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Optimizing Centrate Bioaugmentation Reactors by Monitoring Ph and Do to Produce Maximum Nitrification While Minimizing Aeration Energy

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OPTIMIZING CENTRATE BIOAUGMENTATION REACTORS BY MONITORING PH
AND DO TO PRODUCE MAXIMUM NITRIFICATION WHILE MINIMIZING AERATION
ENERGY

By

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B.S., University of Florida, 2009

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This thesis entitled:
Optimizing Centrate Bioaugmentation Reactors by Monitoring pH and DO to Produce Maximum
Nitrification While Minimizing Aeration Energy

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The final copy of this thesis has been examined by the signatories, and we
Find that both the content and the form meet acceptable presentation standards
Of scholarly work in the above mentioned discipline.

Abstract

Huang, Joyce (M.S, Environmental Engineering)

Optimizing Centrate Bioaugmentation Reactors by Monitoring pH and DO to Produce Maximum Nitrification While Minimizing Aeration Energy

Thesis directed by Professor JoAnn Silverstein

Increased nitrogen loads from anthropogenic sources have led to nutrient enrichment in our nation's waterways. The over-enrichment increases algal growth which can lead to ecological degradation and eutrophication. As a result, there is now increased pressure on point source discharges to remove nitrogen from treated effluent. Nitrogen entering the wastewater stream is typically in the form of ammonia and organic nitrogen. Biological nitrogen removal (BNR) is the most commonly used method for removing excess ammonia from wastewater. The pressure of reducing nutrient concentrations in the effluent has led to improved technological innovations for nitrogen removal, forcing many facilities to upgrade or improve their current systems.

The Metro Wastewater Treatment Facility provides wastewater transmission and treatment services to a large portion of metropolitan Denver and surrounding cities. Their north secondary treatment facility (NSEC) removes excess nutrients from the wastewater. Due to concerns about high ammonia loads from the sludge centrate causing stress on the main system, a sidestream bioreactor known as CaRRB is currently in place. The CaRRB basins receive a portion of the recycled activated sludge which is combined with centrate. There are three zones in each basin, one larger oxic zone and 2 smaller anoxic zones for nitrification and denitrification. Despite consistent operational parameters of CaRRB, large fluctuations in the nitrification performance

are occurring and affecting the main system. This results in an unsteady effluent ammonia concentration. The goal of this project was to identify the causes of the fluctuations by evaluating the basic factors that impact nitrification. Based on recorded CaRRB data, batch experiment results, and system modeling it appears that pH values outside the optimal range of 6.6-8.0 are repressing nitrification and potentially affecting nitrifier growth. Potential resolutions include monitoring pH and DO in the basins or bypassing the sidestream reactors and relying on the nitrifying capacity of the aeration basins. Implementation of these solutions could reduce the ammonia fluctuations in CaRRB and maximize nitrification efficiency while reducing aeration costs, providing the District with a more consistent total nitrogen effluent concentration.

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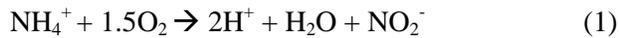
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1. Introduction

1.1 Biological Nitrogen Removal

Biological nitrogen removal (BNR) is one of the most common methods for removing excess ammonia from municipal wastewater. This process is known as nitrification and occurs as a two-step process by autotrophic organisms. The ammonium (NH_4^+) is oxidized to nitrite (NO_2^-) by the ammonia oxidizing bacteria (AOBs) which is followed by nitrite oxidation to nitrate (NO_3^-) by the nitrite oxidizing bacteria (NOBs). The chemical transitions are shown below in equations (1) and (2). The most commonly discussed and reported AOB and NOB genera discussed in literature are *Nitrosomonas* and *Nitrobacter* [1, 2, 9]. Although mixed cultures of AOBs and NOBs are generally found in the nitrifying biomass, these two species are often dominant or at least present in the cultures.



