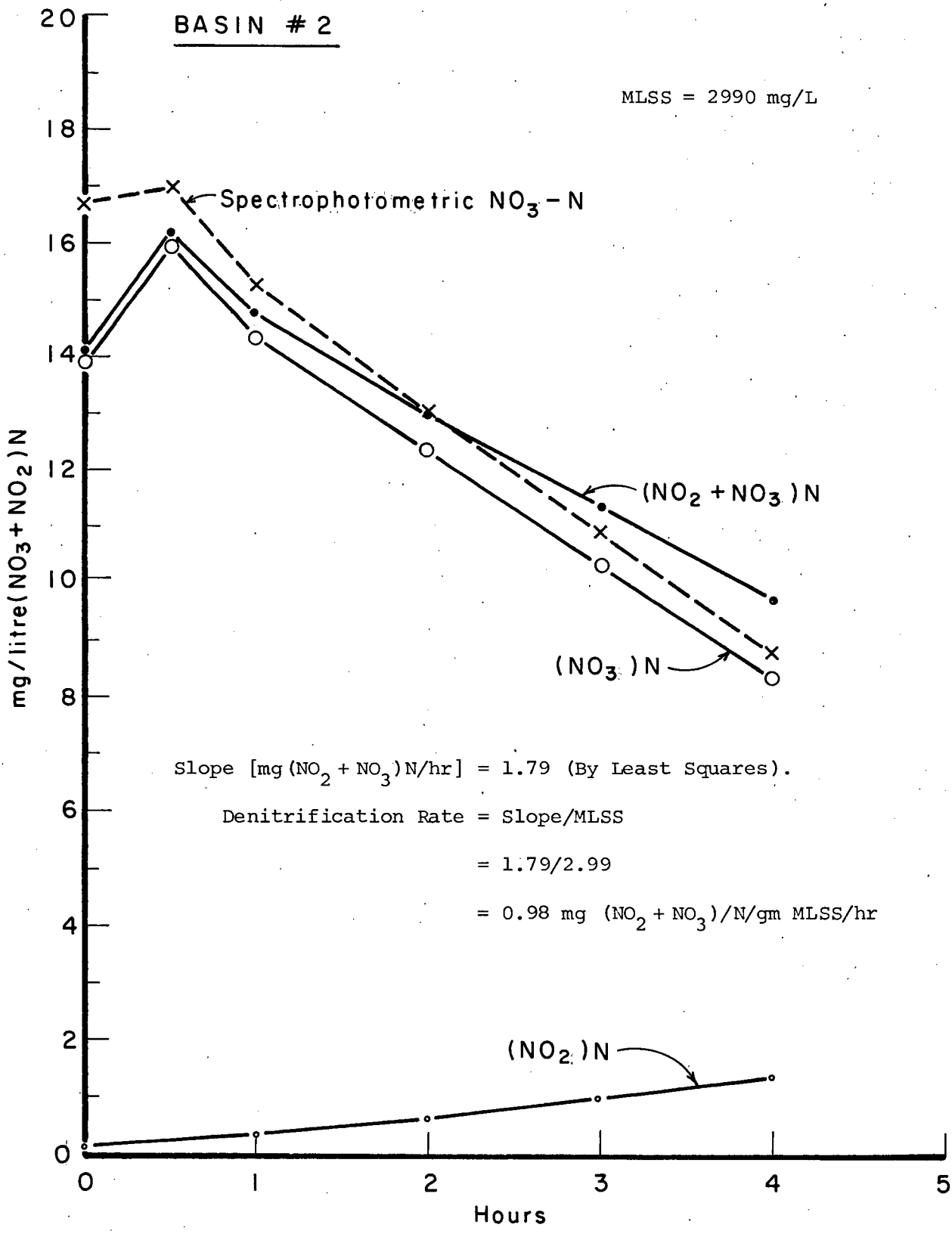


FIG.6.1 BATCH DENITRIFICATION, BASIN #2 AT 18°C.

analyzes for nitrate only, with nitrite being discounted as only an additive interference.

When available, total oxidized nitrogen values reported are those determined by cadium reduction, unless otherwise indicated.

CHAPTER 7

RESULTS AND DISCUSSION

7.1 Startup Operations (Phase 181A):

Initial operation began at room temperature, using raw sewage without recycle, until wall growth was apparent. The temperature was then lowered to 18^{o}C and recycle of "sludge" and "MLSS" initiated. The reactor walls and tubing were brushed to aid in the initial MLSS buildup.

Approximately twelve weeks were needed to achieve an MLSS concentration above 500 mg/L. Shortly after the installation of an improved clarifier (Day 100, Figure 7.1) the MLSS reached 1000 mg/L. With stable MLSS concentrations, good DO control became possible and the basins could be maintained anoxic or aerobic as required. BOD removal reached 90% within six weeks of startup. After ninety days, TKN conversion approached 50%, indicating an initiation of nitrifier buildup. A further two months elapsed before 90% conversion and a 2 mg/L TKN concentration in the process effluent was obtained (Figure 7.1).

7.2 Overall System Performance

Table 6.2 summarizes the feed and recycle rates, hydraulic and estimated solids retention times used in all runs and tests. The percentage removals of BOD, TKN and total Nitrogen, together with the effluent quality are presented in Table 7.1.

7.2.1 Phosphorus Removal:

While the overall average phosphorus removal never exceeded 89%, at each temperature stable operating periods averaging 93% removal were obtained.

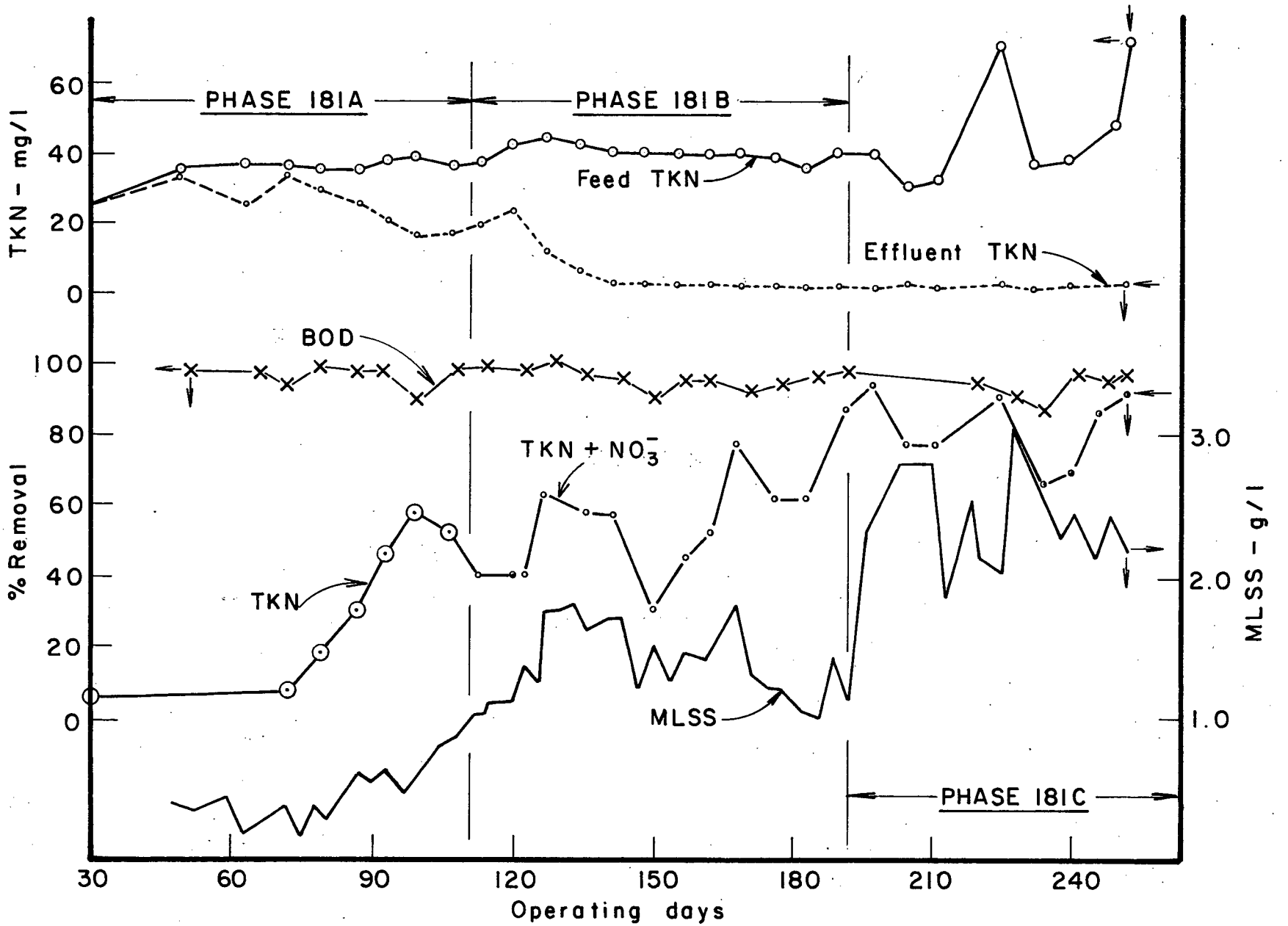


FIG.7.1 SYSTEM PERFORMANCE DURING STARTUP AND OPERATION AT 18°C.

TABLE 7.1

OVERALL SYSTEM PERFORMANCE

Run *	System Removal Percentages						System Effluent Quality (mg/L)					
	Total N		TKN		BOD		NO_3		TKN		SS	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
181B	55	31-87	84	46-96	96	92-99	9.7	2.0-25.8	7.0	1.7-22.8	50	21-260
181C	81	65-95	95	93-98	94	87-97	5.5	0.4-10.5	2.1	1.5-2.5	54	23-102
182A	92	83-94	96	95-97	95	84-99	2.6	1.0-6.8	1.7	1.4-2.2	49	28-80
141A	87	79-93	93	83-96	91	83-97	2.3	1.2-4.8	3.3	1.6-7.7	78	22-110
141B	No Data Available						No Data Available					
141C	67	62-72	70	65-73	91	87-95	1.5	0.2-1.5	13.9	12-16	101	69-142
142A	83	82-86	95	91-96	99	99	4.7	3.8-5.9	2.4	1.7-3.6	39	25-54
101A	50	48-54	53	52-56	93	85-97	1.4	0.8-2.8	23	22-24	81	50-110
061A	70	61-79	80	64-87	91	91	3.9	1.0-7.8	7.9	4.4-14	40	18-72

* See Table 6.2 for explanation.

7.2.2 BOD Removal:

At all temperatures, the BOD removal averaged over 91% and no individual value less than 83% was recorded. Under the "extended aeration" conditions of the model, high removals would be expected. Lower values recorded are most likely due to the exertion of a nitrogenous oxygen demand in the effluent, as nitrification inhibition was not practised in the BOD tests.

7.2.3 Suspended Solids Removal:

From Table 7.1, it is apparent that the clarifier was not capable of producing an effluent of generally acceptable suspended solids quality. Several factors are suggested as major causes:

(i) Scale (size) effects

(ii) Carry over of the "scum" present on all tanks (Section 7.11).

(iii) Dispersion of bioflocs by aeration and stirring in the final aeration basin (Tank #5).

(iv) Denitrification in the clarifier causing floating sludge.

No relationship between the system MLSS and the effluent suspended solids was apparent.

7.2.4 Volatile Suspended Solids:

MLVSS was determined as 80% of MLSS. This factor is used to compare rate data from this work (based on MLSS) with other data based on MLVSS (eg. Figures 5.1 and 5.2).

7.2.5 Heavy Metals:

A comprehensive analysis, spanning three months is attached as Appendix 3.

Nickel ranged from 0.04 to 0.39 mg/L in the feed and was determined at 1.4 mg/L in the MLSS. Chromium in the feed was 0.1 to 0.71 mg/L and 3.8 in the MLSS.

7.2.6 Nitrite Concentrations

While nitrite concentrations were not monitored regularly, concentrations of between 1 and 3 mg/L were observed during several batch tests. During periods of poor overall nitrification performance, nitrite concentrations in basins #3 and #5 sometimes approached the nitrate levels.

7.3 Nitrogen Removal (Table 7.1)

7.3.1 18°C At 18°C, up to 98% TKN conversion and 95% total nitrogen removal was achieved.

Run 181B (Figure 7.1)

This designation coincided with the period during which complete TKN conversion and nitrogen removal was being established. As a consequence, relatively low average TKN removals (84%) and total nitrogen removals (55%) are reported (Table 7.1).

Run 181C (Figure 7.1)

Arbitrarily begun when both nitrification and denitrification were satisfactorily established, this run exceeded 93% TKN conversion throughout. Total nitrogen removal averaged 81%, reaching a 95% maximum. Several periods with relatively high nitrate concentrations in the effluent were responsible for lowering the overall nitrogen removal. These periods corresponded with low system feed BOD values (less than 90 mg/L).

Run 182A (Table 7.1)

During this repeat run at 18°C, TKN oxidation and total nitrogen removals equal to or better than performance during 181C were achieved. Periods of low system performance again coincided with low feed BOD levels (less than 100 mg/L).

7.3.2 14°C At 14°C, TKN oxidation up to 96% and total nitrogen removals up to 94% were achieved.

Run 141A (Figure 7.2)

During this run, which coincided with the period prior to failure of the system (as a result of catastrophic overheating), total nitrogen removal averaged 87% and TKN conversion was 93%. Several short periods of poor performance, which lowered the averages, resulted from mechanical failures in the reactor pumping and feeding systems.

Run 141B (Figure 7.2)

Minimal data was collected during this run which was the period immediately after system failure, in which nitrification did not occur.

Run 141C (Figure 7.2)

This run began when some nitrification ability had apparently returned to the system. The overall performance was poor, mostly due to the slow and incomplete restoration of nitrification. TKN concentrations in the effluent remained in excess of 12 mg/L. Nitrate levels remained low, indicating that the denitrifying ability was at least equal to the nitrification capacity. This run was terminated before a satisfactorily nitrifying sludge had redeveloped in the system.

Run 142A (Figure 7.3)

During this run, a short bridging period between operations at 18°C and at 6°C, a steady state condition was not achieved. However TKN conversions up to 96% and total nitrogen removals up to 86% were obtained; values comparable to the best obtained during run 141A.

