Nitrogen Transformation in Secondary Wastewater Treatment Plants

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NITROGEN TRANSFORMATION IN SECONDARY WASTEWATER TREATMENT PLANTS

BY

MARK LEE MORRIS
B.S., Florida Technological University, 1974

RESEARCH REPORT

Submitted in partial fulfillment of the requirements for the degree of Master of Science in the Graduate Studies Program of the College of Engineering of Florida Technological University

Orlando, Florida
1975
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NITROGEN TRANSFORMATION IN SECONDARY WASTEWATER TREATMENT PLANTS

by

Mark Lee Morris

Abstract

Nitrogen is an essential nutrient for plant and animal life; however, its presence in concentrations exceeding assimilative capacities of receiving water bodies is undesirable. Therefore, the form and concentration of total nitrogen released in wastewater effluents is of great concern.

During the course of this study, the nitrogen analysis was performed on the various unit processes of the Florida Technological University wastewater treatment plant. The average percent removal of nitrogen between plant influent and clarifier effluent was 30.5% during the month of August 1975. It is believed that the nitrogen removal is attributed to luxury uptake by the biomass through the plant. The clarifier effluent was highly nitrified containing an average ammonia nitrogen concentration of 0.76 milligrams per liter and a nitrate nitrogen concentration of 16.47 milligrams per liter. The extent to which nitrification took place was 93 - 98% with an average of 96.5% for the month of August.
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INTRODUCTION

Although the main concern of secondary wastewater treatment plants is the removal of carbonaceous BOD, environmentally speaking, nitrogen transformation and removal is equally important. Provoking an interest in this aspect of treatment is the Florida Technological University secondary wastewater treatment plant, an extended aeration facility, which has a design capacity of five hundred thousand gallons per day. During the month of August 1975, it received an average daily flow of approximately one hundred thousand gallons while servicing a student population of 5,400. Previous reports had indicated that nitrification and possibly denitrification phenomena may be taking place within the plant at a higher degree than would normally be expected. The usual effects that a conventional secondary wastewater treatment process has on various forms of nitrogen are: first, that soluble organic nitrogen in the form of urea and amino acids is 15-25% removed; second, that ammonia ($NH_2/NH_4^+$) is less than 10% removed; third, that nitrate ($NO_3^-$) is unaffected; and fourth, that removal of total nitrogen entering the process is 10-20%.  

An increasing interest has developed to study nitrogen transformation occurring in the Florida Technological University secondary wastewater treatment plant. The facility and stations
where sampling took place are presented in Figure 1 with the wastewater flow diagram being shown in Figure 2. At the time of analysis no sludge was being mechanically wasted from the system; therefore, digester 3 and 4 (Figure 1) were not in use. Thus, wastewater enters the plant, in the raw, at the wet well where it is pumped to the contact stabilization tank for aeration. From here it passes to the clarifiers where separation of solids and liquor takes place. Air pumps lift the solids from the bottom of the clarifiers to the reaeration tank where they are concentrated and recycled to the contact stabilization tank. Clarifier supernatant passes to the chlorination tank from which it is pumped to the polishing pond or lagoon and then to irrigation fields.

**Objectives**

The broad objective of this study is to evaluate changes in nitrogen forms within the various processes of secondary wastewater treatment plants. Specifically, samples were collected from various units of the Florida Technological University wastewater treatment plant to investigate:

1. Nitrogen forms within the liquor and solid fractions of wastewater samples collected from various processes in the system. The units sampled include raw, contact tank, reaeration tank, final clarifier and lagoon.

2. Possible nitrification and denitrification phenomena taking place in the system.
Fig. 1. FTU Secondary Wastewater Treatment Plant, with Sampling Stations

1. 63000 gallon contact tank
2. 45000 gallon final clarifiers (a & b)
3. 62000 gallon digester #2
4. 30000 gallon digester #1
5. 130000 gallon reaerator
6. 5000 gallon chlorinator
7. polishing pond
8. irrigation pump
9. air blowers
10. sewage lift pumps
11. wet well
12. chlorine supply
13. screen and comminutor
14. sampling stations
Fig. 2. Flow Diagram for FTU Secondary Wastewater Treatment Plant
3. Conceivable kinetic relationships with respect to nitrogen utilization taking place within the system.
CHAPTER II

LITERATURE REVIEW

Recent awareness of the effects of nitrogenous compounds on receiving water bodies has stimulated much research to determine those forms of nitrogen which should be considered potential pollutants and to find various methods for their control. One of the major sources of nitrogenous wastes is found in domestic wastewater, commonly treated by primary and secondary biological processes. These types of treatment usually do not control, nor are they required to remove nitrogenous pollutants. The following is a review of domestic wastewater makeup and biological conditions necessary for nitrogen transformation and removal.

Domestic Wastewater Composition

Protein, or organic nitrogen, present in plants and animals is assimilated by man and passed into wastewater in the form of urine and feces. These excretions are two of the three major constituents found dispersed in domestic wastewater, the third being cellulose. The organic matter present in domestic wastewater is composed of approximately 40% protein, 50% carbohydrates, and 10% fats. Close to 80% of the total nitrogen introduced into domestic wastewater is in the form of urea which is the bulk component found in urine. Organic fecal matter and urine are transformed by bacteria as follows:
The mechanism whereby organic and ammonia nitrogen is converted to nitrite and nitrate nitrogen is referred to as nitrification. Denitrification occurs after nitrification, converting nitrate nitrogen to nitrogen gas.

**Nitrification**

Wild, et al. (1971), made the following statements about process design with respect to nitrification:

With the development and widespread application of the biochemical oxygen demand (BOD) test, it became apparent to many design engineers that high degrees of waste treatment, in terms of BOD removal, could be accomplished at marked saving in capital and operating costs by designing to avoid nitrification.

Although the nitrogenous oxygen demand (NOD) of unnitrified effluents was well understood, sanitary engineers generally dismissed this matter on the basis of three premisses:

1. Nitrification is caused by special organisms, the population of which is minimal in surface waters.

2. The reaction constant for nitrogenous oxidation is small in relation to the constant for carbonaceous matter.

3. Oxidation of ammonia to nitrates simply converts dissolved oxygen (DO) to a form in which it is still available to prevent development of anaerobic conditions.

Thus, from 1940 until the late 1960's the main objective in the U.S. was to design to minimize nitrification.

Today, the need for systems capable of nitrification is becoming more and more understood. It is known that the presence
of ammonia in treatment plant effluents has several undesirable effects: 10, 11 (1) ammonia is oxidized to nitrate in receiving waters, depleting dissolved oxygen. The ammonia nitrogen oxygen demand may be as much as three times that of the carbonaceous oxygen demand in the effluent of conventional secondary wastewater treatment plants. (2) The reaction of ammonia with chlorine forms chloramines, which are less effective disinfectants than free chlorine. (3) Under certain conditions, ammonia is toxic to fish life.