A synergistic and competitive relationship exists between the two organisms, the AOBs produce the nitrite needed by the NOBs but both microorganisms must compete for oxygen (O_2) as their electron acceptor. Research has shown AOBs to be the stronger scavenger of O_2 and as a result the accumulation of nitrite has been observed at low dissolved oxygen (DO) concentrations ($k_{\text{DO}} = 0.5$ mg/l AOBs, 0.68 mg/l NOBs). A few key factors that influence the rate and efficiency of nitrification are pH, alkalinity, temperature, DO, and inhibitory compounds [4, 8, 13].

Alkalinity and pH are large factors for optimizing the oxidation and growth rate of nitrifiers. For every 1 mg of ammonium that is oxidized to nitrate, 7.1 mg of alkalinity as CaCO_3 (or 12 mg of alkalinity as NaHCO_3) is consumed. During nitrification, hydrogen ions are produced therefore adequate alkalinity is required to maintain an acceptable pH range. The carbonate species in the system will vary depending on the pH value. At normal operating conditions of pH 7, a large portion of the carbonate will be in the

form of bicarbonate (HCO_3^-) which can take up 1 proton produced from nitrification. A more desirable form is carbonate (CO_3^{2-}) because it is capable of accepting 2 protons which means this species provides a larger buffering capacity. Alkalinity from a bicarbonate dominated system may result in a decrease in pH that occurs sooner and more rapidly than a CO_3^{2-} dominated system. Sufficient alkalinity also provides inorganic carbon to the nitrifiers to support cell growth and biomass production.

The optimal pH range for nitrification is 6.6 to 8.0. Environments with pH less than 6.0 experience slowed nitrification rates while complete inhibition can occur once the pH is less than 4.5 [11]. Several research studies have found pH affects on nitrification to begin at higher values. Decreased rates of nitrification were reported to start at pH 6.5 with severely decreased rates once the pH declined to 6.0. [14]. It should be noted that pH values greater than 7.0 are not commonly maintained in wastewater treatment and most facilities are capable of nitrifying effectively at pH 6.5-7.0.

Increasing temperatures yield increasing nitrification rates with an optimal temperature range of 30-35°C. Once temperatures exceed 35 °C the rate of nitrification begins to decrease. As a reference for the impact of temperature, a drop from 20°C to 10°C results in a nitrification rate decrease of approximately 30% which means three times the mass of the mixed liquor suspended solids (MLSS) will be needed to produce an equivalent effluent ammonia concentration.

Nitrification is an aerobic process therefore DO concentrations will play a large role in the rate of oxidation. As DO increases, the rate of oxidation also increases until a plateau is reached. Depending on the system's conditions, DO concentrations that are too low can result in nitrite accumulation or incomplete nitrification. Bae et al. found NOBs to have a significantly higher max specific oxidation rate compared to AOBs at DO = 2.5 mg/l which means that although AOBs are better O_2 scavengers once the NOBs acquire O_2 , they will quickly convert NO_2^- to NO_3^- [9, 18].

1.2 Inhibition and Limitations

In the absence of inhibitions and limitations, *nitrobacter* grows almost twice as fast as *nitrosomonas* therefore ammonium oxidation would be seen as the rate limiting step. Once inhibitions come into play, it is no longer obvious which step decides the pace of nitrification. Inhibitory compounds include certain heavy metals and organic compounds, unionized free ammonia (NH_3) and nitrous acid (HNO_2) [20, 21]. The amount of free ammonia and nitrous acid will vary depending on pH, temperature, and the concentration of ammonium and nitrite in the system. Due to the equilibrium of the $\text{NH}_3/\text{NH}_4^+$ and $\text{NO}_2^-/\text{HNO}_2$ systems, as pH increases, the concentration of NH_3 will increase while the concentration of HNO_2 will decrease and vice versa [2].