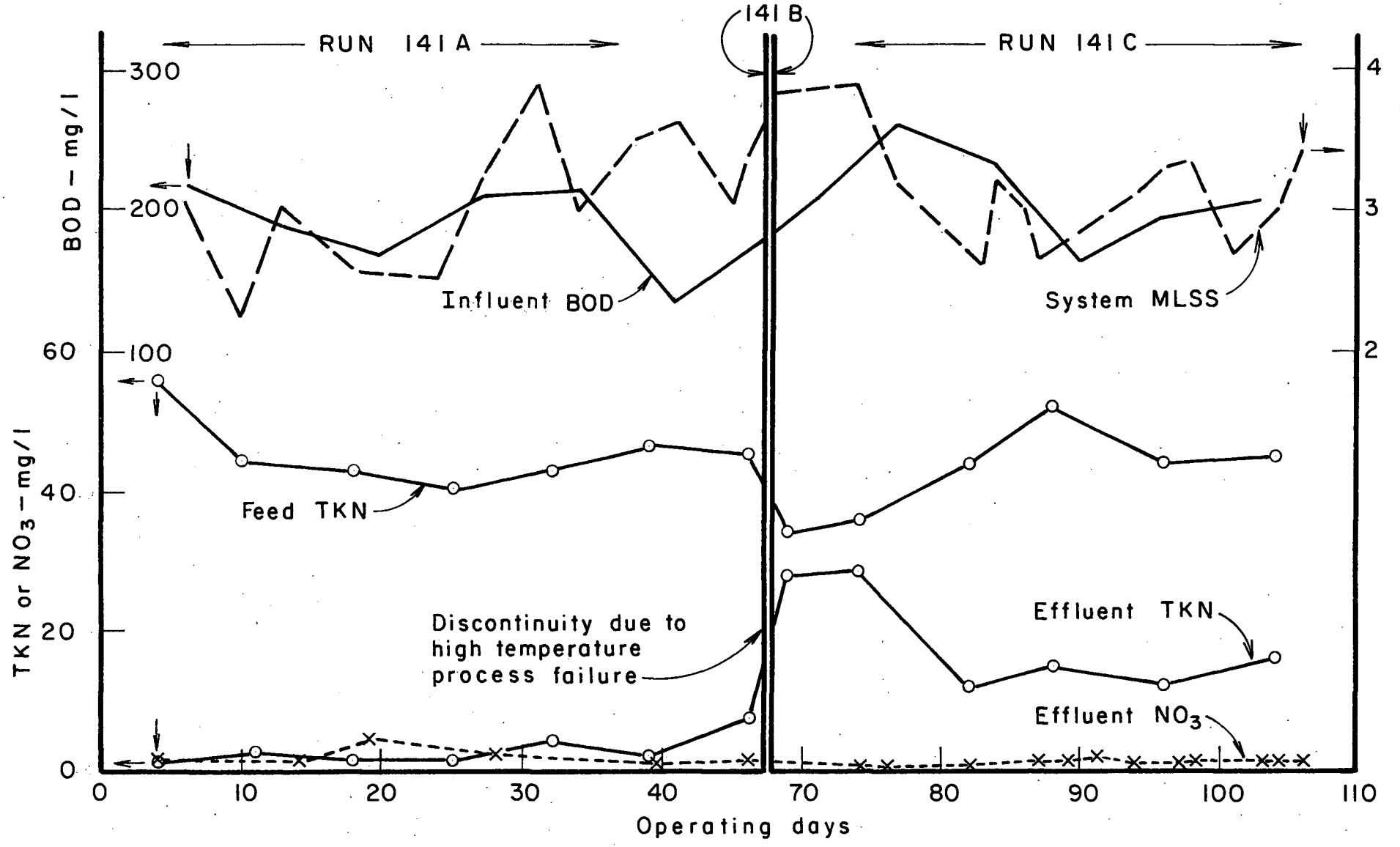


FIG.7.2 OVERALL SYSTEM PERFORMANCE AT 14°C (RUNS 141 A, B AND C).

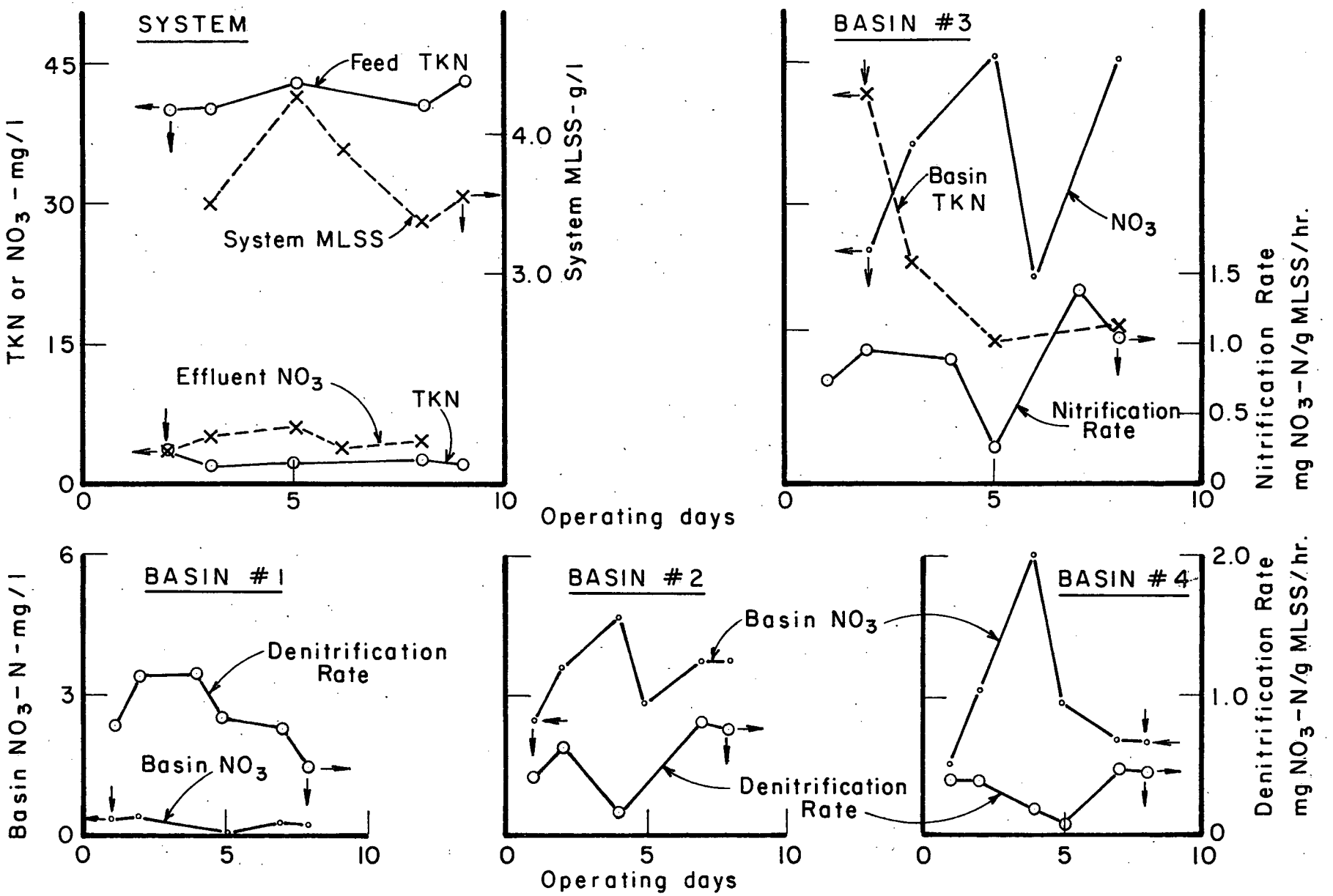


FIG.7.3 SYSTEM AND BASIN PERFORMANCE AT 14°C (RUN 142).

7.3.3 10°C (Figure 7.4)

At 10°C, TKN conversions up to 56% and total nitrogen removals up to 54% were achieved. Overall, at this temperature, performance was steady but poor, principally as a result of an unsatisfactory nitrifying ability (apparently a legacy of its incomplete restoration during the immediately preceding run, 141C). However, as was the case during 141C, the denitrification ability was sufficient to maintain low effluent nitrate levels.

7.3.4 6°C (Figure 7.5)

At 6°C, TKN conversion reached 87% and total nitrogen removal reached 79%. Effluent nitrate levels were initially high, as a result of relatively poor removal during the late stages of run 142A. However, the concentration fell with time at 6°C, due to the deteriorating nitrification ability of the system relative to denitrification. From Figure 7.5, it appears probable that the nitrification capability was steadily failing and that the run was terminated before this trend could be verified. As a consequence, the reported average efficiencies are probably somewhat high. Nonetheless, the data indicates that good nitrogen removal can be maintained for a significant period of time at such a reduced mixed liquor temperature.

7.4 Nitrification and Denitrification Rates

7.4.1 Batch nitrification tests:

Nitrification rates in basin #3 as determined from batch tests are summarized in Table 7.2. The variation of these rates with temperature is shown in Figure 7.6.

7.4.2 Nitrification rates calculated from a system flow-through mass balance:

Table 7.3 summarizes the calculated nitrification rates using basin #3, while the variation with temperature is shown in Figure 7.7.

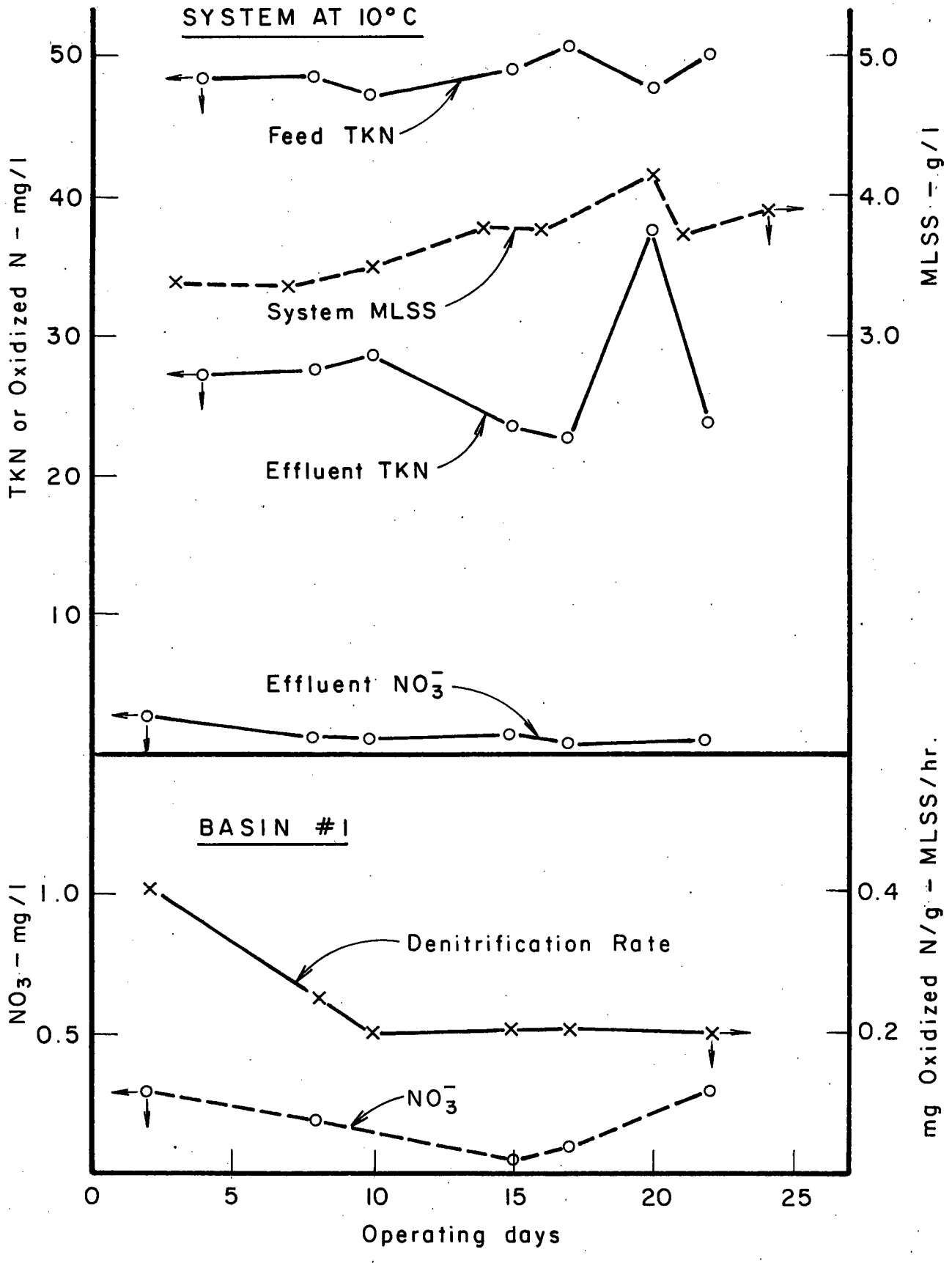


FIG.7.4 SYSTEM PERFORMANCE AND #1 BASIN DATA AT 10°C.

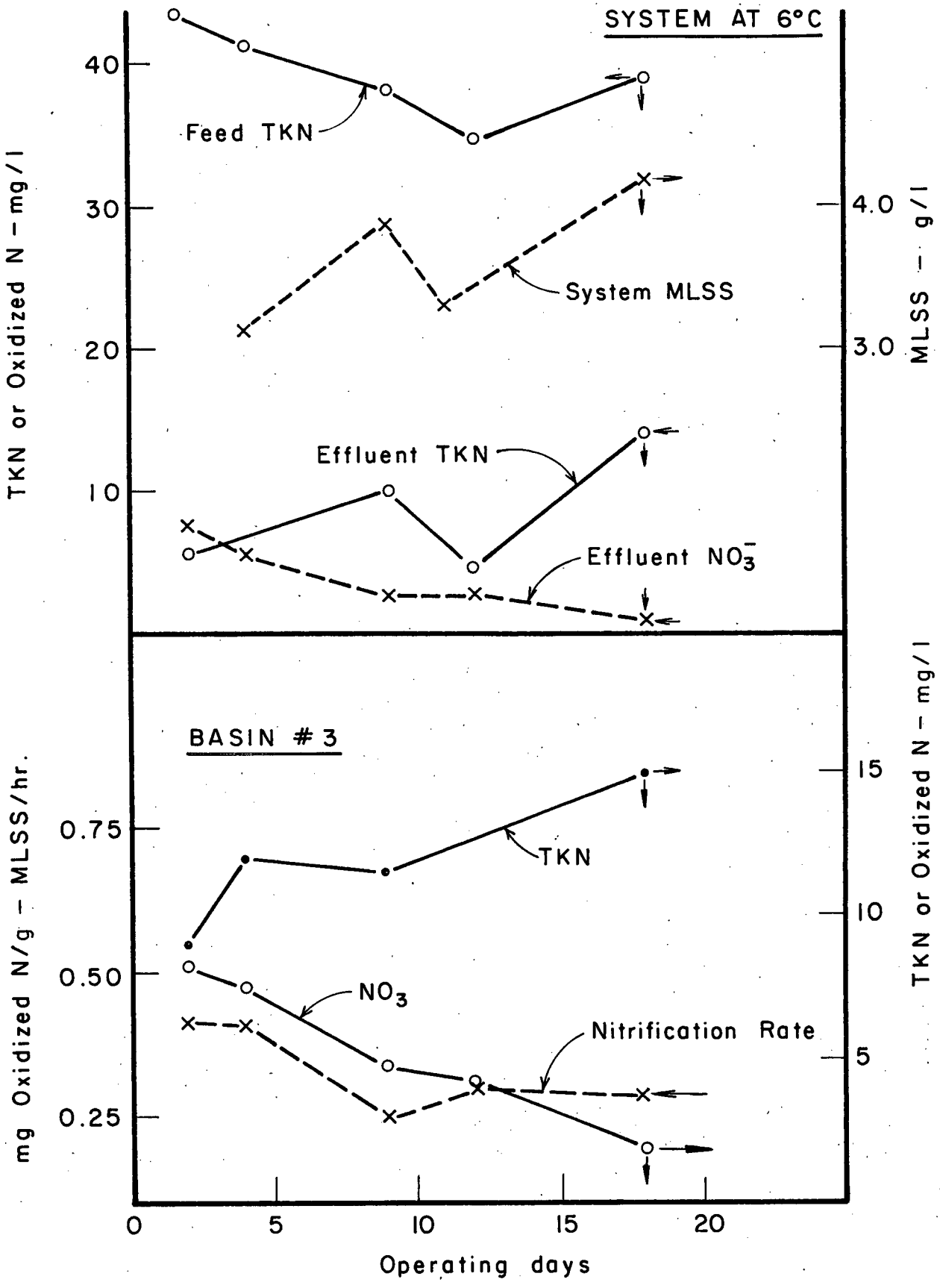


FIG.7.5 SYSTEM PERFORMANCE AND #3 BASIN DATA AT 6°C.