Conditions Necessary for Nitrification

Ammonia nitrogen is predominant in domestic wastewater influents. If environmental conditions are conducive, nitrification will occur because certain chemoautotrophic bacteria (Nitrosomonas Spp. and Nitrobacter Spp.) have the ability to use carbon dioxide as a carbon source, along with this oxidizable substrate as their source of energy for growth and metabolism. The two steps in nitrification are: 12, 13, 14, 15

I. \[2\text{NH}_3 + 3\text{O}_2 + \text{Nitrosomonas} \rightarrow 2\text{NO}_2^- + 2\text{H}_2\text{O} + 2\text{H}^+ + \text{Cells}\]

II. \[2\text{NO}_2^- + \text{O}_2 + \text{Nitrobacter} \rightarrow 2\text{NO}_3^- + \text{Cells}\]

The biological kinetics of growth based on limiting substrate, as proposed by Monod, is as follows: 16

\[\mu = \mu_0 \frac{S}{K_s + S}\]
where: \( \mu = \text{growth rate of microorganisms, day}^{-1} \)
\( \hat{\mu} = \text{maximum growth rate of microorganisms, day}^{-1} \)
\( K_s = \text{half velocity constant} = \text{substrate concentration, mg/l, at half the maximum growth rate} \)
\( S = \text{growth limiting substrate concentration, mg/l} \)

Considering reactions I and II, the reaction involving \textit{Nitrosomonas Spp.} is the rate-controlling step. Under steady-state conditions, very little nitrite will be present in the effluent due to rapid oxidation to nitrate after formation.\(^{17,18}\) Thus, the Monod equation would indicate (if written for the rate-limiting step) that ammonia is the limiting substrate and the growth rate of \textit{Nitrosomonas Spp.} is dependent on its concentration.

The growth rate of \textit{Nitrosomonas Spp.} can be related to the mean cell residence time or solids retention time by the following equations:\(^{19,20}\)

\[
Q_c = \frac{VX_1}{FX_2 + WX_r}
\]

and

\[
Q_c = \frac{1}{\mu}
\]

where:
\( X_1 = \text{MLVSS concentration, mg/l} \)
\( X_2 = \text{effluent VSS, mg/l} \)
\( X_r = \text{return sludge VSS, mg/l} \)
\( W = \text{waste sludge flow, mgd} \)
\( V = \text{volume of aeration plus secondary sedimentation tanks, mg} \)
\( Q_c = \text{mean cell residence time, days} \)
\( F = \text{influent flow rate, mgd} \)
This indicates that the operation or the design of activated sludge systems can be such that nitrification will be promoted by allowing the mean cell residence time or the solids retention time to be greater than the reciprocal growth rate for *Nitrosomonas Spp.*21,22 Beckman, et al. (1972), found that a mean cell residence time of 6.5 days at 18°C and 13°C averaged 90-95% ammonia removal.23 More realistic values for sludge systems are 10-15 days at temperatures above 20°C.24,25

The degree and rate of nitrification can be determined based on detention time and volatile suspended solids concentration by using the following relation proposed by Associated Water and Air Resources Engineers, Inc.:26

\[
\frac{N_e}{N_0} = e^{-K_nX_vt}
\]

where:  
- \(N_e\) = desired effluent ammonia concentration, mg/l  
- \(N_0\) = influent ammonia concentration, mg/l  
- \(K_n\) = gross nitrification rate coefficient, l/mg-day  
- \(X_v\) = concentration of VSS in aeration basin, mg/l  
- \(t\) = hydraulic detention time, days

Typical gross nitrification rate coefficients \((K_n)\) values for various ammonia concentrations and wastes ranged from 0.00039 - 0.00086 liters per milligram day (base e).27

Nitrification can be greatly effected by changes in temperature and pH. The effect of temperature on both maximum growth rate, \(\mu\), and the half saturation constant, \(K_s\) for *Nitrosomonas Spp.* and *Nitrobacter Spp.*, as presented by Downing and Coworkers, is shown
in Figures 3 and 4.\textsuperscript{28,29} Values found by other researchers for \( \mu \) and \( K_s \) are summarized in Tables 1 and 2, respectively.\textsuperscript{30} Courchaine (1968) states optimum temperatures for growth of nitrifiers as 25-28\textdegree C.\textsuperscript{31} Temperatures from 20-30\textdegree C have shown nitrification in the range of 60-100\%.\textsuperscript{32} Investigation of hydrogen ion concentration has indicated that pH values above 10 and below 6 can limit the rate of nitrification critically, as shown in Figure 5.\textsuperscript{33} Optimum pH for nitrifiers for 90-100\% removal of ammonia nitrogen at 20\textdegree C was found by Wild, et al. (1971), to be 7.8-8.9.\textsuperscript{34}

One of the most carefully done studies to determine the effects of dissolved oxygen (DO) on the rate of nitrification was carried out by the Los Angeles County Sanitation District at its Pomona Water Renovation Plant. Nitrification rates determined from the data indicated that nitrification was inhibited as dissolved oxygen concentration decreased, as shown in Figure 6.\textsuperscript{35} Wild, et al. (1971), indicated that nitrification was inhibited if dissolved oxygen levels fell below one milligram per liter.\textsuperscript{36}

Other environmental conditions affecting nitrification are:

1. Concentrations of ammonia nitrogen which should be below 60 milligrams per liter, not to be toxic to nitrifying bacteria.\textsuperscript{37,38}
2. Concentrations of inhibiting heavy metals such as zinc, nickel, chromium, and copper which should be low to favor nitrification.\textsuperscript{39}
3. Barth, et al. (1968), also indicates that toxic materials in wastewater could cause failure of nitrifiers, even though the majority of bacteria in the sludge are not impaired.\textsuperscript{40}
4. Food-to-mass ratio (pounds of BOD removed per pound of mixed liquor volatile
Fig. 3. Temperature Dependence of the Maximum Growth Rates of Nitrifiers

Fig. 4. Temperature Dependence of the Half Saturation Constants of Nitrifiers
<table>
<thead>
<tr>
<th>Organism</th>
<th>$\hat{\alpha}_N$, day$^{-1}$ at Stated Temperature, $^\circ$C</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrosomonas</td>
<td>0.40 0.34 0.57</td>
<td>Activated sludge, wash out</td>
</tr>
<tr>
<td></td>
<td>0.85 0.65 0.17</td>
<td>Activated sludge, math model</td>
</tr>
<tr>
<td></td>
<td>0.57 0.37 0.17</td>
<td>Activated sludge</td>
</tr>
<tr>
<td></td>
<td>0.71 0.48 0.55</td>
<td>Activated sludge</td>
</tr>
<tr>
<td></td>
<td>1.08 1.44</td>
<td>Activated sludge</td>
</tr>
<tr>
<td>Nitrobacter</td>
<td>0.25 0.28 0.34 0.53</td>
<td>Synthetic river water</td>
</tr>
<tr>
<td></td>
<td>0.5 0.53 1.44</td>
<td>Activated sludge</td>
</tr>
</tbody>
</table>
### Table 2

**Half-Saturation Constants for Nitrifiers in Various Environments**

<table>
<thead>
<tr>
<th>Organism</th>
<th>K_s, mg/l-N at Stated Temperature, C</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Nitrosomonas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.8</td>
<td>0.37</td>
<td>3.4</td>
</tr>
<tr>
<td>0.5 to 1.0</td>
<td>3.5</td>
<td>1.0</td>
</tr>
<tr>
<td>0.5</td>
<td>0.25</td>
<td>0.7</td>
</tr>
<tr>
<td>Nitrobacter</td>
<td>0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>0.07</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Activated sludge
- Synthetic river water
- Lab culture
- Warburg analyses
- Lab culture and activated sludge
- Lab culture
- Activated sludge
- Synthetic river water
- Lab culture
- Lab culture
- Lab culture
- Lab culture
- Lab culture
- Lab culture
Fig. 5. Effect of pH on Nitrification Rate (after Sawyer, et al.)
Fig. 6. Effect of Dissolved Oxygen on Nitrification Rate
suspended solids (MLVSS) per day) in the activated sludge tank of
0.25 days$^{-1}$ or less is optimum for nitrification to occur.\textsuperscript{41} Johnson
and Schroepfer (1964) indicated that nitrification is an all-or-nothing
phenomena, and the load factor limit for obtaining reasonably com­
plete nitrification is probably in the range of 0.25 - 0.35 days$^{-1}$;
and at higher load factors, good nitrification may occur, but is
unlikely.\textsuperscript{42}

Knowledge of these parameters and their effects can be used
in order to produce operational or design conditions which favor a
low ammonia effluent.