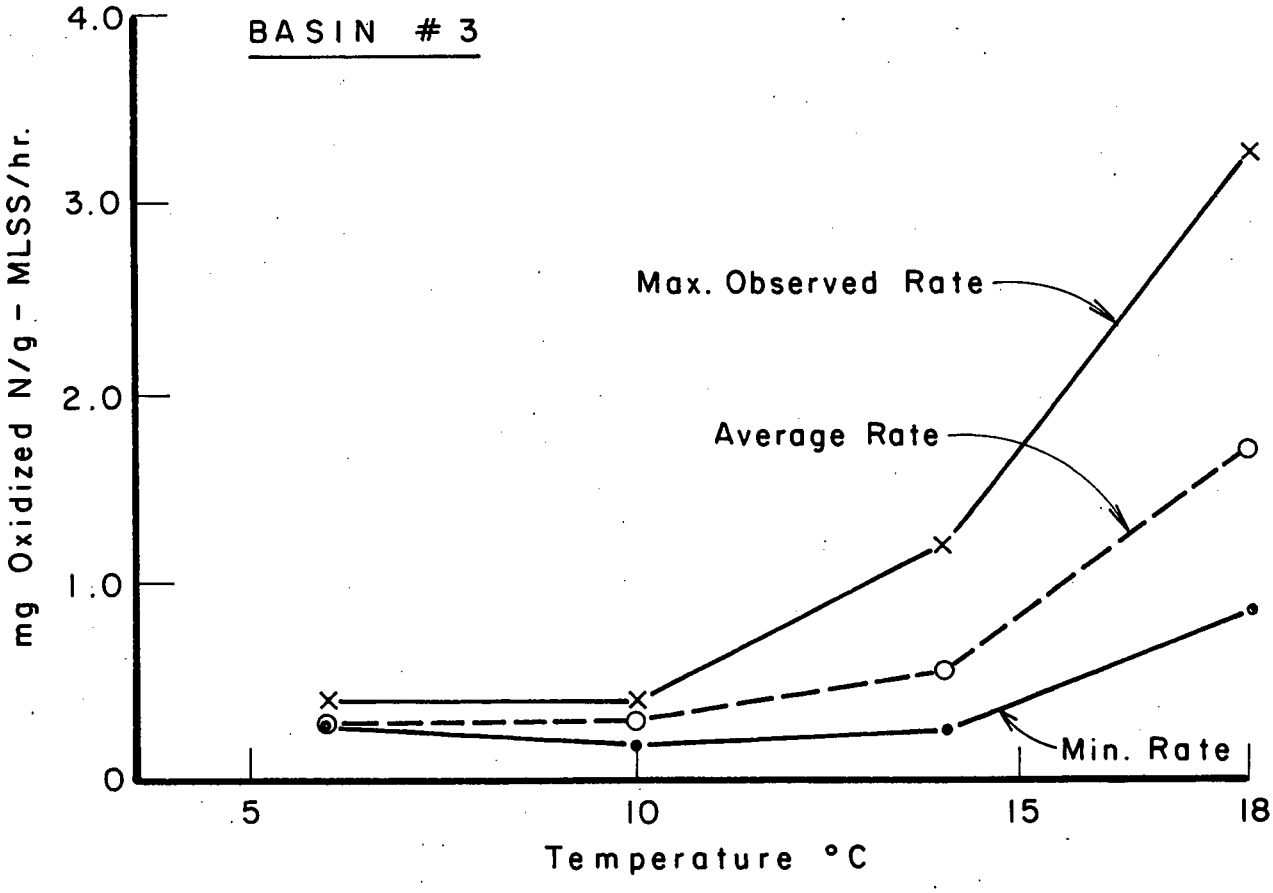


FIG.7.6 BATCH NITRIFICATION RATES IN BASIN # 3.

TABLE 7.2

BATCH NITRIFICATION RATES IN #3 BASIN

Run	Day	Temp °C	MLSS	TKN (sol)	BOD Feed	Nitrification Rate mg (NO_3 + NO_2 - N) /hr/gm MLSS		pH Range	Δ Alkalinity / TKN
			mg/L			maximum[t]	average		
181	220	18	2410	14.9	150	3.3*	3.3*	7.0-6.8	ND
182	6	18	3500	18.2[+]	140	1.33	.87/.8*	6.6-5.6	6.67
182	16	18	4020	27.2[+]	290	147	1.03	[o]8.9-7.1	7.63
141	98	14	3370	47.6	200	0.30*	0.23*	7.1-7.0	ND
141	106	14	3470	25.2	200	.44/.36*	.42/.32*	7.2-6.8	ND
142	9	14	3540	19.3[+]	160	1.21	1.08	[o]8.6-7.1	8.08
101	10	10	3290	44.3	180	.38/.19*	.38/.19*	7.2-7.1	ND
101	20	10	4160	41.2	240	0.2	0.2	7.2-7.0	ND
061	9	6	3870	25.0[+]	140	0.29	0.29	7.3-7.0	7.43

[+] Ammonia only

[*] Spectrophotometric nitrate analysis

[Δ] Ratio of Alkalinity consumed to Nitrate produced

[t] The maximum observed rate between two sampling times

[ND] Not Determined

[o] Initial alkalinity spike made

TABLE 7.3

NITRIFICATION RATE BY FLOW THROUGH MASS BALANCE CALCULATIONS IN BASIN #3

[mg(NO_2+ NO_3) -N/hour/gram MLSS]

Run	Temperature	Mean	Low	High	Number of Observations
181A	18°C	No Nitrification			-
181B*	18°C	4.9	0.72	14.5	10
181C	18°C	1.26	0.75	1.76	9
182A	18°C	1.04	0.52	1.50	13
18° Average		1.15	0.52	1.76	22
141A	14°C	0.57	0.40	0.86	6
141B	14°C	No Nitrification			-
141C*	14°C	0.34	0.22	0.46	11
142A	14°C	0.96	0.73	1.44	8
14° Average		0.79	0.40	1.44	14
101A	10°C	0.17	0.13	0.26	6
061A	6°C	0.33	0.25	0.42	5

* Not included in mean due to unstable operating conditions.

7.4.3 Denitrification rates calculated from a system flow-through mass balance:

In Table 7.4 the calculated denitrification rates for basin #1, #2 and #4 are summarized. The data for basin #1 have mostly been estimated by using average values for nitrate concentrations in the raw sewage and #1 basin overflow (which were generally very low) when actual nitrate analyses were unavailable. Because a good correlation was found between the nitrate concentration in the system effluent and in the recycled sludge, the former was used to give a conservative estimate of the nitrate returning to basin #1 when no actual return sludge data was available. Figures 7.8 and 7.9 illustrate the variation in denitrification rates with temperature.

7.4.4 Batch Denitrification Tests:

Table 7.5 summarizes the denitrification rates calculated from batch tests for basins #2 and #4. In Figure 7.10, the variation in denitrification rates with temperature is shown.

7.4.5 Example Batch Rate Calculation

Figure 6.1 shows a typical variation of nitrite and nitrate concentration with time, as observed in a batch denitrification test. The accompanying calculation illustrates the way in which the batch rates were calculated.

7.4.6 Individual Basin Operating Data

As summarized in Sections 7.4.2 and 7.4.3, the nitrate levels were frequently monitored in most basins and from this data, plus a knowledge of basin HRT and MLSS, a mass balance was carried out and individual nitrification or denitrification rates were calculated. Some of this monitoring data is summarized in Figures 7.3, 7.4, 7.5 and

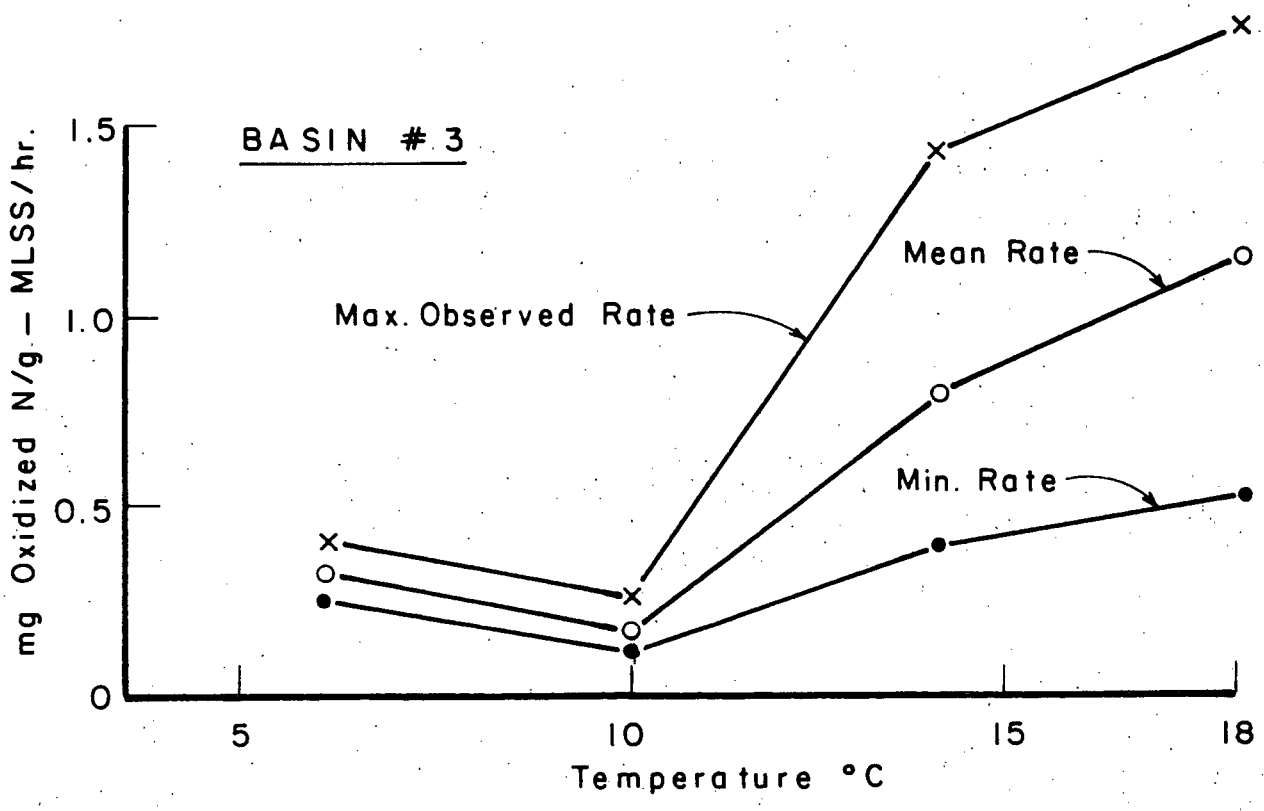


FIG.7.7 CALCULATED NITRIFICATION RATE IN #3 BASIN. (FLOW-THROUGH BASIS)

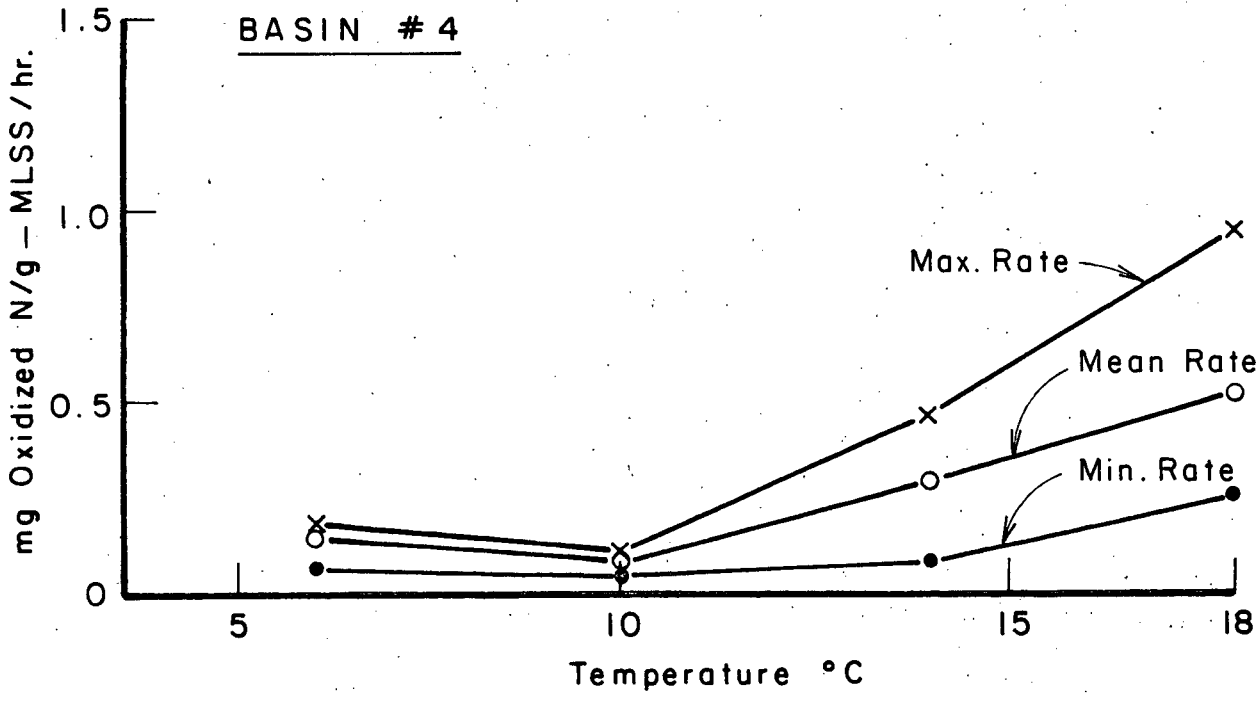
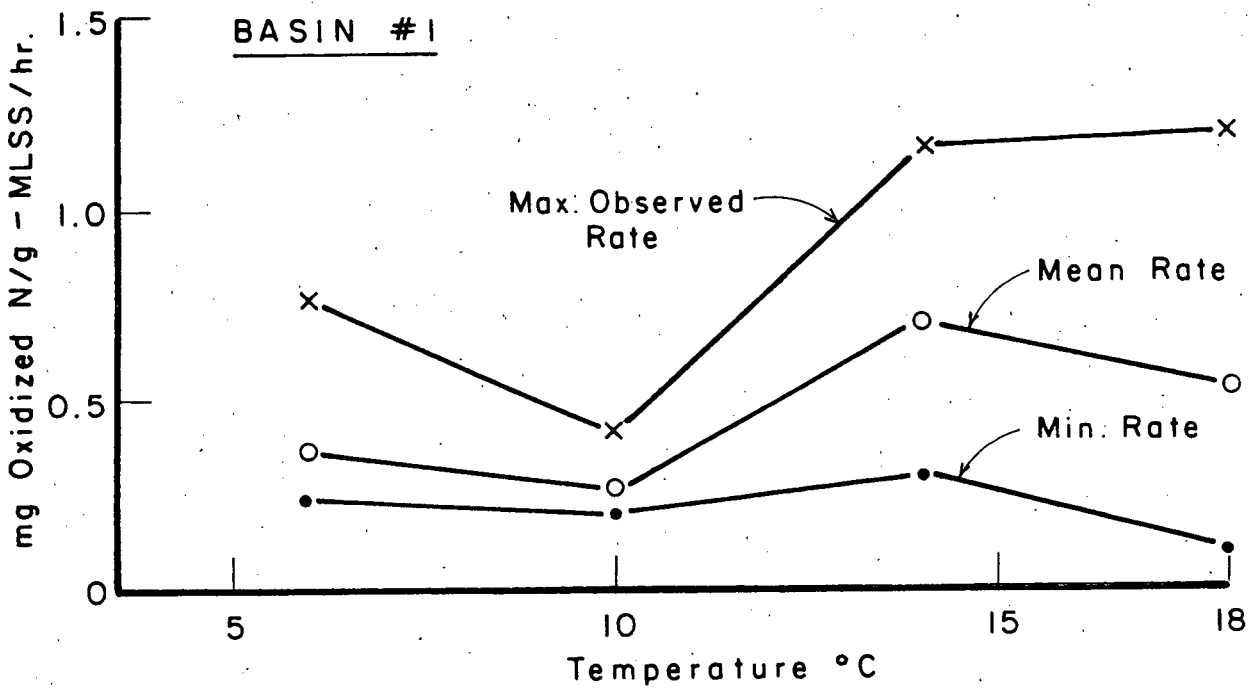


FIG.7.8 CALCULATED DENITRIFICATION RATE IN #4 BASIN.



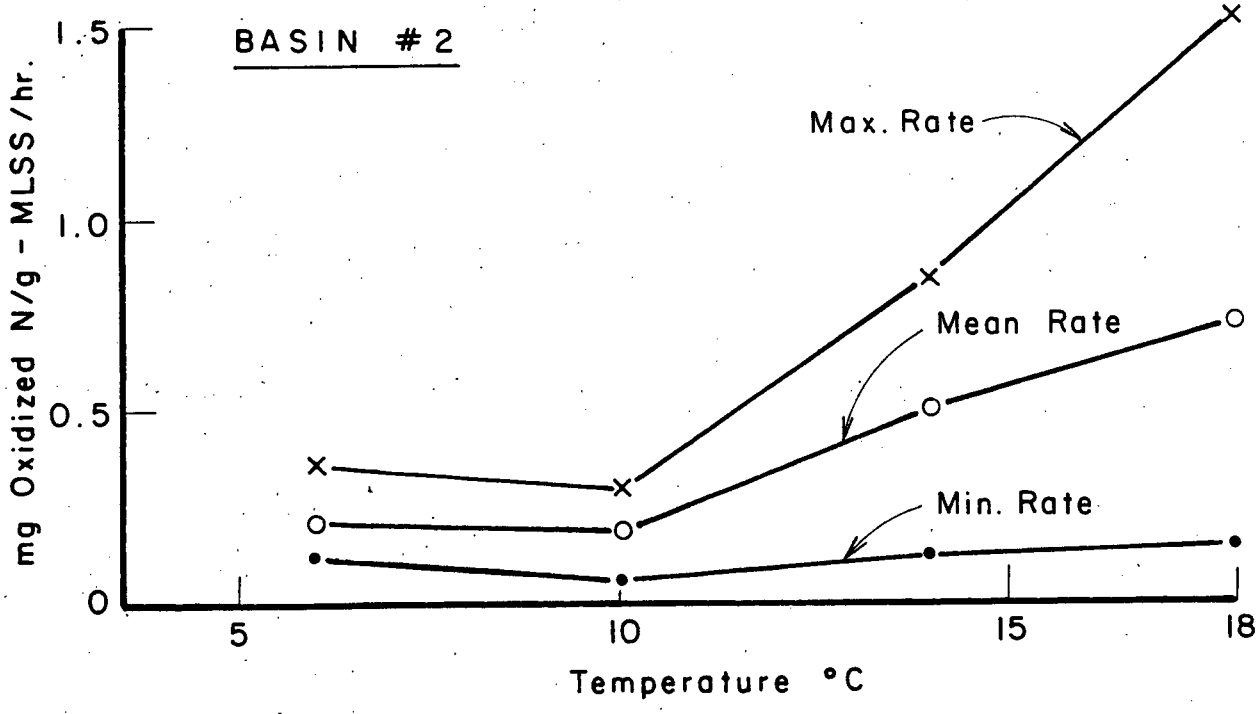
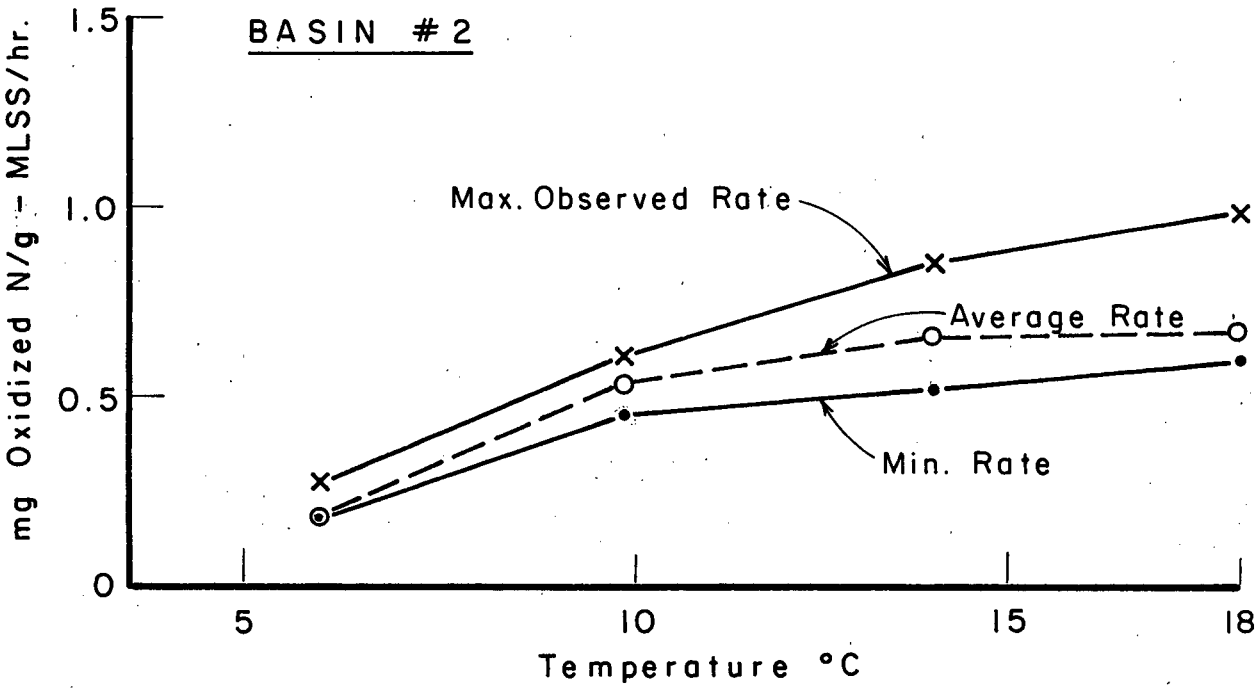


FIG.7.9 CALCULATED DENITRIFICATION RATES
BASIN #1 AND #2.



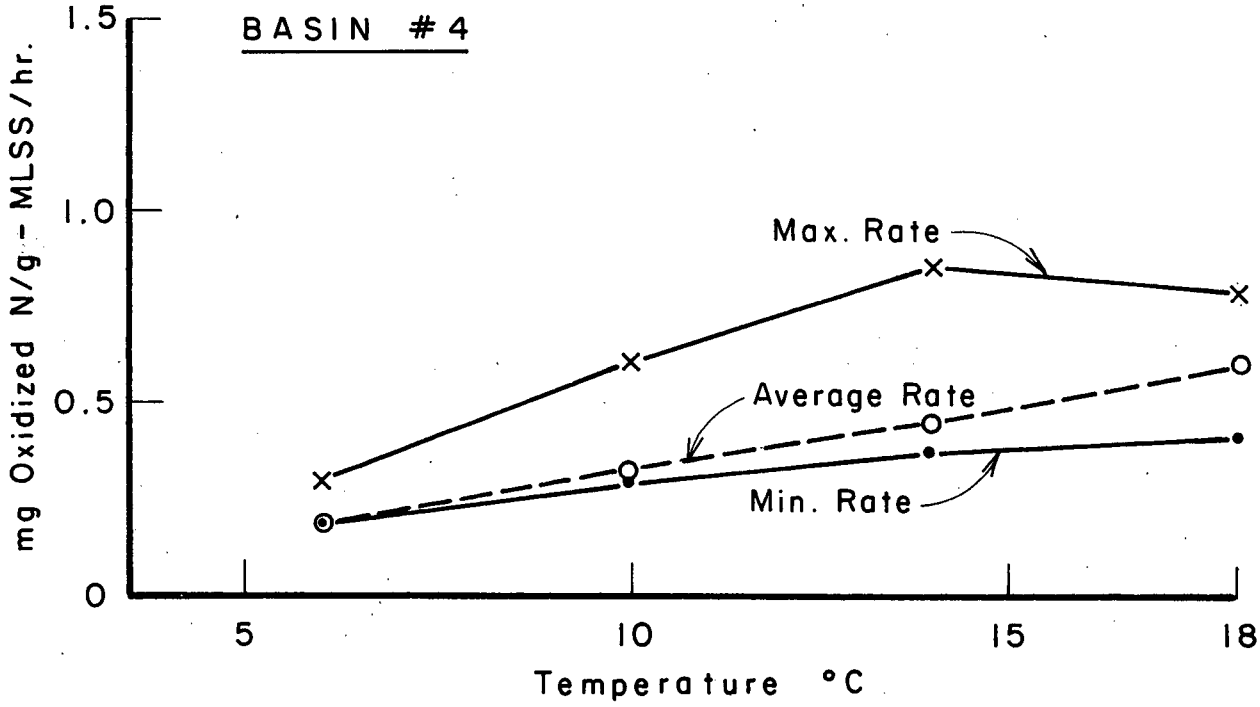


FIG.7.10 BATCH DENITRIFICATION RATES IN BASINS #2 AND #4.

TABLE 7.4

DENITRIFICATION RATES BY FLOW THROUGH MASS BALANCE CALCULATION

[mg (NO_2 + NO_3) - N (hour/gram MLSS]

Run	#1 Basin[t]			#2 Basin			#4 Basin		
	Mean	Low	High	Mean	Low	High	Mean	Low	High
181A	No Nitrification Occurring								
181B*	4.0	0.7	7.8	3.8	-0.4	17.8	0.65	0.17	1.96
181C	0.8	0.1	1.2	0.54	0.15	1.09	0.61	0.32	0.95
182A	0.34	<0.1	0.93	0.92	0.55	1.52	0.42	0.26	0.54
18°C Mean	0.53	<0.1	1.2	0.73	0.15	1.52	0.52	0.26	0.95
141A	0.5	0.3	1.07	0.44	0.31	0.68	0.22	0.16	0.36
141B	Negligible Nitrification Occurring								
141C*	0.43	0.35	0.45	0.29	0.07	0.34	0.15	0.11	0.26
142A	0.87	0.48	1.16	0.56	0.12	0.83	0.34	0.08	0.47
14°C Mean	0.70	0.3	1.16	0.50	0.12	0.83	0.28	0.08	0.47
101A	0.25	0.2	0.41	0.18	0.06	0.3	0.08	0.06	0.11
061A	0.35	0.23	0.77	0.2	0.12	0.36	0.14	0.07	0.18

* Data not included for determination of mean due to lack of steady state conditions.

[t] Estimated (See Section 7.4.3)

TABLE 7.5

BATCH DENITRIFICATION RATES: BASINS #2 AND #4

Batch	Day	Temp °C	MLSS (mg/L)	Feed BOD (mg/L)	Denitrification Rate (mg N/hour/gm MLSS) Maximum[t]	Denitrification Rate (mg N/hour/gm MLSS) Average	pH Range	Δ Alk/ NO_3
Basin #2 (Wastewater Carbon Source)								
181	256	18	2720	80	0.63*	0.60*	7.2-7.4	5.3
182	6	18	2990	100	0.98/1.14*	0.60/0.72*	6.9-7.0	3.3
182	17	18	3450	230	0.79	0.77	7.1-7.2	3.8
141	14	14	3170	190	0.82*	0.59*	6.9-8.2	2.3
141	98	14	3352	195	0.88*	0.72*	7.2-7.3	2.5
141	106	14	3210	205	0.86/1.0*	0.80/0.89*	7.1-7.2	4.0
142	9	14	3280	160	0.60	0.51	7.2-7.5	3.9
101	17	10	3390	187	0.45	0.45	7.1-7.3	3.5
101	23	10	3940	200	0.71	0.60	7.1-7.2	4.9
061	9	6	3090	140	0.27	0.18	6.9-7.0	2.0
Basin #4 (Endogenous Denitrification)								
181	262	18	3780	-	0.79*	0.73*	7.0-7.1	5.38
182	6	18	3630	-	0.53/0.63*	0.41/0.53*	6.7-6.8	4.78
182	17	18	3670	-	0.80	0.64	7.1-7.2	3.18
141	25	14	2890	-	0.86*	0.56*	6.7-6.9	2.61
141	106	14	3210	-	0.57/0.68*	0.42/0.50*	7.1-7.2	3.88
142	9	14	3540	-	0.39	0.38	7.1-7.2	3.46
101	17	10	3570	-	0.30	0.30	7.1-7.3	3.84
101	23	10	3650	-	0.6	0.33	7.1	4.83
161	9	6	3440	-	0.31	0.19	6.9-7.0	4.05

Notes:

* Spectrophotometric nitrate analysis used.