\textbf{Denitrification}

As a result of increased research in the field, stemming
from the need for nitrification, another form of nitrogen trans­
formation has been recommended. This type of nitrogen conversion
is found in systems which are capable of producing a denitrified
or nitrogen-free effluent. The reason for this is based on the
following problems associated with waters receiving nitrogenous
effluents: (1) Nitrogen supplies an inorganic nutrient source for
the growth of nuisance algae and aquatic weeds.\textsuperscript{43,44} (2) In concen­
trations above ten milligrams per liter, nitrogen is a potential
health danger, causing Methemoglobinemia in infants if present in
public drinking water or in receiving waters used for public con­
sumption.\textsuperscript{45,46}
Limiting Nutrients

Ericsson \(^4^7\) and Miller and Maloney \(^4^8\) indicate that phosphorus, not nitrogen, is the limiting factor in natural waters for controlling nuisance algae. It has also been stated that certain types of blue-green algae have the ability to fix atmospheric nitrogen to use as an energy source when nitrogen is limiting; therefore, phosphorus must be controlled. \(^4^9\) Gibson (1971) points out that nitrogen to phosphorus ratios of between 10:1 and 15:1 are reasonable for algae cells and that if either nitrogen or phosphorus drops below this ratio, it becomes limiting and therefore growth of the organism does not proceed at as fast a rate as theoretically possible. Thus, depending on the environmental conditions and on economics, it may be more sensible to limit nitrogen rather than phosphorus for controlling nuisance algae. \(^5^0\)

Nitrogen Removal in Wastewater Treatment Plants

Nitrogen removal from a system can occur either as a form of luxury uptake by bacteria and/or by denitrification. Approximately one pound of nitrogen is necessary for every twenty pounds of BOD removed to insure bacterial growth. \(^5^1\) Mulbarger (1971) points out that nitrogen removal caused by sludge synthesis in high-rate systems totals 20-40% before entering nitrification process. \(^5^2\) Barth, et al. (1966), in a study of several existing activated sludge plants, shows removals of 13-61%. \(^5^3\) Denitrification has been noted to occur in secondary wastewater treatment plant clarifiers and in oxidation ditches where the interior of the sludge particle becomes
anaerobic in liquors containing low DO's. This is usually indicated by floating sludge which can produce a problem in sludge recovery.\(^5^4,^5^5,^5^6\)

**Conditions Necessary for Denitrification**

Several common types of facultative heterotrophic bacteria under anaerobic conditions are able to reduce nitrate to gaseous \(N_2, NO,\) or \(N_2O.\) These organisms are of the genera *Pseudomonas Spp.*, *Micrococcus Spp.*, *Achromobacter Spp.*, *Bacillus Spp.*, and *Spirillum Spp.*\(^5^7\) The reaction is represented in the following equation where nitrate serves as an oxygen source and methanol as the substrate:\(^5^8\)

\[
\text{NO}_3^- + \text{CH}_3\text{OH} \rightarrow \text{CO}_2 + 0.5\text{N}_2 + 2\text{H}_2\text{O}
\]

Monod's relationship for the influence of nitrate on the growth rate of denitrifiers followed the same basic equation as presented in the case of nitrification:\(^5^9\)

\[
\mu_D = \tilde{\mu}_D \frac{D}{K_D + D}
\]

where:

- \(\mu_D\) = growth rate, day\(^{-1}\)
- \(\tilde{\mu}_D\) = maximum denitrifier growth rate, day\(^{-1}\)
- \(D\) = concentration of nitrate nitrogen, mg/l
- \(K_D\) = half saturation constant, mg/l \(\text{NO}_3-N\)

Denitrification rates can be related to microbial growth rates and solids retention time by the following equations:\(^6^0,^6^1,^6^2\)

\[
q_D = \mu_D/v_D
\]

and
\[
\frac{1}{Q_c} = y_D \, q_D - K_d
\]

where: 
- \( q_D = \) nitrate removal rate, \( lb \) \( NO_3^-\)-N removed/\( lb \) VSS/day
- \( y_D = \) denitrifier gross yield, \( lb \) VSS grown/\( lb \) \( NO_3^-\)-N removed
- \( Q_c = \) solids retention time, days
- \( K_d = \) decay coefficient, \( day^{-1} \)

These types of relationships allow for operational parameters or design parameters to be adjusted so that stable populations of denitrifiers can exist, promoting denitrification. Various kinetic constants for denitrification are presented in Table 3 by a number of investigations.\(^6\) The net yield coefficient, \( \overline{y}_D \), can be related to the gross yield coefficient, \( Y_D \), by the equation:\(^6\)

\[
\overline{y}_D = \frac{Y_o \, q_D - K_d}{q_D} = \frac{Y_D}{(1 + Q_c \, K_d)}
\]

where: \( \overline{y}_D = \) denitrifier net yield, \( lb \) VSS/lb \( NO_3^-\)-N removed

Typical solids retention times of 4 days at temperatures of 20°C and 30°C and 8 days at 10°C have been shown necessary to prevent denitrifier washout.\(^6\)

Both denitrifier growth rate and nitrate removal rate are significantly affected by temperature and pH as presented in Figures 7 and 8, respectively.\(^6\) A temperature of 10°C or higher was shown by Sutton, et al. (1975), to produce nitrate plus nitrite nitrogen removal of less than one milligram per liter in a stirred tank reactor.\(^6\) Denitrification is suppressed by the presence of dissolved oxygen adjacent to denitrifying microbes. This is due to the rapid rate of aerobic respiration versus the slower rate of assimilatory...
**TABLE 3**

VALUES OF DENITRIFICATION YIELD AND DECAY COEFFICIENTS FOR VARIOUS INVESTIGATIONS USING METHANOL

<table>
<thead>
<tr>
<th>Process Description</th>
<th>$q_{D'}$ (-1) days</th>
<th>$\overline{Y}_{D'}$ lb VSS (\frac{lb \ NO_3^-N \ rem.}{lb \ VSS})</th>
<th>$Y_{D'}$ lb VSS (\frac{lb \ NO_3^-N \ rem.}{lb \ VSS})</th>
<th>$K_{d'}$ (-1) days</th>
<th>Temp, C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended growth, no solids recycle, continuous</td>
<td>Variable</td>
<td>Variable</td>
<td>0.57</td>
<td>0.05</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Variable</td>
<td>Variable</td>
<td>0.63</td>
<td>0.04</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>0.12 to 0.32</td>
<td>0.55 to 1.4</td>
<td>-</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>0.16 to 0.9</td>
<td>0.57 to 0.73</td>
<td>-</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>Suspended growth, batch</td>
<td>0.24 to 3.8</td>
<td>0.45 to 1.43</td>
<td>-</td>
<td>-</td>
<td>5 to 27</td>
</tr>
<tr>
<td></td>
<td>Variable</td>
<td>0.53</td>
<td>-</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>Suspended growth, solids recycle, continuous</td>
<td>- (b)</td>
<td>0.58</td>
<td>0.77</td>
<td>0.04 (d)</td>
<td>10 to 20</td>
</tr>
<tr>
<td></td>
<td>0.131 to 0.347</td>
<td>0.542 to 0.703</td>
<td>0.84</td>
<td>0.04</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.49</td>
<td>0.65</td>
<td>0.04 (d)</td>
<td>16 to 18</td>
</tr>
<tr>
<td></td>
<td>- (e)</td>
<td>0.7 to 1.4</td>
<td>0.83 to 1.67</td>
<td>0.04 (d)</td>
<td>10 to 20</td>
</tr>
<tr>
<td>Suspended growth, solids recycle, continuous, aerated stabilization</td>
<td>0.30</td>
<td>0.061</td>
<td>0.65</td>
<td>0.19</td>
<td>10 to 20</td>
</tr>
</tbody>
</table>