[t] The maximum observed rate between two adjacent sampling times.

Δ Ratio of alkalinity produced to nitrate consumed.

For the denitrification rate 'N' is NO_2 plus NO_3.

Figures 7.11 to 7.16 and gives an insight into the fluctuations in basin and hence system performance.

7.5 Summary of Results

The process efficiencies and rates reported in Sections 7.2 through 7.4 are summarized below. The rates are the maximum observations taken from the pooled batch and flow through data.

Process Removal Efficiencies (%)

Temperature °C	Total N		TKN		Total P		BOD	
	Mean	Max	Mean	Max	Mean	Max	Mean	Max
18	92	95	95	98	87	96	95	99
14	87	93	93	96	88	97	91	99
10	50	54	53	56	89	94	93	97
6	70	79	80	87	81	93	91	91

Maximum Observed Nitrification or Denitrification Rates
(mg oxidized N/gm MLSS/hr)

Temperature °C	Nitrification	Denitrification	
		Wastewater Substrate	Endogenous
18	1.52 (14.5)*	1.52 (14.5)*	0.95 (1.96)*
14	1.44	0.88	0.86
10	0.38	0.71	0.60
6	0.42	0.36	0.31

* This peak rate was observed during the establishment of nitrifier and denitrifier populations but not subsequently. (See Section 7.6.2)

7.6 Discussion of Model Performance

7.6.1 Reactor Startup (Phase 181A)

The startup phase could have been significantly reduced by using an activated sludge from a secondary treatment plant or by initially using the model as a draw and fill reactor and growing a suitable mixed liquor on the sewage being tested.

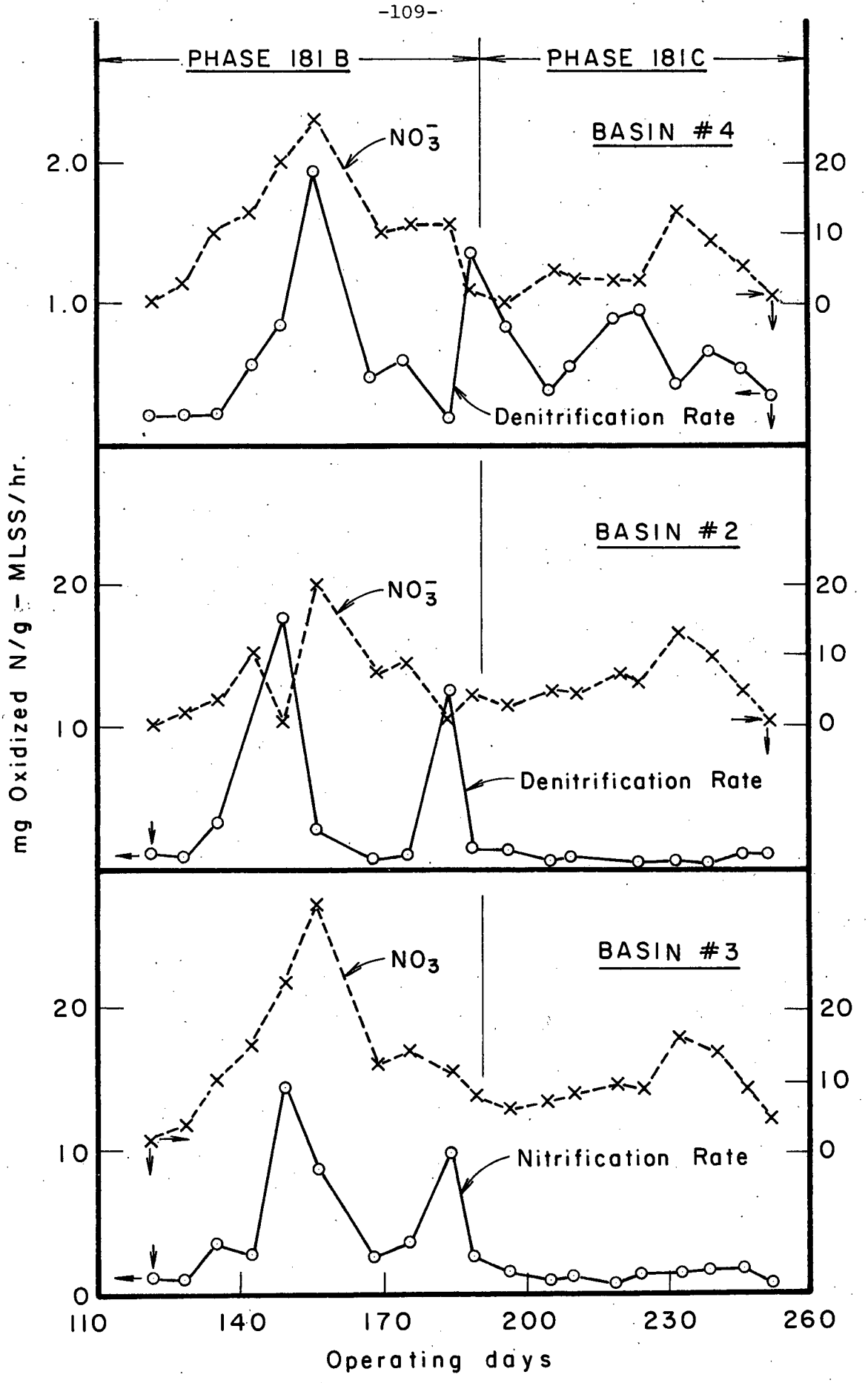


FIG.7.11 OPERATING DATA FOR BASINS #2,3 AND 4 AT 18°C.

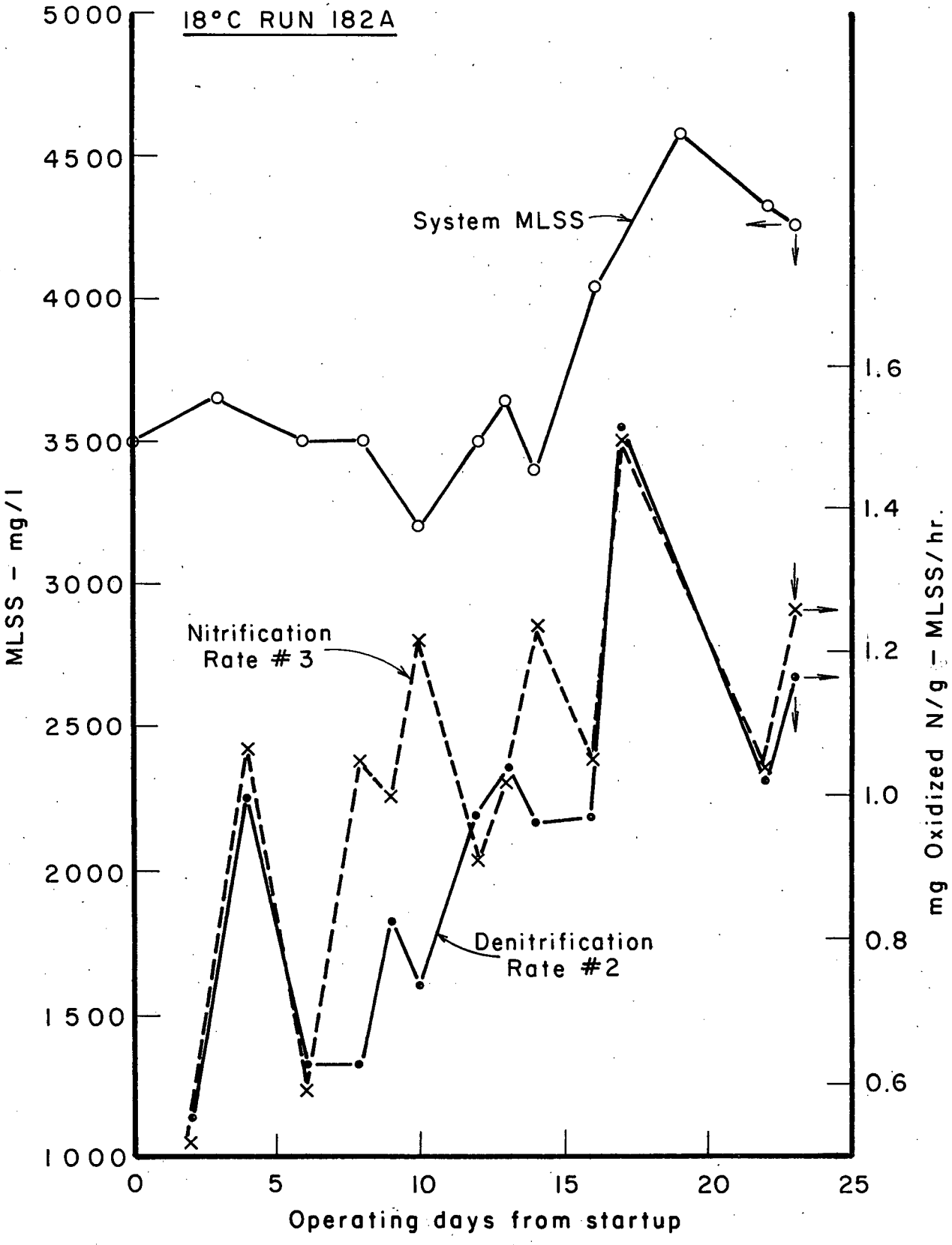


FIG.7.12 PERFORMANCE OF BASINS #2 AND #3 AT 18°C.

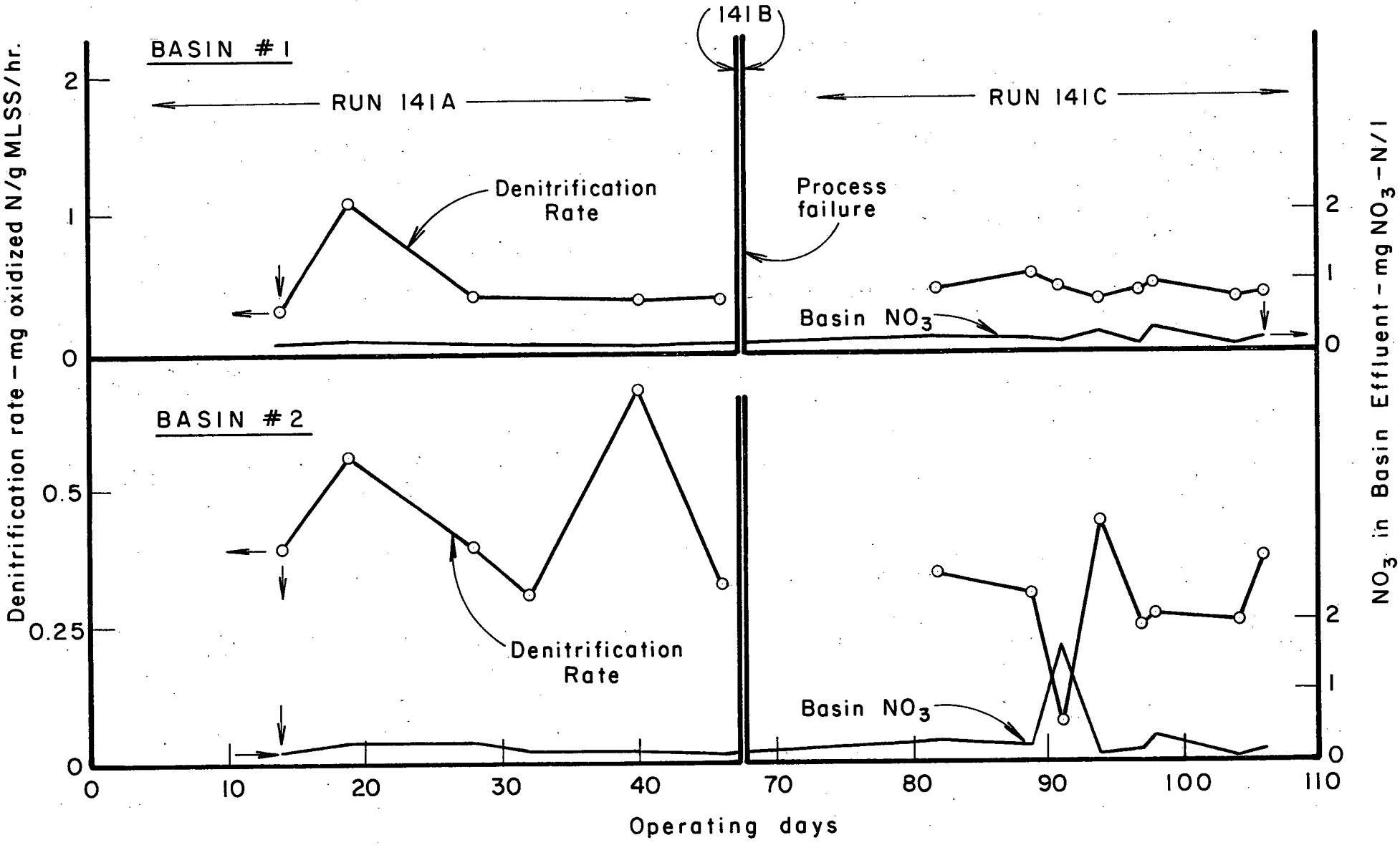


FIG.7.13 PERFORMANCE OF BASIN #1 AND #2 AT 14°C(RUN 141).

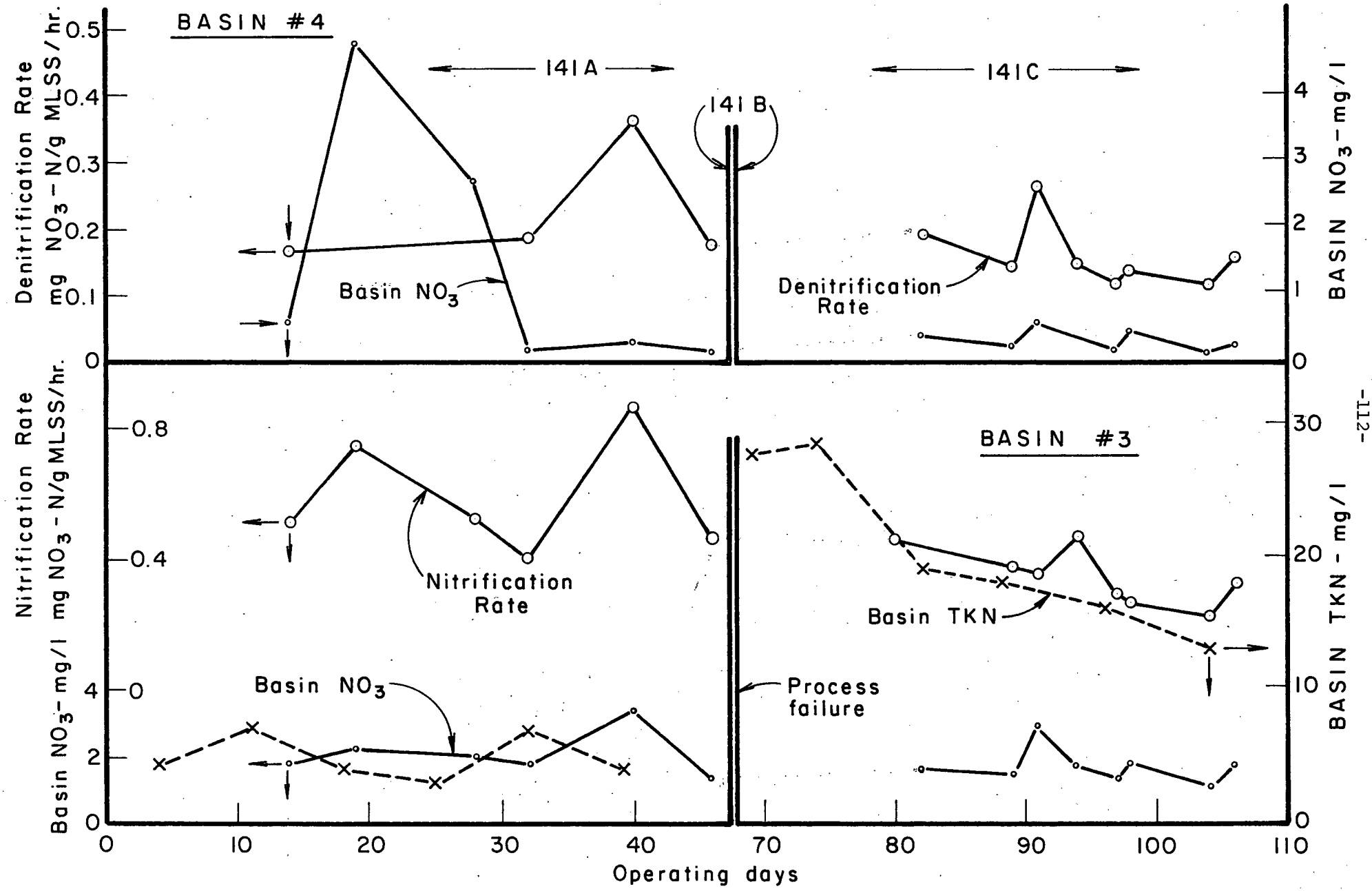


FIG.7.14 PERFORMANCE OF BASINS # 3 AND #4 AT 14°C (RUN 141).

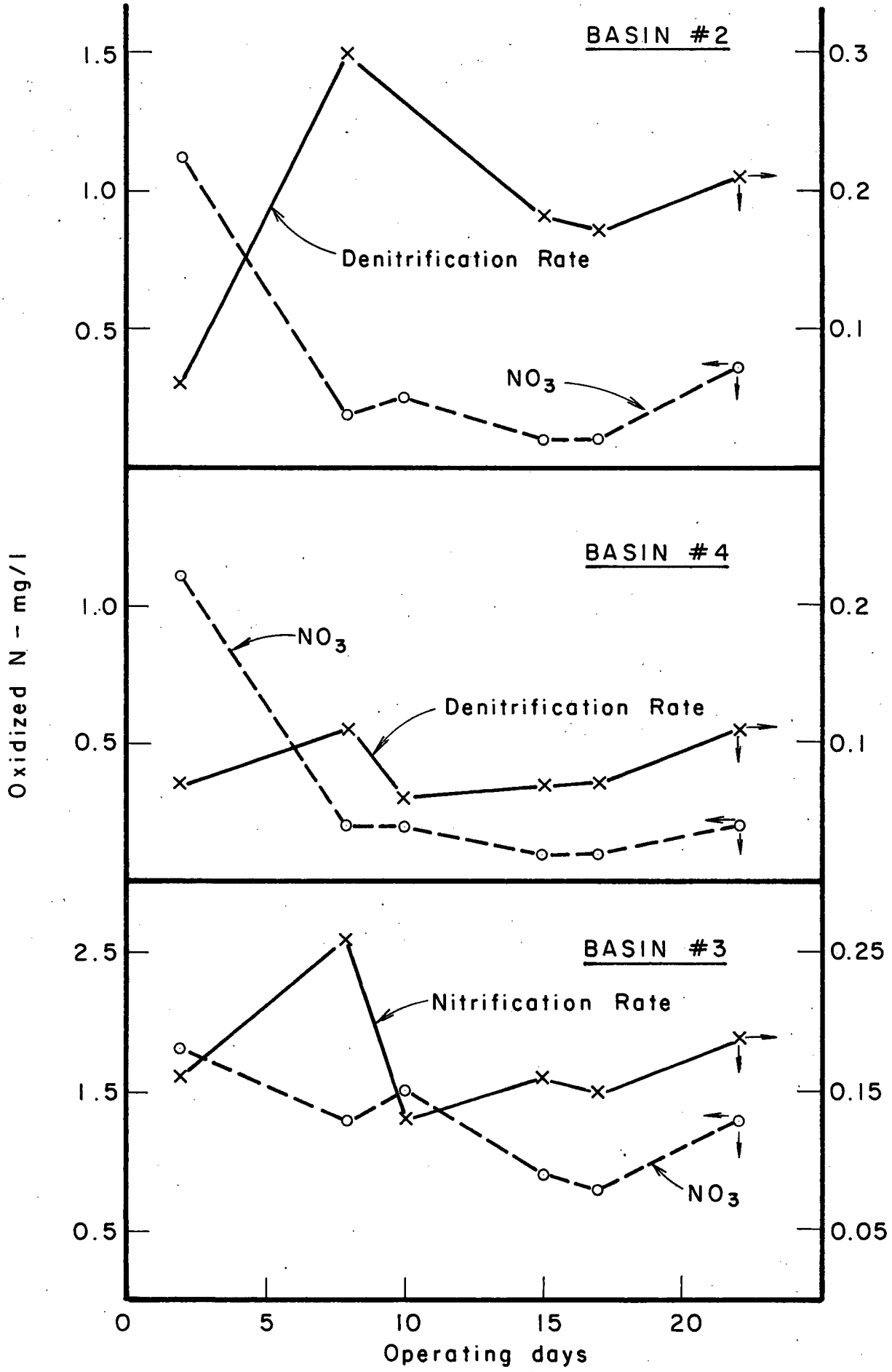


FIG.7.15 OPERATING DATA FOR BASINS #2,3 AND 4 AT 10°C.

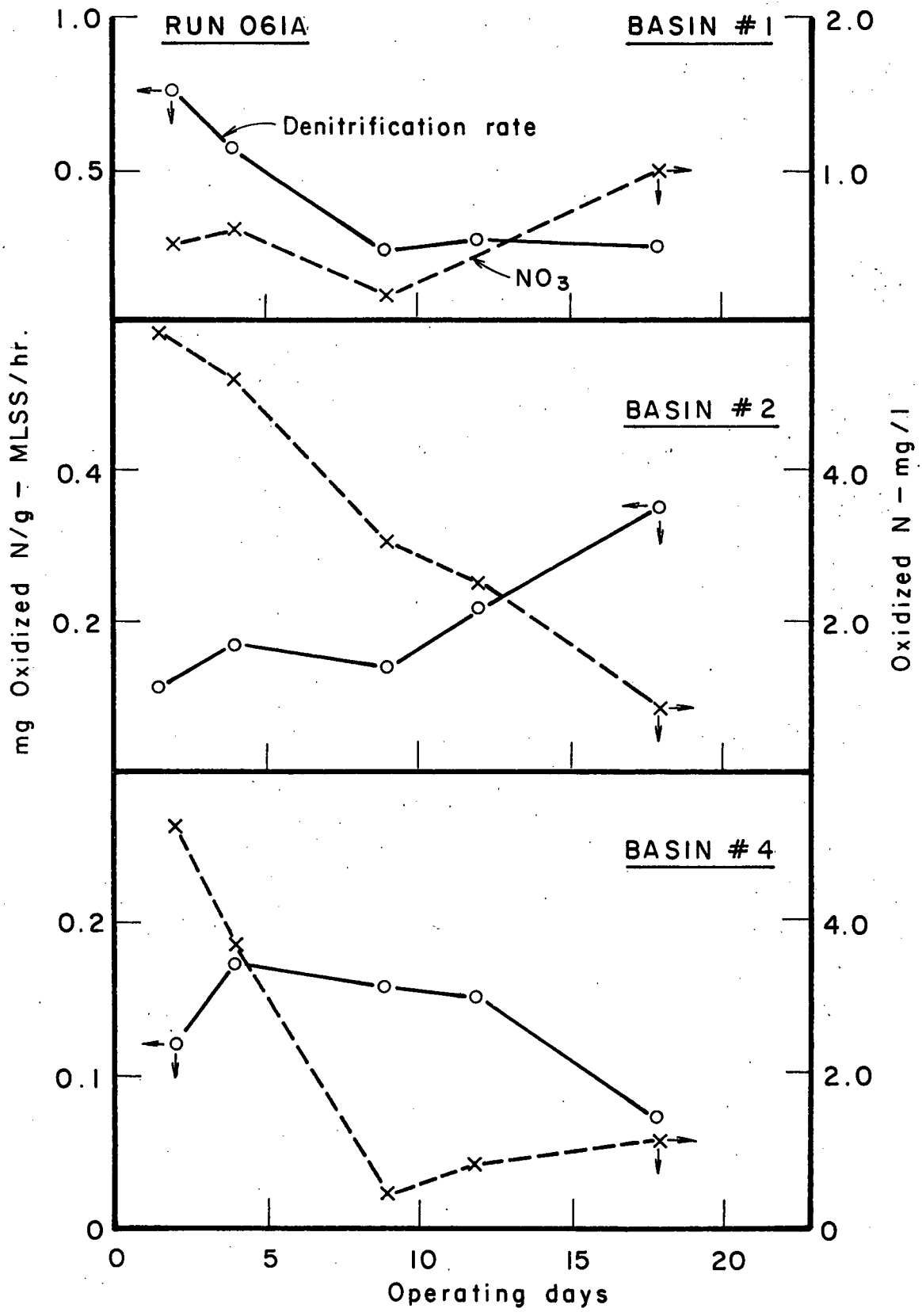


FIG.7.16 PERFORMANCE OF BASINS #1, #2 AND #4 AT 6°C.

The presence of a more efficient clarifier to provide a higher percentage of solids recycle would also have shortened the startup time.

7.6.2 Phase 181B and 181C

During the establishment of the nitrifier population (181B) the observed nitrification rates were periodically an order of magnitude greater than any rate achieved during the subsequent 181C and 182A phases (Figure 7.11; Table 7.3). Coincident with these high rates, the system effluent TKN's were above 3 mg/L, while during the periods of lower average rates they were below 3 mg/L (Figure 7.1). This supports the theory that nitrification rates are dependent of substrate concentration below the 2-3 mg/L level. Even though the observed nitrification rates were low at these smaller TKN concentrations, they were adequate to maintain the desired low TKN concentrations (Table 7.1). A batch nitrification test carried out late in run 181C (Table 7.2) showed that the available nitrification capacity of the mixed liquor was at least three times greater than actually being utilized at this time (Table 7.3).

Also during 181B, both denitrification rates (endogenous and waste-water carbon substrate) had significantly higher peak values than those subsequently observed during phases 181C and 182A (Figure 7.11). However, in this instance, the lower rates were firmly established as "normal", particularly for basin #2, while the nitrate level in the system was still excessive at 12 mg/L. At this time, the BOD concentrations in the raw sewage were quite low (<100 mg/L) and probably the denitrification rate was limited by the shortage of readily available short chain hydrocarbons in basin #2.

7.6.3 Run 141A

The addition of BOD spikes near the end of run 181C and early in run 141A brought about a rapid decline in the overall nitrate levels,

the concentration in the effluent being reduced to 1 mg/L and the total nitrogen removal exceeding 90% (Figure 7.2; Table 7.1). Because at this time the rates were not monitored, no conclusions can be drawn as to the effect of BOD supplementation on the denitrification rate.

7.6.4 Adequate Nitrification and Denitrification Achieved

Once the initial nitrifier and denitrifier populations were established and an adequate external carbon source was available for denitrification, the unit reaction rates fell to low values, because of the conservative design of the system. Both mechanisms performed at the rates demanded by the loads imposed on them and a high level of nitrogen removal was maintained.

7.6.5 Recovery from Overheating (141B and 141C)

Both BOD removal and denitrification ability appeared relatively unaffected by the catastrophic overheating, or else recovered rapidly. However, the TKN conversion, 4 days after the event, was only 31% in contrast to the 93% average before. When run 141C was terminated two months later, the TKN removal had reached only 70% (Figure 7.2). Calculated nitrification rates from batch tests and from flow-through data were similar, tending to show that the poor TKN conversion was due to a low nitrifier population in the sludge rather than to any substrate concentration limitations. Both of these nitrification rates were significantly lower than the flow-through calculations made during 141A prior to overheating (Table 7.2 and 7.3).

During 141C, the denitrification rates calculated from flow-through mass balances were only half those determined before "overheating" (Run 141A). However, the maximum rates calculated from batch tests during both 141C and 141A were similar, indicating the existence of unused denitrification capacity during 141C; unused because of the poor nitrifica-

tion performance, consequent low nitrate levels and, thus, minimal need for denitrification (Tables 7.4 and 7.5).

7.6.6 Run 101A

At 10°C, relatively constant performance was maintained, particularly with regard to TKN transformation which stayed fixed in the 50% to 55% range. The aerobic basin SRT appeared adequate to prevent nitrifier washout (Tables 4.3 and 6.2). BOD concentrations and BOD:TKN ratios remained high and unfavourable to a nitrifier population increase.

The two batch nitrification tests carried out yielded conflicting information. In the first, the rate calculated from the batch data was 2.7 times greater than the flow-through calculated rate on the same day, while in the second, both calculations gave a similar rate (Table 7.6). This second test gave the expected result. The poor nitrification performance was most probably due to the low nitrifier fraction in the sludge, and not due to a substrate deficiency. The first result, however, suggests a possible problem with poor TKN hydrolysis in the continuous reactor, at the time of testing.

From Table 7.6, it can be seen that the denitrifying capacity of the biomass was up to 5.7 times greater in batch tests than was actually being utilized in the flow-through reactor. As a consequence, nitrate levels throughout this run were kept low (Figures 7.4 and 7.15).