\(b\) $q$ not given, but $\Theta_C = 8.0$

\(c\) calculated

\(d\) assumed

\(e\) $\Theta_C = 3$ to 6 days
Fig. 7. Effect of Temperature on Denitrification Rate
Fig. 8. Effect of pH on Denitrification Rate
nitrate reduction. 68 Baumann (1972) indicates that dissolved oxygen concentrations less than 0.5 milligrams per liter at a pH of about 6.5 are necessary for denitrification. 69 A possible physical condition which may have to be introduced into the system is a source of hydrogen in the form of an organic carbon substrate such as methanol or glucose. 70 Nitrate nitrogen must also be present as an oxygen source before denitrification can take place; therefore, complete nitrification is desirable prior to denitrification. 71

According to past and recent research studies, biological nitrification and denitrification are both environmentally and physically sensitive means of nitrogen transformation. In addition, future investigation should prove that they are also the most sensible when compared to other methods of nitrogen control.
EXPERIMENTAL PROCEDURE

Samples were collected every three hours for a period of twelve hours from the wet well, the contact tank, the clarifier supernatant, the reaeration tank and the lagoon, as shown in Figure 1. Flow-weighted, twelve-hour composite samples, to be analyzed for ammonia nitrogen, organic nitrogen, and nitrate nitrogen, were preserved with eight milliliters per liter concentrated sulfuric acid; while those analyzed for nitrite nitrogen were preserved with forty milligrams per liter mercuric chloride. The samples were transported directly to the FTU environmental chemistry laboratory, where they were refrigerated at $4^\circ C$ and analyzed within 48 hours.

In order to determine the ammonia and organic nitrogen concentrations in the liquor fraction of each sample, an aliquot from a stirred sample was taken, filtered through Whatman No. 1 filter paper, then analyzed. The ammonia and organic nitrogen associated with the solid fraction of the sample were determined by blending the sample for sixty seconds in a Waring blender (to release nitrogen bound within the solids) and then by analyzing an unfiltered aliquot.

Nitrate and nitrite nitrogen present in the liquor fraction of the sample were determined on an unblended aliquot which was filtered through Whatman No. 1 filter paper and then through Milli-
pore 0.45\(\mu\) pore-size filter paper. Nitrate and nitrite nitrogen in the solids fraction of the sample were determined by blending for sixty seconds in a Waring blender (to release nitrate and nitrite ions bound in the solids), then filtered through Whatman No. 1 filter paper, followed by filtration through millipore 0.45\(\mu\) pore-size filter paper prior to analysis.

The procedures used in analyzing for the four forms of nitrogen present in wastewater were taken from Standard Methods for the Examination of Water and Wastewater\(^7\) and the Environmental Protection Agency's Methods for Chemical Analysis of Water and Wastes.\(^7\)

Organic and ammonia nitrogen were analyzed by the Kjeldahl distillation procedure with a titrimetric finish using 0.02 normal sulfuric acid as a titrant. The Brucine Method was used to determine nitrate nitrogen. Temperature was controlled at 100\(^\circ\)C using a steam bath. The standard curve is presented in Figure 9. The correlation coefficient (\(R\)) for the data is 99.62% with a standard deviation (\(\sigma\)) of \(\pm 0.03\) milligrams per liter. Nitrite nitrogen was analyzed using a modification of the Griess-Ilosvay Diazotization Method employing two reagents: sulfanilic acid and 1-naphthylamine hydrochloride. The standard curve for this procedure is presented in Figure 10. The correlation coefficient for the data is 99.99% with a standard deviation of \(\pm 0.00\) milligrams per liter. A Beckman DB-GT Spectrophotometer was used for colorimetric analysis.
$\text{Absorbence} = 1.07 \times \text{Concentration} - 0.026$

$R = 99.6\%$

$\sigma = \pm 0.03 \text{ mg/l}$

**Fig. 9.** Standard Curve for the Determination of Nitrate Nitrogen
Absorbance = 6.56 x Concentration - 0.009

\[ R = 99.99\% \]

\[ \sigma = 0.00 \text{ mg/l} \]

Fig. 10. Standard Curve for the Determination of Nitrite Nitrogen
CHAPTER IV

RESULTS AND DISCUSSION

The four forms of nitrogen, namely organic nitrogen, ammonia nitrogen ($\text{NH}_3$-$\text{N}$), nitrite nitrogen ($\text{NO}_2$-$\text{N}$), and nitrate nitrogen ($\text{NO}_3$-$\text{N}$), occurring in the various stages of the Florida Technological University secondary wastewater treatment plant for the month of August 1975 are presented in Table 4. Additional data taken from the plant's monthly report are shown in Table 5. Pie diagrams of nitrogen transformations taking place within the various processes of the plant are presented in Figure 11. Also, the percentages and average concentrations of each form of nitrogen which occurs in the liquor and solids fractions of the wastewater at each stage of treatment are shown in Figure 12. Nitrogen enters the plant in the raw wastewater predominantly in the liquor fraction as ammonia nitrogen. Nitrogen present in the contact stabilization tank and the reaeration tank is mainly in the form of organic nitrogen in the solids fraction, and nitrate nitrogen in the liquor fraction. Finally, nitrogen in the liquor fraction leaves the plant through the final clarifier in the nitrate form.

Average nitrogen concentrations through the Florida Technological University Plant for the month of August are presented in Table 6. The nitrogen removal between the raw and final clarifier effluent averaged 6.0 pounds per day or 30.5%. The average $\text{BOD}_5$
<table>
<thead>
<tr>
<th>Process</th>
<th>Form</th>
<th>Fraction</th>
<th>Concentration in mg/l-N of Composite Samples, Collected on</th>
<th>Average Nitrogen Concentrations mg/l-N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>8/04</td>
<td>8/06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic-N</td>
<td>Liquor</td>
<td>2.00</td>
<td>2.00</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>Solid</td>
<td>1.88</td>
<td>1.94</td>
<td>2.65</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>Liquor</td>
<td>21.72</td>
<td>23.04</td>
<td>25.17</td>
</tr>
<tr>
<td></td>
<td>Solid</td>
<td>0.00</td>
<td>0.44</td>
<td>0.00</td>
</tr>
<tr>
<td>Raw</td>
<td>Liquor</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>NO₂-N</td>
<td>Solid</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>NO₃-N</td>
<td>Liquor</td>
<td>0.18</td>
<td>0.22</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>Solid</td>
<td>0.09</td>
<td>0.04</td>
<td>0.06</td>
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<tr>
<td>Total N</td>
<td></td>
<td></td>
<td>25.87</td>
<td>27.70</td>
</tr>
</tbody>
</table>
TABLE 4 (cont'd.)