7.6.7 Run 182A

Within one day of raising the temperature from 10°C to 18°C, the TKN conversion rose from 50% to 70% and reached 95% within 4 days. Both the nitrification and denitrification rates increased steadily for the duration of this run (see Figure 7.12). The batch and the mass balance

TABLE 7.6

RATIO OF BATCH RATE TO CALCULATED FLOW-THROUGH MASS BALANCE RATE ON SAME DAY (DATA FROM TABLES 7.2 TO 7.5)

Basin #2				Basin #4				Basin #3			
Run	Ratio		NO_3	Run	Ratio		NO_3	Run	Ratio		TKN
	Max.	Avg.	Mg/L		Max.	Avg.	Mg/L		Max.	Avg.	Mg/L
061	1.9	1.3	3.0	061	1.9	1.2	0.4	061	1.5	1.2	11.5
101	2.6	2.6	0.1	101	4.3	4.3	0.1	101	2.7	2.7	25.2
101	3.4	2.9	0.4	101	5.7	3.1	0.2	101	1.2	1.0	23.5
141	2.1	1.5	0.2	141	-	1.0*	2.0*	141	1.1	1.0	<3.0
141	3.3	2.7	0.4	141	3.8	2.8	0.2	141	1.2	0.9	16*
141	2.3	2.2	0.2	142	0.9	0.9	2.0	142	1.4	1.3	13*
142	0.8	0.7	3.7	181	0.9	0.8	1.1	181	2.7	2.7	2.0
181	0.8	0.7	0.8	182	1.8	1.4	0.5	182	2.2	1.5	2.0
182	1.6	1.0	0.7	182	2.0	1.6	0.3	182	1.4	1.0	<4.0
182	0.5	0.5	0.5								

Notes: * Estimated

Maximum and Average refer to those rates determined in batch tests (Tables 7.2 and 7.4).

rates stayed in close agreement (see Table 7.6). With the rapid increase in nitrification ability, the nitrate levels in the effluent rose appreciably, due to the rapid use of the excess denitrifying capacity observed at 10°C and an apparent "lag-time" needed for growth of additional denitrifiers to respond to this nitrate surge.

Although the feed characteristics during this run were more favourable to nitrifier growth than at 10°C, it is apparent that there was a large difference in the system behaviour between operation at 18°C and 10°C.

Because this run was not monitored during the first few days at 18°C, it is not possible to comment on the existence of high peak rates similar to those achieved during 181B. Generally the rates and performance achieved confirmed those obtained during 181C.

7.6.8 Run 142A

The results exceeded those obtained during the previous 14°C period. A good performance was expected because the detrimental effects of overheating had been completely erased by the time of this run. Because of the enhanced nitrification performance, unlike 141C, there was no excess denitrification capacity (Table 7.6). For the duration of 142A, a comparison of the batch and the flow-through mass balance calculations showed no unused denitrification capacity to be present and only a small excess nitrification capacity, probably carrying over from 182A.

7.6.9 Run 061A

During this short run at 6°C, an effort was made to stress the system to the point of failure by lowering the HRT in each basin. Because the short duration of the run and several changes in operating parameters allowed insufficient time to fully evaluate the steady-state performance, the results are tentative, but informative.

Figure 7.5 shows a marked build-up in TKN concentration in basin #3 and in the effluent, together with a slight but perceptible decline in the nitrification rate. Table 7.6 shows the nitrification rate calculated from a batch test to be slightly higher than from a flow-through mass balance calculation; perhaps resulting from ammonia being more readily available in the batch reactor (due to spiking) than in the model, where, at 6°C organic nitrogen hydrolysis has slowed down. Tables 4.3 and 6.3 show that the estimated solids retention time should be sufficient to maintain nitrification.

The nitrate concentrations fell from initially higher values and then remained low indicating the existence of an adequate denitrification capacity (see Figures 7.5 and 7.16). From Table 7.6, adequate reserve nitrogen removal capability is apparent.

An unanswered question remains as to how the system performance would have looked at 6°C given several more weeks of operation under the high feed-rate conditions imposed shortly before shut-down. Such long-term performance at low temperature could be important under some climatic conditions in British Columbia.

7.7 Dependence of Nitrification and Denitrification Rates on Temperature

In Figure 7.17, an envelope of the maximum and minimum unit nitrification rates observed in this study is compared to the results of other investigations in the 4°C to 25°C temperature range. Similarly, Figures 5.1 and 5.2 compare results for endogenous and waste-water carbon substrate denitrification respectively.

It is immediately apparent that the nitrification results determined in this work are significantly lower than most data previously reported in the literature. The endogenous denitrification rates compare well, but are slightly lower while the rates using sewage substrate are similar to some reported work, but significantly lower than the data of Barnard.

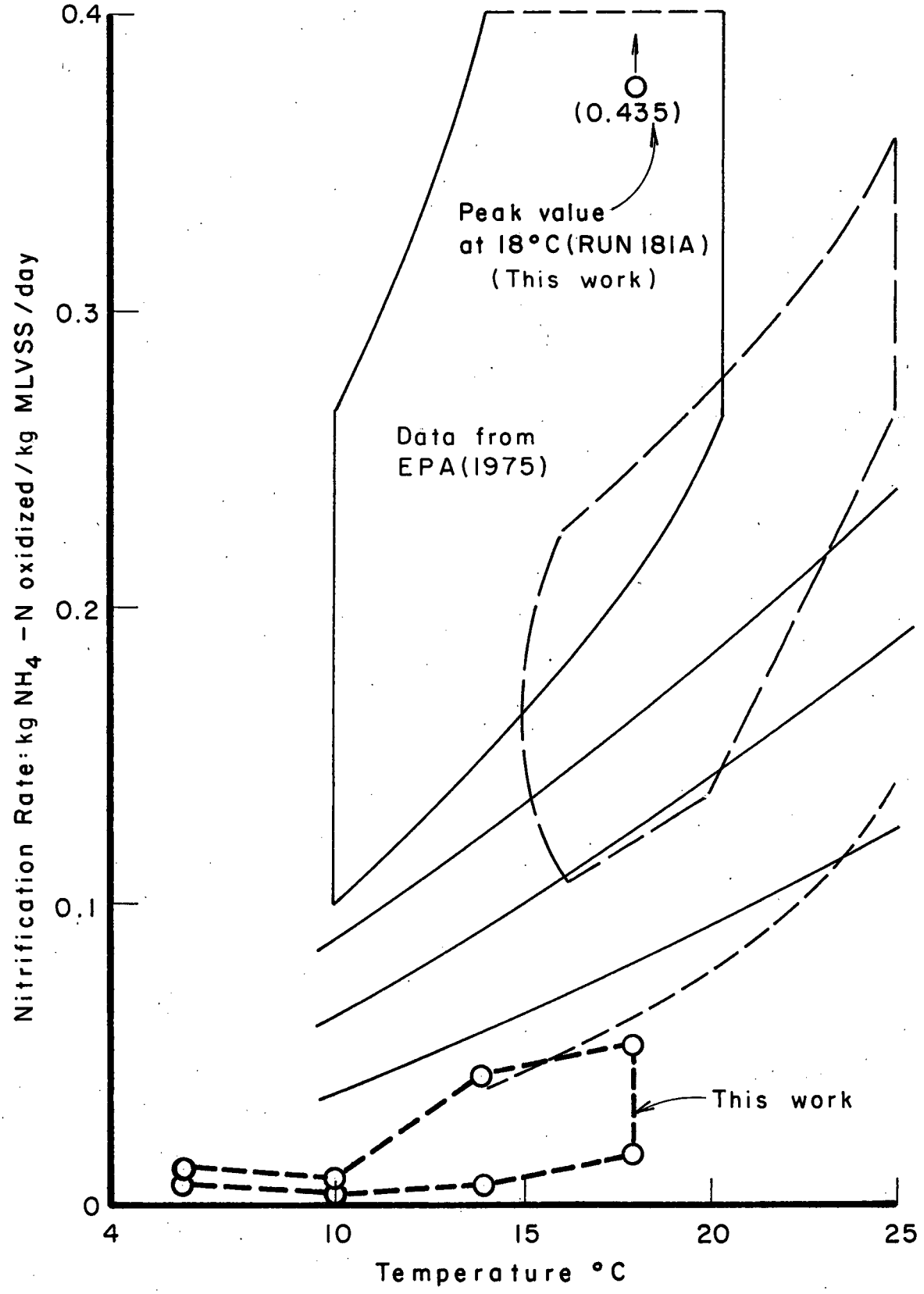


FIG.7.17 NITRIFICATION RATES : THIS WORK AND OTHERS.
(See FIG.4.1 for References).

An examination of the factors regarded as having significance in establishing rates may provide an explanation for this discrepancy.

7.8 Factors Potentially Influencing the Observed Unit Reaction Rates

7.8.1 Dissolved Oxygen:

Only rarely did "aerobic" DO concentrations leave the 1-4 mg/L range, or anoxic concentrations exceed 0.2 mg/L, and thus oxygen had minimal effect on the observed average unit rates.

7.8.2 pH and Alkalinity

In basin #3, the observed pH ranged between 6.5 and 7.3 over the course of the experiment, with basins #2 and #4 usually being 0.2 to 0.3 units higher. Using Equation 4.7 and an average pH of 6.7, the nitrification rate at pH 6.7 would be 58% of the maximum rate at pH 7.2 (EPA 1975). Thus in this work, the low system pH has probably lowered the maximum possible nitrification rate. The pH has probably had negligible effect on denitrification due to the adequately high values.

7.8.3 Anoxic Residence Time

At no time in this work was the actual anoxic HRT deliberately maintained above three hours in the model (see Table 6.3). Thus, according to Section 4.3.5 nitrification ability should have remained unaffected. However, during batch denitrification tests or system malfunction, this limit was exceeded and may have caused some biomass mortality.

7.8.4 Combined Sludge

As indicated by Sutton (1978a), a combined sludge performing carbon oxidation, nitrification and denitrification operations will exhibit lower substrate removal rates per unit of biomass than a separate sludge performing only one of these operations. Where unit rates are being

compared, the type of sludge is a major, indeed probably the most important consideration.

7.8.5 MLSS Concentration

Although Christensen (1977a) showed a decrease in unit denitrification rate with increased MLSS concentration, this work shows no trends in this relationship.

7.8.6 Steady-state Conditions

From the literature, it appears that one to two sludge ages after a process change or, two weeks for a temperature change, are adequate to allow sufficient time for a system to reach steady-state (Wild 1971; Sutton 1977b). Several runs in this work fell short of this requirement, (i.e. 101A, 182A, 142A and 061A).

7.8.7 SRT

As indicated in Section 5.5.3, the denitrification rate decreases at higher SRT. Nitrification rates increase as the SRT increases (Sutton 1977b). Because of the fact that only estimated sludge ages are available in this work, it is not possible to comment on any relationship between sludge age and unit rate. However, as discussed elsewhere in this chapter (Section 7.5), the SRT in #3 basin was probably inadequate to allow adequate nitrifier growth during several runs under the conditions prevailing at the time (eg. runs 141C and 101A).

7.8.8 Fraction of Viable Micro-organisms

A major criticism of most published data on unit nitrification and denitrification rates revolves around the choice of a parameter to quantify the viable biomass. There is ample evidence that numerous factors (eg. sludge age, C:N ratio and environment) affect the fraction and activity of nitrifiers in a sludge. However, most commonly used

measurements of biomass (MLVSS, MLSS) do not adequately quantify this fraction, indeed there is negligible evidence of any practical system that (for biological waste-treatment) does. Thus, in order to compare unit nitrification rates in a rational way a litany of other process variables should presently be attached as qualifiers.

The case for denitrification is different in that the population is more diversified and adaptable, with a higher fraction of potential nitrate users, which allows unit rate comparisons to be made with less qualification.

In this work, system SRT varied randomly with time as did BOD:TKN ratios and BOD concentrations. Mixed liquor and sludge from spillage, batch test and filtering operations, all with indeterminate fractions of viable biomass, were also returned to the system. The criteria used to quantify the biomass was MLSS. The unit rates observed must therefore be seen in the light of these experimental variations and the factors, previously discussed, that determine the activity of the relevant components of the viable biomass.

7.8.9 Toxicity and Inhibition

Nitrifiers are more susceptible to inhibition than denitrifiers, which in turn are more sensitive than carbon oxidizers (Section 4.4). In this work possible sources of inhibitors or toxicants included:

(i) Components of the raw sewage;

(ii) Products of sewage or sludge biodegradation;

(iii) Any material in contact with the sewage or mixed liquor;

(iv) Plant air supply.

While no data is available on (ii), (iii), or (iv), an analysis of feed and mixed liquor for metals (see Appendix 3) revealed the following:

(i) A build-up of many elements in the mixed liquor;

(ii) The concentration of several metals in the feed (Zn, Cu, Ni, Cr) and the mixed liquor (Pb) periodically exceeded the "threshold concentration" for nitrification inhibition (WPCF 1977).

There was, therefore, a potential for inhibition of nitrification by heavy metals, but no data are available to indicate if in fact inhibition occurred, or if it did not.

7.8.10 Substrate Limitations

7.8.10.1 Nitrification

Both the C:N ratio and the TKN or ammonia concentration may influence the observed unit nitrification rate. Generally, with higher C:N ratios, nitrifier fractions are smaller, unit rates lower, and longer minimum sludge ages are needed to maintain a nitrifying sludge. Throughout this work, BOD:TKN ratios in the raw sewage ranged between 3:1 and 6:1, although passage through basins #1 and #2 accompanied by dilution, oxidation, assimilation and dissimilation events probably changes this ratio by basin #3. The relatively low nitrification rates obtained in this work result, in part, from the relatively high C:N ratios.

As previously discussed, zero order nitrification rates occur at ammonia concentrations in excess of 2-3 mg/L. Sutton (1978a) and Keller (1978) show about 2 mg/L of refractory soluble TKN inevitably passes untransformed into the process effluent. TKN in excess of 4 to 5 mg/L, should thus prevent substrate limitation of nitrification. For much of this work at 18°C and 14°C, this criteria was not met. Table 7.6 compares the ratios of nitrification rates calculated from batch tests and from flow-through mass balances on the same day. Generally, where the TKN in basin #3 exceeded 3 mg/L, this ratio was relatively close to unity, which indicates that the system is operating close to its maximum

nitrifying ability. Conversely, at lower TKN concentrations, the ratio is higher, probably showing a substrate shortage in the model. The high ratios at 18°C (181B and 181C) may well result from the growth of a high nitrifier fraction in the mixed liquor, (resulting from temporary high TKN concentrations) and its gradual dissipation once low TKN concentrations were established, thus leaving a temporary excess nitrification capacity. The high initial ratio at 10°C is less easily explained, but may be due to a temporary TKN hydrolysis inhibition.

7.8.10.2 Denitrification Using Wastewater Substrate (Basin #2)

Here, one or both of nitrate and wastewater carbon may be limiting. For run 142A and generally at 18°C, the batch rates were less than the calculated flow-through rates, even at low nitrate concentrations in basin #2. It appears that while carbon substrate was continually supplied in the model by overflow from basin #1, the wastewater spikes in the batch test were inadequate and thus these tests were carbon limited.

At 10°C and for two runs during 141C at 14°, all with low reactor nitrate concentrations, and all taken when the nitrification performance was inadequate, the batch rates were markedly higher than those calculated from the flow-through mass balances. Nitrate was most probably limiting, in the reactor although how much the flow-through denitrification rates could have been increased until carbon became limiting is not determinable.

Similarly for one run at 14°C, when nitrification was good, the ratio, while closer to unity, still showed some denitrifying capacity unused in the reactor model.

At 6°C, with an adequate NO_3^- level in basin #2, the higher batch rate may be related to factors other than nitrate or carbon substrate (eg. better DO control in the batch reactor).

From Table 7.4, it can be seen that the unit denitrification rates in basin #1 (calculated from a flow-through mass balance), although based in some instances on estimated data (see Section 7.4.3), are often higher than in basin #2, even though the nitrate concentrations in #1 basin were generally extremely low (see Figures 7.4, 7.14, 7.16). Possibly, in #1 a lower O.R.P. (resulting from sewage septicity and anaerobic hydrocarbon breakdown in that reactor) provides for a more rapid denitrification than in #2 where the O.R.P. is raised by the high rate of recycle from basin #3 of aerobic and nitrified mixed liquor. This recycle would also dilute the short-chain hydrocarbon concentration in basin #2.

7.8.10.3 Endogenous Denitrification (Basin #4)

For endogenous nitrate respiration, the biomass provides an ample carbon source; only nitrate is of concern. The concentration in #4 basin was usually less than 2 mg/L and thus potentially limiting. From Table 7.6, it can be seen that with low system nitrate levels, batch rates are usually much higher than those calculated from flow-through data, but with high system nitrate levels in the model, the rates are generally similar. There is thus a good indication that endogenous denitrification rates in the flow-through system might have been higher if a higher nitrate concentration existed in the #4 reactor (and thus in the process effluent).

7.8.11 Summary of Rate Limiting Factors

7.8.11.1 Nitrification

As a general rule, the system performed with the maximum nitrification rate possible, under the conditions of design and operation. The supplementation of pH and minimization of potential toxicity problems may have increased the unit rates that were observed. Improved design of the experiment, optimization and better process control (eg. SRT) in the model would also have had positive benefits.

However, the apparently superior unit rates reported by other investigators (Figures 4.1 and 7.17) are for peak rates in systems using single stage nitrifying sludges with optimum pH, low C:N ratio and uninhibitory environments. Such systems possess high fractions of nitrifiers and thus have a much greater potential nitrifying capacity per unit weight of sludge.

7.8.11.2 Wastewater Substrate Denitrification

Throughout most of this work the denitrification rate was limited by low nitrate concentrations, due to poor nitrification performance, or to overly long anoxic HRT's. However, where low effluent nitrate concentration is the operating objective, a less than maximum denitrification rate is inevitable, because of this restriction on the electron receiver. In some instances at 18°C and 14°C, carbon substrate was apparently limiting and may possibly have been overcome by adding some raw sewage directly to basin #2.

From Figures 5.2 and 5.3, it is apparent that many observations of denitrification, using wastewater substrate, achieved results comparable to average or good endogenous rates, and this work fitted into the same pattern. Given higher BOD levels, improved nitrification and a process optimized for maximum denitrification rate, the observations of Barnard (1975a) may have been approached.

7.8.11.3 Endogenous Denitrification

Some improvement in the endogenous rates could probably have been obtained by:

(i) Maintaining higher nitrate levels, but thereby sacrificing final effluent quality.

(ii) Operating at a lower SRT in the endogenous reactor by minimizing

the endogenous HRT in a system with optimized SRT.

7.9 Minimum Solids Residence Time

An inadequate data base does not allow comparisons to be made between nitrification and denitrification rates and SRT. However, from Table 6.2 it is possible to tabulate the estimated minimum SRT's at which nitrification and denitrification were maintained (see Table 7.7).

TABLE 7.7

ESTIMATED MINIMUM SOLIDS RESIDENCE TIME
FOR NITRIFICATION AND DENITRIFICATION

Temperature (°C)	Nitrification	Denitrification (Wastewater)	Denitrification (Endogenous)
18	>5 days	4 days	>5 days
14	>10 days	4 days	>5 days
10	>13 days	6 days	>10 days
6	30 days	18 days	>18 days

A minimum SRT for denitrification (particularly endogenous) is seldom reported in the literature, presumably on the assumption that a healthy biomass will be able to move facultatively between oxygen and nitrogen respiration as circumstances demand.

With the exception of the recorded value for 6°C, the minimum SRT's reported here for nitrification agree well with the data reported in Table 4.3.

7.10 Effect of Basin #5 on Nitrogen in the Effluent

In the aerobic basin #5, ammonia released from lysing cells and auto-oxidation in #4 basin is oxidized to nitrate; some TKN not transformed in #3 basin may also be removed. As pointed out by Sutton

(1978a) and Keller (1978), between 1 and 3 mg/L of refractory soluble TKN is not removed by normal biological treatment. Such was the case here. As a general rule, nitrate levels in the system effluent were increased by 0.5 to 2.0 mg/L over those leaving the endogenous denitrification basin, due to the oxidation in the final aerobic basin.

In this work the aerobic period in #5 basin has been ignored in assessing the system aerobic SRT. It is suggested that the long SRT in basin #4 and the good BOD removal in #3 result in significant endogenous loss of both heterotrophs and nitrifiers in basin #4 and #5. Any nitrifier growth in #5 will at best only replace these losses in basin #4 and #5.

7.11 Scum Layer:

Through most of the experiment (at all temperatures), a 1-2 cm thick dark scum remained on the surface of the main aerobic tank (#3). The scum was not dispersed by commercial defoamers (Dow Antifoam C) but could be removed by stirring it into the mixed liquor, when aeration was halted, or by skimming it off. However, in both instances, the scum rapidly returned after resumption of aeration.

Hadeed (1978) discusses "a dense and somewhat greasy and scummy layer of deep tan to brown foam" that may indicate an old or an over-oxidized sludge. Pipes (1978) indicates that "some activated sludge processes develop a persistent viscous brown scum..." which coincides with the presence of large numbers of actinomycetes. Both overcame the problem by lowering the MLSS, increasing the F/M ratio and effectively decreasing the sludge age.

Because no investigation was made of the scum in this instance, nothing can be said about its influence, if any, on nitrogen removal. It

was, however, noted that the onset of the layer coincided with an increased loading of fish packing waste into the sewage system from which the process feed was obtained.

7.12 Nitrogen Analysis:

The literature on biological nitrification and denitrification indicates a wide variation in the form of nitrogen monitored and in the analytical techniques used. This variation, in part, results from the difficulty of achieving rapid and accurate determinations of nitrogen values in complex solutions, eg. sewage, due to interferences and to the many nitrogen containing constituents that may be present. In turn, the variety of analytical techniques reflects efforts to overcome these problems. Thus, among numerous other factors, it is important to consider the form of nitrogen and the method of its determination when comparing nitrogen transformation rates reported in the literature.

In this work, nitrification and denitrification rates were determined in terms of the appearance and disappearance of "nitrate" - on the somewhat suspect assumption that nitrite concentrations were negligible or at least remained constant.

During the course of this work, the use of a nitrate probe and of cadmium columns was hampered by unknown soluble materials in the sewage which were capable of affecting the cadmium powder and the probe sensing head. Spectrophotometric analysis was also hampered by nitrite and other interferences, and by the development of coatings on sample cuvettes.

Many of these analytical problems were intermittent, of varying and unpredictable effect and thus difficult to eliminate.

7.12.1 Alternative Monitoring

When determining nitrification rates, a reasonable alternative might be to monitor soluble TKN or ammonia removal. It must be recalled, however, that:

(i) Ammonia will be assimilated by growing biomass

(ii) Ammonia will be released from lysing biomass and then oxidized

(iii) If the pH is high, aeration may strip out any free ammonia present

(iv) A limitation may be imposed by the slow or incomplete hydrolysis of TKN to ammonia

(v) Relatively large sample requirements for analysis may unduly stress small bench-scale reactors.

For denitrification, possible analyses are limited to nitrate disappearance or to dinitrogen appearance. As discussed in "Standard Methods" (APHA, 1977), nitrate analysis is difficult and prone to interference, while the monitoring of nitrogen evolution is complicated by problems of leakage, oxide formation, solubility and entrainment, and by the high nitrogen component of the air.

In summary, any program to determine nitrogen transformation rates must carefully choose the parameters to monitor and must have sufficient resources and manpower to enable the development of a satisfactory analytical technique.

This programme was hampered by an initial lack of appreciation of the difficulties associated with nitrogen analysis and by an inadequate manpower budget to develop the necessary techniques. As a consequence, neither the chosen nitrogen parameter nor the accuracy of its determination were fully optimized.

CHAPTER 8

CONCLUSIONS

A benchscale Bardenpho reactor averaged 95% total Nitrogen removal at 18°C, 93% at 14°C, 54% at 10°C and 79% at 6°C. Average BOD removals in excess of 91% were observed at all temperatures. Average phosphorus removals exceeded 87% except for 81% recorded at 6°C.

The maximum unit nitrification rates observed in this work were 1.76, 1.44, 0.38 and 0.42 (mg oxidized N/gm MLSS/hr), recorded at 18°C, 14°C, 10°C and 6°C respectively.

The maximum unit rates for wastewater substrate denitrification and endogenous denitrification were 1.52, 0.88, 0.71, 0.36 and 0.95, 0.86, 0.60, 0.31 (mg oxidized N/gm MLSS/hr) at 18°C, 14°C, 10°C and 6°C respectively.

The apparently low unit nitrification rates reflect the actual operating conditions of this work and of combined sludge nitrification generally. The most influential factors included: high system C:N ratios (typical of combined sludges), giving rise to small nitrifier fractions in the biomass; suboptimum system pH; possible heavy metal inhibition; the unreliability of MLSS and MLVSS as active-biomass monitoring parameters; and non-optimization of the system operation and control.

At soluble TKN concentrations below 3 to 4 mg/L, nitrification rates became substrate limited. The observed denitrification rates may have been increased by shorther HRT in the anoxic reactors, higher nitrate concentrations and higher BOD concentrations in the wastewater substrate denitrification basin (#2).

Given higher BOD concentrations in basin #2 to improve denitrification, nitrification in basin #3 would probably suffer unless the BOD:TKN ratio was decreased to, or maintained at, a low value.

Maintenance and control of nitrification poses a greater operational difficulty than does denitrification. Carbon:Nitrogen ratio and sludge age are the key factors in determining the relative ability of a combined sludge to nitrify and denitrify.

With a change in operating temperature from 18°C to 6°C, the average unit nitrification and unit (wastewater substrate) denitrification rates decreased by 75% while the endogenous denitrification decreased by 67%.

Comparisons of unit rates between investigators are handicapped by the lack of consensus on analysis for nitrogen forms and viable biomass. Development of such consensus requires improved techniques for nitrogen and biomass determination in the sewage treatment context.

Comprehensive, small scale, continuous flow experiments of this nature require adequate budgeting for long-time operation and for extensive analysis. Good experimental design is mandatory to adequately and efficiently control and evaluate the system performance.

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A P P E N D I C E S

APPENDIX 1.

LULU ISLAND RAW SEWAGE AND SYNTHETIC SEWAGE COMPOSITION

Lulu Island Raw Sewage

Component	Average Composition
BOD	168 mg/L
COD	-
TKN	43.2 mg/L
Ammonia	-
Nitrate	<0.2 mg/L
Nitrite	0 mg/L
Total Phosphorus	7.5 mg/L
Soluble Phosphorus	5.6 mg/L
Alkalinity	200 mg/L
pH	6.5 - 8.5

Synthetic Sewage Composition

Solution A	NaCl	12,000 mg	
	KCl	2,800 mg	dissolved in 1 litre
	$NaHCO_3$	67,200 mg	
Solution B	$CaCl_2$	2,800 mg	in 1 litre
Solution C	$MgSO_4$	2,000 mg	in 1 litre
Solution D	Nutrient Broth	10 grams	in 5 litres of feed
Solution E	Soap	20,000 mg	in 1 litre
Solution F	Urea	12,000 mg	in 1 litre
Solution G	Starch	40,000 mg	in 1 litre
Solution H	Na_2HPO_4	10,000 mg	in 1 litre
Solution I	$Al_2(SO_4)$ $18H_2O$	10,000 mg	in 1 litre

250 mL of each solution diluted to 5 litre total gave a theoretical BOD of 4000 mg/L of synthetic feed.

APPENDIX 2

COMPARISON OF DETERMINATIONS ON FILTERED AND UNFILTERED SAMPLES INDICATING THE SIGNIFICANT DIFFERENCES IN THE MEASURED ALKALINITY AND pH

Sample	Filtered		Unfiltered	
	pH	Alkalinity	pH	Alkalinity
Feed	7.1	185	7.1	187
#1	7.2	142	7.15	186
#2	7.3	108	7.12	152
#3	7.1	84	7.0	134
#4	7.1	102	6.9	150
#5	7.5	96	7.2	142
Effluent	7.4	96	7.2	96
Sludge	7.3	96	7.2	174

APPENDIX 3

METAL ANALYSES (mg/L)

Date Sample	10/3 Feed	7/4 Feed	21/4 Feed	21/4 Storage	21/4 Effluent	21/4 MLSS	5/5 Feed	19/5 Feed	16/6 Feed	M.O.P.
Na	59	65	-	81	84	89	-	-	-	
K	7.7	7.3	-	7.7	6.9	36.4	-	-	-	
Fe	4.9	6.3	5.6	4.0	2.1	85	-	-	-	
Zn	0.83	0.54	0.37	0.42	0.32	9.64	-	-	-	0.08
Mg	5.19	3.94	4.7	3.97	3.86	24.4	-	-	-	
Cu	0.17	0.25	0.19	0.2	0.14	3.9	-	-	-	0.005
Ni	0.39	0.29	0.15	0.29	0.25	1.4	0.037	0.08	0.06	0.25
Mn	0.17	0.18	0.17	0.16	0.12	1.5	-	-	-	
Cr	0.6	0.18	0.14	0.14	0.12	3.8	0.15	0.10	0.71	0.25
Pb	0.102	0.15	0.137	0.103	0.004	2.39	-	-	-	0.5
Al	0.82	1.52	0.94	1.15	0.6	21.7	-	-	-	
Cd	0.005	0.008	0.004	0.005	0.003	0.120	-	-	-	
Ca	14.4	15.4	15.1	13.3	12.2	65.0	-	-	-	
Hg	0.0006	0.001	0.0014	0.0012	0.0008	0.0101	-	-	-	

NOTES: Feed refers to a sample of fresh sewage taken immediately prior to cold storage.
Storage refers to a sample taken from the feed line to the reactor model.
Effluent refers to unfiltered effluent from the model.
MLSS refers to unfiltered mixed liquor from basin #3.
M.O.P. indicates the minimum threshold concentration for nitrification inhibition. (WPCF, 1977).
All analyses were carried out using Methods for Chemical Analysis of Water and Waste. USEPA Water Quality Lab, Connecticut, Ohio 1971, or modification thereof.