NITROGEN ANALYSES FOR COMPOSITE SAMPLES FROM FTU WASTEWATER TREATMENT PLANT

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Organic-N</th>
<th>NH$_3$-N</th>
<th>NO$_2$-N</th>
<th>NO$_3$-N</th>
<th>Total N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquor</td>
<td>0.48</td>
<td>0.22</td>
<td>0.48</td>
<td>0.22</td>
<td>0.30</td>
</tr>
<tr>
<td>Solid</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Liquor</td>
<td>0.13</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Liquor</td>
<td>0.24</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Liquor</td>
<td>0.17</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Solid</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Liquor</td>
<td>0.26</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Solid</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Liquor</td>
<td>0.26</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Solid</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Liquor</td>
<td>0.26</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Solid</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Liquor</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Solid</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Liquor</td>
<td>0.25</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Solid</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Liquor</td>
<td>0.25</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Solid</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Liquor</td>
<td>0.25</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Solid</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Liquor</td>
<td>0.25</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
TABLE 4 (cont'd.)

NITROGEN ANALYSES FOR COMPOSITE SAMPLES FROM
FTU WASTEWATER TREATMENT PLANT

<table>
<thead>
<tr>
<th>Process</th>
<th>Form</th>
<th>Fraction</th>
<th>Concentration in mg/l-N of Composite Samples, Collected on</th>
<th>Average Nitrogen Concentrations mg/l-N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>8/04  8/06  8/11  8/13  8/18  8/20  8/25  8/27</td>
<td></td>
</tr>
<tr>
<td>Contact Stabilization Tank</td>
<td>Organic-N</td>
<td>Liquor</td>
<td>1.18  1.09  0.60  0.83  0.89  0.79  0.75  0.86</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solid</td>
<td>58.03  58.40  58.13  56.39  57.09  55.33  57.44  56.48</td>
<td>57.16</td>
</tr>
<tr>
<td></td>
<td>NH₃-N</td>
<td>Liquor</td>
<td>1.92  1.65  1.59  1.58  1.60  0.80  0.93  0.35</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solid</td>
<td>2.61  2.91  4.04  2.55  1.78  1.45  5.52  1.84</td>
<td>2.84</td>
</tr>
<tr>
<td></td>
<td>NO₂--N</td>
<td>Liquor</td>
<td>0.02  0.02  0.01  0.01  0.02  0.02  0.03  0.03</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solid</td>
<td>0.00  0.00  0.00  0.01  0.00  0.01  0.00  0.01</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solid</td>
<td>0.00  0.00  1.27 1.42 0.00 2.17 0.00 2.86</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>Total N</td>
<td></td>
<td>75.33 78.37 84.54 70.00 78.26 68.90 83.11 78.86</td>
<td>77.29</td>
</tr>
</tbody>
</table>
TABLE 4 (cont'd.)

NITROGEN ANALYSES FOR COMPOSITE SAMPLES FROM FTU WASTEWATER TREATMENT PLANT

<table>
<thead>
<tr>
<th>Process</th>
<th>Form</th>
<th>Fraction</th>
<th>Concentration in mg/l-N of Composite Samples, Collection on</th>
<th>Average Nitrogen Concentrations mg/l-N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>8/04</td>
<td>8/06</td>
</tr>
<tr>
<td>Reaeration Tank</td>
<td>Organic-N</td>
<td>Liquor</td>
<td>1.25</td>
<td>1.23</td>
</tr>
<tr>
<td>Solid</td>
<td></td>
<td>Solid</td>
<td>67.74</td>
<td>68.58</td>
</tr>
<tr>
<td>NH\textsubscript{3}-N</td>
<td>Liquor</td>
<td>0.40</td>
<td>0.38</td>
<td>0.13</td>
</tr>
<tr>
<td>Solid</td>
<td></td>
<td>Solid</td>
<td>3.51</td>
<td>4.40</td>
</tr>
<tr>
<td>NO\textsubscript{2}-N</td>
<td>Liquor</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Solid</td>
<td></td>
<td>Solid</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>NO\textsubscript{3}-N</td>
<td>Liquor</td>
<td>12.51</td>
<td>13.98</td>
<td>18.19</td>
</tr>
<tr>
<td>Solid</td>
<td></td>
<td>Solid</td>
<td>1.08</td>
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<tr>
<td>Total N</td>
<td></td>
<td></td>
<td>86.51</td>
<td>88.59</td>
</tr>
</tbody>
</table>
### TABLE 4 (cont'd.)

**NITROGEN ANALYSES FOR COMPOSITE SAMPLES FROM FTU WASTEWATER TREATMENT PLANT**

<table>
<thead>
<tr>
<th>Process</th>
<th>Form</th>
<th>Fraction</th>
<th>Concentration in mg/l-N of Composite Samples, Collection on</th>
<th>Average Nitrogen Concentrations mg/l-N</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>8/04</td>
<td>8/06</td>
</tr>
<tr>
<td>Lagoon</td>
<td>Organic-N</td>
<td>Liquor</td>
<td>0.30</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solid</td>
<td>0.30</td>
<td>0.29</td>
</tr>
<tr>
<td>Lagoon</td>
<td>NH₃-N</td>
<td>Liquor</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solid</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Lagoon</td>
<td>NO₂⁻-N</td>
<td>Liquor</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solid</td>
<td>0.11</td>
<td>0.01</td>
</tr>
<tr>
<td>Lagoon</td>
<td>NO₃⁻-N</td>
<td>Liquor</td>
<td>2.45</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solid</td>
<td>2.45</td>
<td>1.38</td>
</tr>
<tr>
<td>Lagoon</td>
<td>Total N</td>
<td></td>
<td>3.32</td>
<td>3.00</td>
</tr>
</tbody>
</table>
### TABLE 5

**PARAMETERS MEASURED BY THE STAFF AT FTU SECONDARY WASTEWATER TREATMENT PLANT, TAKEN FROM THEIR MONTHLY REPORT**

<table>
<thead>
<tr>
<th>Date</th>
<th>Day</th>
<th>Daily Flow MGD</th>
<th>Daily BOD&lt;sub&gt;5&lt;/sub&gt; Raw mg/l</th>
<th>BOD&lt;sub&gt;5&lt;/sub&gt; Final mg/l</th>
<th>BOD&lt;sub&gt;5&lt;/sub&gt; Removal mg/l</th>
<th>MLSS Contact Tank mg/l</th>
<th>MLSS Reaeration Tank mg/l</th>
<th>DO Raw mg/l</th>
<th>DO Final mg/l</th>
<th>Temp WW °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/04/75</td>
<td>Mon</td>
<td>0.1003</td>
<td>165.0</td>
<td>0.8</td>
<td>164.2</td>
<td>4529</td>
<td>5187</td>
<td>4.7</td>
<td>10.7</td>
<td>26.7</td>
</tr>
<tr>
<td>8/06/75</td>
<td>Wed</td>
<td>0.0870</td>
<td>165.0</td>
<td>0.8</td>
<td>164.2</td>
<td>4444</td>
<td>5009</td>
<td>0.7</td>
<td>10.3</td>
<td>28.3</td>
</tr>
<tr>
<td>8/11/75</td>
<td>Mon</td>
<td>0.0818</td>
<td>165.0</td>
<td>0.8</td>
<td>164.2</td>
<td>4387</td>
<td>4808</td>
<td>2.5</td>
<td>11.3</td>
<td>27.8</td>
</tr>
<tr>
<td>8/13/75</td>
<td>Wed</td>
<td>0.1135</td>
<td>165.0</td>
<td>2.3</td>
<td>137.7</td>
<td>4294</td>
<td>4976</td>
<td>2.1</td>
<td>10.1</td>
<td>27.8</td>
</tr>
<tr>
<td>8/18/75</td>
<td>Mon</td>
<td>0.0924</td>
<td>165.0</td>
<td>2.3</td>
<td>137.7</td>
<td>4660</td>
<td>5266</td>
<td>0.2</td>
<td>7.6</td>
<td>28.9</td>
</tr>
<tr>
<td>8/20/75</td>
<td>Wed</td>
<td>0.1003</td>
<td>165.0</td>
<td>4.7</td>
<td>118.3</td>
<td>4504</td>
<td>5173</td>
<td>1.1</td>
<td>10.8</td>
<td>27.8</td>
</tr>
<tr>
<td>8/25/75</td>
<td>Mon</td>
<td>0.0792</td>
<td>165.0</td>
<td>1.6</td>
<td>123.4</td>
<td>4422</td>
<td>4892</td>
<td>2.2</td>
<td>8.5</td>
<td>27.2</td>
</tr>
<tr>
<td>8/27/75</td>
<td>Wed</td>
<td>0.0870</td>
<td>165.0</td>
<td>1.6</td>
<td>123.4</td>
<td>4927</td>
<td>4914</td>
<td>2.5</td>
<td>10.3</td>
<td>28.9</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>0.0927</td>
<td>138.3</td>
<td>2.4</td>
<td>135.9</td>
<td>4521</td>
<td>5028</td>
<td>2.0</td>
<td>10.0</td>
<td>27.9</td>
</tr>
</tbody>
</table>
Fig. 11. Transformation of Nitrogen Through Various Stages of the FTU Secondary Treatment Plant Based on Four Week Mass Balance
Fig. 12. Concentrations and Percentages of Nitrogen Present in Solids and Liquors at Various Stages of the FTU Secondary Treatment Plant
### TABLE 6

**AVERAGE NITROGEN CONCENTRATIONS THROUGH FTU WASTEWATER TREATMENT PLANT**

<table>
<thead>
<tr>
<th>Position</th>
<th>Raw</th>
<th>Clarifier</th>
<th>Contact Stabilization</th>
<th>Reaeration</th>
<th>Lagoon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Form</td>
<td></td>
<td>Liquor</td>
<td>Solids</td>
<td>Liquor</td>
<td>Solids</td>
</tr>
<tr>
<td>$\text{NH}_3\text{-N}$</td>
<td>20.19</td>
<td>0.68</td>
<td>0.08</td>
<td>1.30</td>
<td>2.84</td>
</tr>
<tr>
<td>Org-N</td>
<td>1.82</td>
<td>0.25</td>
<td>0.07</td>
<td>0.87</td>
<td>57.16</td>
</tr>
<tr>
<td>$\text{NO}_3\text{-N}$</td>
<td>0.66</td>
<td>16.06</td>
<td>0.41</td>
<td>14.16</td>
<td>0.97</td>
</tr>
<tr>
<td>$\text{NO}_2\text{-N}$</td>
<td>0.03</td>
<td>0.03</td>
<td>0.00</td>
<td>0.02</td>
<td>0.00</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>22.70</strong></td>
<td><strong>17.02</strong></td>
<td><strong>0.55</strong></td>
<td><strong>16.32</strong></td>
<td><strong>60.97</strong></td>
</tr>
<tr>
<td><strong>Average Nitrogen</strong></td>
<td><strong>22.70</strong></td>
<td><strong>2.57</strong></td>
<td><strong>17.02</strong></td>
<td><strong>0.55</strong></td>
<td><strong>16.32</strong></td>
</tr>
</tbody>
</table>
removal for the plant is 105.1 pounds per day or a ratio of 17.7:1 pounds of BOD$_5$ removed per pound of nitrogen removed (see Appendix A). This ratio is in good agreement with value stated in literature review.

A high degree of nitrification was shown to have taken place within the plant for the month of August. Ammonia transformation between plant influent and clarifier effluent ranged from 93-98% with an average value of 96.5%. Other average environmental and physical parameters under which the FTU plant operated, shown in Table 5, compared favorably with those established as necessary for nitrification by other researchers in the literature review. Plant environmental and physical conditions noted as responsible for such a high degree of nitrification are: (1) greater solids retention time than the reciprocal growth rate of nitrifiers (due to very small amounts of sludge being wasted in the plant effluent); (2) average wastewater temperature of 27.9°C (which is favorable to nitrifiers); (3) ammonia nitrogen concentration present in the influent well below the toxic level for nitrifiers; (4) an average dissolved oxygen concentration in the influent and effluent of 2.0 and 10.0 milligrams per liter respectively; and (5) an average food-to-mass ratio of 0.059 in the contact tank (assuming 75% of MLSS equals MLVSS - see Appendix B). The pH would be the only questionable parameter which might be expected to inhibit nitrification. It averaged 7.0 entering the plant and 6.3 in the effluent. In a study of the effect of pH on nitrification it was found that abrupt changes in pH from 7.2 to 6.4 caused no adverse effects. However, when the pH dropped below 6.4,
nitrification was impaired considerably. This short-range change in pH exhibited by the FTU plant is a good indicator that nitrification is taking place and not inhibited. As alkalinity is destroyed by the oxidation of ammonia, carbonic acid is produced, lowering the pH as indicated by the reaction:

\[ \text{NH}_4^+ + 2\text{O}_2 + 2\text{HCO}_3^- \rightarrow \text{NO}_3^- + 2\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \]

The average gross nitrification rate coefficient for the month was determined for the contact stabilization tank, where nearly all ammonia nitrogen transformation occurs as indicated by Figure 11 and Table 4. Calculations (see Appendix C) produced a gross nitrification rate (K_n) of 0.00069 liter per milligram-day, in good agreement with values cited in literature review.

The percentage transformation of ammonia nitrogen with varying concentrations of ammonia nitrogen in the influent is shown in Figure 13 (see Appendix D). Linear regression analysis was performed on the data which produced the following straight line relation:

\[ \% \Delta \text{NH}_3-N = -0.27 \times \text{Influent NH}_3-N \text{ lb/day} + 100.74\% \]

The correlation coefficient for the data was 97.18% with a standard deviation of ±26.26% \( \Delta \text{NH}_3-N \). From this relationship it is obvious that the percentage ammonia nitrogen removal decreases by increasing the ammonia nitrogen concentration in the influent. Theoretical examination of the data indicated that at the present flow, approximately 0.1 MGD, ammonia nitrogen removal would be greater than or equal to 90% for concentrations less than 40 pounds per day as am-
\[ \% \Delta \text{NH}_3\text{-N} = -0.27 \times \text{Influent NH}_3\text{-N lb/day} + 100.74\% \\
R = 97.18\% \\
\sigma = \pm 26.26 \% \Delta \text{NH}_3\text{-N} \]

Fig. 13. Percentage of Ammonia-Nitrogen Removal Occurring in the FTU Secondary Treatment Plant with Increasing Ammonia Nitrogen in Influent
monia nitrogen entering the plant. Further investigation indicated that if the plant were operating at maximum flow of 0.5 MGD with the present average influent ammonia nitrogen concentration of 20.38 milligrams per liter, that 77.8% ammonia nitrogen removal would occur.

Graphical analysis of nitrogen removed to mass (mixed liquor suspended solids) ratio versus food to mass ratio present in Figure 14 produced the following linear relation (see Appendix E):

\[ \Delta N/\text{day}/\text{MLSS} = 0.182 \times \text{BOD}_5/\text{day}/\text{MLSS} - 0.0057 \]

The correlation coefficient for the data is 93.5% with a standard deviation of ±0.00159 lb/lb/day. Examination of the graph shows substrate removal taking place at zero change in nitrogen. This would occur at times when zero nitrogen would enter the plant; therefore, the microbial population would remove the substrate by utilizing nitrogen released from dead cells. Theoretically, the amount of \( \text{BOD}_5 \) which could be removed if such a situation existed and mixed liquor suspended solids were held at 4500 milligrams per liter with an average flow of 0.1 MGD would be 89.2 milligrams per liter or 74.4 pounds per day.

The FTU treatment plant has a lagoon which had recently been filled with effluent from the plant prior to the analysis. The lagoon exhibited nitrogen removals in the range of 67 - 83% (see Appendix F). The nitrogen present in the lagoon was predominantly in the nitrate and organic nitrogen form, liquor and solid fractions, respectively.
Fig. 14. Pounds of Nitrogen Removal Occurring in FTU Wastewater Treatment Plant with Respect to BOD₅ Removal and Mixed Liquor Suspended Solids
CHAPTER V

CONCLUSIONS

The nitrogen analysis performed on the Florida Technological University secondary wastewater treatment plant for the month of August 1975 yielded the following conclusions:

1. Nitrogen entered the system mainly in the liquor as ammonia. In the contact stabilization unit and the reaeration unit, nitrogen occurred mostly as organic and nitrate, in the solids and liquor fractions, respectively. When leaving the plant through the final clarifier, nitrate nitrogen in the liquor fraction predominated.

2. The nitrogen removal between the plant influent and clarifier effluent was due to a luxury uptake by the bacteria which averaged 30.5%. The total nitrogen in the plant influent during the month of August 1975 averaged 25.27 milligrams per liter and the clarifier effluent averaged 17.58 milligrams per liter.

3. The ratio of 5-day BOD removed to nitrogen removed through the plant averaged 17.7:1.

4. Ammonia nitrogen removal between plant influent and clarifier effluent averaged 96.5%. The ammonia nitrogen influent concentration averaged 20.38 milligrams per liter, and in the clarifier effluent averaged 0.76 milligrams per liter. Nitrate nitrogen concentration increased; however, from 0.98 milligrams per liter
in the influent to 16.47 milligrams per liter in the clarifier effluent. This indicates a high degree of nitrification taking place in the plant.

5. The average gross nitrification rate coefficient ($K_N$) for the contact stabilization tank under field conditions was 0.00069 liter per milligram-day.

6. The average nitrate nitrogen concentration in the liquor fraction for the month of August from the contact tank, reaeration tank, and final clarifier are approximately equal. The contact stabilization tank averaged 14.13 milligrams per liter, the reaeration tank averaged 14.16 milligrams per liter and the final clarifier effluent averaged 16.06 milligrams per liter.

7. A reduction in total nitrogen concentration in the lagoon effluent when compared to clarifier effluent was detected. Under test conditions, the total nitrogen decreased from 17.58 milligrams per liter to 4.67 milligrams per liter through the lagoon, or an average removal of 73.4%.
APPENDIX A

CALCULATIONS FOR EXPERIMENTAL AND THEORETICAL
NITROGEN REMOVAL BASED ON AVERAGE
VALUES FROM TABLES 4 AND 5

Experimental Analysis:

Nitrogen Removal = Influent Nitrogen - Effluent Nitrogen

thus:

\[
\text{Nitrogen Removal} = (25.271 \text{ mg/l N} - 17.575 \text{ mg/l N}) \times Q \times (8.34 \text{ lb-l/MG-mg})
\]

where: \( Q = \) average flow for month of August, MGD. Therefore:

\[
\text{Nitrogen Removal} = 5.950 \text{ lb/day}
\]

and

\[
\% \text{ Nitrogen Removal} = 30.5\%
\]
(based on average influent nitrogen from Table 6)

Average removal of BOD₅ for the month of August:

\[
\text{BOD₅ Removal} = \text{BOD₅} \times Q \times (8.34 \text{ lb-l/MG-mg})
\]

where: \( \text{BOD₅} = \) average BOD₅ removed for the month of August, mg/l.

Thus:

\[
\text{BOD₅ Removal} = 135.9 \text{ mg/l} \times 0.0927 \text{ MGD} \times (8.34 \text{ lb-l/MG-mg})
\]

Therefore:

\[
\text{BOD₅ Removal} = 105.1 \text{ lb/day}
\]
Food to nitrogen removal ratio:

\[
\text{BOD}_5 \text{ Removal/Nitrogen Removal} = \frac{105.1 \text{ lb/day}}{5.950 \text{ lb/day}}
\]

Therefore:

\[
\text{BOD}_5 \text{ Removal/Nitrogen Removal} = 17.7:1
\]
APPENDIX B

CALCULATIONS TO DETERMINE FOOD TO MASS RATIO IN THE CONTACT STABILIZATION TANK OF THE FTU WASTE-WATER TREATMENT PLANT BASED ON DATA TAKEN FROM TABLES 4 AND 5

Equation, Food to Mass Ratio:
\[
F/M = \frac{(\text{lb } \text{BOD}_5 \text{ Removed/day})}{(\text{lb } \text{MLVSS in Contact Tank})}
\]

If, MLVSS = 75% of MLSS, then:
\[
F/M = \frac{(135.9 \text{ mg/l } \times 0.0927 \text{ MGD } \times (8.34 \text{ lb-1/MG-mg}))}{(4521 \text{ mg/l } \times 0.75 \times 0.063277 \text{ MG } \times (8.34 \text{ lb-1/MG-mg}))}
\]

Therefore:
\[
F/M = 0.059 \text{ lb/lb/day}
\]
APPENDIX C

CALCULATIONS TO DETERMINE AVERAGE GROSS NITRIFICATION RATE COEFFICIENT ($K_N$) FOR THE CONTACT STABILIZATION UNIT OF THE FTU WASTEWATER TREATMENT PLANT

BASED ON DATA TAKEN FROM TABLES 4 AND 5

Equation:

$$ \frac{N_e}{N_o} = e^{-K_n X_v t} $$

where:

- $N_e$ = Ammonia nitrogen concentration leaving the contact stabilization tank, mg/l
- $N_o$ = Ammonia nitrogen concentration in the raw entering the contact stabilization tank, mg/l
- $K_n$ = Average gross nitrification rate coefficient for the month of August, l/mg-day
- $X_v$ = Mixed liquor volatile suspended solids concentration assuming 75% of mixed liquor suspended solids is in this form, mg/l
- $t$ = Detention time, contact tank volume divided by average flow, days

Thus:

$$ \frac{4.14 \text{ mg/l NH}_3\text{-N}}{20.38 \text{ mg/l NH}_3\text{-N}} = e^{-K_n \times 4521 \text{ mg/l} \times 0.75 \times (0.063277 \text{ MG}/0.0927 \text{ MGD})} $$

Therefore:

$$ K_n \text{ (base } e) = 0.000689 \text{ l/mg-day} $$
APPENDIX D

DATA, CALCULATIONS, AND LINEAR REGRESSION

ANALYSIS USED TO OBTAIN FIGURE 13

BASED ON DATA TAKEN FROM

TABLES 4 AND 5

Data:

<table>
<thead>
<tr>
<th>NH₃-N Influent mg/l</th>
<th>NH₃-N Influent lb/day</th>
<th>NH₃-N Removal mg/l</th>
<th>NH₃-N Percentage Removal, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.72</td>
<td>18.17</td>
<td>20.32</td>
<td>93.6</td>
</tr>
<tr>
<td>23.48</td>
<td>17.04</td>
<td>22.60</td>
<td>96.3</td>
</tr>
<tr>
<td>25.17</td>
<td>17.17</td>
<td>24.04</td>
<td>95.5</td>
</tr>
<tr>
<td>23.42</td>
<td>22.17</td>
<td>22.59</td>
<td>96.5</td>
</tr>
<tr>
<td>20.03</td>
<td>15.44</td>
<td>19.14</td>
<td>95.6</td>
</tr>
<tr>
<td>16.15</td>
<td>13.51</td>
<td>15.71</td>
<td>97.3</td>
</tr>
<tr>
<td>20.82</td>
<td>13.75</td>
<td>20.47</td>
<td>98.3</td>
</tr>
<tr>
<td>12.30</td>
<td>8.92</td>
<td>12.14</td>
<td>98.7</td>
</tr>
</tbody>
</table>

Calculation:

I. NH₃-N Removal = Influent NH₃-N - Effluent NH₃-N

II. NH₃-N Influent = NH₃-N Raw x Q x (8.34 lb-1/MG-mg)

III. NH₃-N Effluent = NH₃-N Clarifier Effluent x Q x (8.34 lb-1/MG-mg)

IV. % ANH₃-N = (NH₃-N Removal x Q x (8.34 lb-1/MG-mg)) / (NH₃-N Influent lb/day)

where: NH₃-N = ammonia nitrogen, mg/l

Q = daily plant flow, MGD
Linear Regression Analysis, Least-Squares Method:

\[
\text{Intercept } b = \left( \sum YX^2 - \frac{\sum X \sum XY}{\sum X^2} \right)
\]

\[
\text{Slope } M = \left( \frac{\sum XY}{\sum X^2} \right) - \left( \frac{\sum X \sum XY}{\sum X^2} \right)
\]

Thus:

\[
b = 100.74\%
\]

\[
M = -0.27 \% \text{ day/lb}
\]

Correlation Coefficient (R value) = 97.18%

Standard Deviation (\(\sigma\)) = \(\pm 26.26\% \Delta N_H_3-N\)

Therefore:

\[
\% \Delta N_H_3-N = -0.27 \times \text{Influent } N_H_3-N \text{ lb/day} + 100.74
\]
APPENDIX E

DATA, CALCULATIONS, AND LINEAR REGRESSION ANALYSIS

USED TO OBTAIN FIGURE 14 BASED ON VALUES

TAKEN FROM TABLES 4 AND 5

Data:

<table>
<thead>
<tr>
<th>BOD(_5) Removal, mg/l</th>
<th>Nitrogen Removal, mg/l</th>
<th>MLSS, mg/l</th>
<th>(\Delta\text{BOD}_5), lb/lb/day</th>
<th>(\Delta\text{N}), lb/lb/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>164.2</td>
<td>9.564</td>
<td>4444</td>
<td>0.0508</td>
<td>0.00296</td>
</tr>
<tr>
<td>137.7</td>
<td>12.449</td>
<td>4294</td>
<td>0.0575</td>
<td>0.00520</td>
</tr>
<tr>
<td>118.3</td>
<td>5.904</td>
<td>4504</td>
<td>0.0416</td>
<td>0.00208</td>
</tr>
<tr>
<td>123.4</td>
<td>2.389</td>
<td>4929</td>
<td>0.0344</td>
<td>0.00067</td>
</tr>
</tbody>
</table>

Calculations:

I. 1 lb BOD\(_5\) Removal/Day/lb MLSS = \(\frac{(\Delta\text{BOD}_5 \times Q \times (8.34 \text{ lb-1/MG-mg}))}{(\text{MLSS} \times V \times (8.34 \text{ lb-1/MG-mg}))}\)

II. 1 lb Nitrogen Removal/Day/lb MLSS = \(\frac{(\Delta\text{N} \times Q \times (8.34 \text{ lb-1/MG-mg}))}{(\text{MLSS} \times V \times (8.34 \text{ lb-1/MG-mg}))}\)

where: \(\Delta\text{BOD}_5\) = influent BOD\(_5\) minus effluent BOD\(_5\), mg/l

\(\Delta\text{N}\) = influent nitrogen minus effluent nitrogen, mg/l

\(Q\) = flow, MGD

\(V\) = volume, MG

Linear Regression Analysis, Least-Squares Method:

Intercept = \(b = \frac{(\Sigma EX^2 - \Sigma EXY)}{(\Sigma EX^2 - (\Sigma X)^2)}\)

Slope = \(M = \frac{(\Sigma EXY - \Sigma XY)}{(\Sigma EX^2 - (\Sigma X)^2)}\)

thus:
\[ b = 0.0057 \text{ lb/lb/day} \]

\[ M = 0.182 \]

Correlation Coefficient = 93.53%

Standard Deviation = ± 0.00159 lb/lb/day

Therefore:

\[ \text{lb Nitrogen Removal/day/lb MLSS} = 0.182 \times (\text{lb BOD}_5 \text{ Removal/day/lb MLSS}) - 0.0057 \]
### APPENDIX F

DATA AND CALCULATIONS USED TO DETERMINE NITROGEN REMOVAL IN LAGOON BASED ON DATA TAKEN FROM TABLES 4 AND 5

#### Data:

<table>
<thead>
<tr>
<th>Clarifier Effluent Nitrogen (lb/day)</th>
<th>Lagoon Effluent Nitrogen (lb/day)</th>
<th>Percentage Nitrogen Removal in Lagoon, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.08</td>
<td>2.56</td>
<td>83.0</td>
</tr>
<tr>
<td>11.51</td>
<td>2.51</td>
<td>78.2</td>
</tr>
<tr>
<td>13.50</td>
<td>4.37</td>
<td>67.6</td>
</tr>
<tr>
<td>12.93</td>
<td>4.12</td>
<td>68.1</td>
</tr>
</tbody>
</table>

#### Calculations:

\[
\% \text{ Nitrogen Removal in Lagoon} = \left( \frac{\text{Clarifier Effluent Nitrogen} - \text{Lagoon Effluent Nitrogen}}{\text{Clarifier Effluent Nitrogen}} \right) \times 100
\]

Where:

- Clarifier Effluent Nitrogen = total nitrogen present in the supernatant leaving the clarifier, lb/day
- Lagoon Effluent Nitrogen = total nitrogen leaving the lagoon, lb/day
FOOTNOTES


4 Hanson, p. 2271.


12 Stenquist, p. 2328.


17 Beckman, p. 1917.


21 Wild, p. 1850.

22 Murray, p. 29.

23 Beckman, pp. 1921-1922.


27 Ibid., p. 218, 225.


32 Wild, p. 1852.


34 Wild, p. 1851.


36 Wild, p. 1848.

37 Stenquist, p. 2334.

38 Wild, p. 1854.

39 Beckman, p. 1921, 1930.

40 Barth, p. 2041.

41 Beckman, p. 1930.

42 Johnson, p. 1023.

43 Reeves, p. 1895.

44 Johnson, p. 1015.


Stenquist, p. 2331.

Mulbarger, p. 2062.


Murray, p. 29.


Reeves, p. 1900.

Monod, p. 3-36.


64 Ibid., p. 3-37.
65 Stensel, p. 253-254, 260.
71 Stensel, p. 249.
74 Methods for Chemical Analysis of Water and Wastes, p. 159-216.
75 Sawyer, p. 429.
78 Sawyer, p. 396.
BIBLIOGRAPHY


Gibson, C. E. "Nutrient Limitation." Journal Water Pollution Control Federation 43 (December 1971): 2436-2440.


Jeris, John S. and Owens, Roger W. "Pilot-Scale, High-Rate Biological Denitrification." Journal Water Pollution Control Federation 47 (August 1975): 2043-2057.


Schwinn, Donald E. and Dickson, Conneau H., Jr. "Nitrogen and Phosphorus Variations in Domestic Wastewater." Journal Water Pollution Control Federation 44 (November 1972): 2059-2065.


Sutton, P. M.; Murphy, K. L.; and Dawson, R. N. "Low-Temperature Biological Denitrification of Wastewater." Journal Water Pollution Control Federation 47 (January 1975): 122-134.