Anthonisen's research reported inhibitory concentrations of NH_3 and HNO_2 for AOBs and NOBs and developed a chart with several defining zones. Zone 1 defined the inhibition of *nitrobacter* by unionized ammonia (NH_3 is greater than 0.1- 1.0 mg/l), zone 2 defined the inhibition of *nitrosomonas* by unionized ammonia (NH_3 is greater than 10-150 mg/l), and zone 3 defined the inhibition of *nitrobacter* by nitrous acid (HNO_2 is greater than 0.2-2.8 mg/l). Although Anthonisen did not discuss the inhibitory effects of nitrous acid on AOBs, inhibitory concentrations of 0.1 to 0.56 mg/l HNO_2 have been reported in literature. Inhibition concentrations may vary from one study to the next since nitrifiers have the ability to acclimate to inhibitory compound concentrations depending on their environmental conditions. Also, pure cultures of *nitrosomonas* and *nitrobacter* will have lower tolerances than mixed cultures therefore a range of culture compositions between studies will yield varying results [21].

1.3 Sidestream Bioreactors and Bioaugmentation

Sidestream bioreactors are commonly used in wastewater treatment facilities to reduce a concentrated stream such as centrate (high ammonia loads) before it's fed back into the main system. This is beneficial because treating high ammonia waters on the side before feeding it into the main system can prevent the main system from becoming "overwhelmed" and as a result improve the effluent water quality.

Bioaugmentation has been researched as a solution to upgrading the nitrification capabilities in sidestream reactors. The concept of bioaugmented side reactors is to increase the growth of nitrifying bacteria in the system which will decrease the effective required solids retention time (SRT) and therefore decrease the required aerobic volume. The BABE (Bio Augmentation Batch Enhanced) process combines the treatment of the sludge liquor and the augmentation of the nitrifier population. This is achieved by combining a fraction of the RAS (return activated sludge) which contains nitrifying organisms in the biomass flocs with the reject water that contains elevated temperatures and a high ammonia load. The concept behind BABE is that the increased temperature and large amount of substrate will increase the nitrifying activity of the activated sludge and return to the main process carrying a larger load of nitrifiers which will provide a larger nitrifying capacity in the main system and improve effluent ammonia water quality [3].

The Metro Wastewater Reclamation District (also referred to as Metro or The District) began operation in 1966. It was originally known as the Robert W. Hite Treatment Facility (RWHTF). The secondary treatment operation is split into the north secondary treatment system (NSEC) and the south secondary treatment system (SSEC). The SSEC removes excess BOD and TSS while the NSEC is responsible for sufficient dissolved organic carbon (DOC) and nutrient removal. The effluents from the NSEC and SSEC are then blended to meet permit standards.

The NSEC receives an average influent flowrate of 86 mgd and operates a sidestream bioreactor known as CaRRB (Centrate and RAS Re-aeration Basin) whose design was based upon the BABE process. These basins were implemented into the NSEC due to concerns that the main system would be stressed by the high ammonia loads from the centrate (~1350 mg/l $\text{NH}_4\text{-N}$). The CaRRB tanks receive a portion of the return activated sludge (30 mgd) from the secondary clarifier underflow along with ammonia-rich centrate from the centrifuges (1mgd). The basin was designed to achieve a high volumetric oxidation rate due to the high concentration of AOBs and NOBs along with the high aeration rate in the reactor. The high concentration of nitrifiers is reflected in the MLVSS of the system, CaRRB contains a

concentration of ~ 4850 mg/l while the more diluted aeration basins contain an MLVSS ~3100 mg/l. The goal of the original design was to oxidize half to two-thirds of the centrate mass ammonia load to nitrate.

The CaRRB process train consists of three parallel basins. Each basin is divided into three sections, one aerated compartment, 0.46 MG, and two swing zones, 0.11 MG each, which can be operated as an aerated or unaerated zone (Figure 1). During 2011, both swing compartments were operated without aeration to allow for denitrification before leaving the basins. The CaRRB effluent is then mixed with settled wastewater (primary effluent) and additional recycled activated sludge (RAS) before entering the main activated sludge process train, which is operated as a Modified Ludzack Ettinger process for additional nitrification and denitrification before discharge. Schematic shown below in Figure 2.

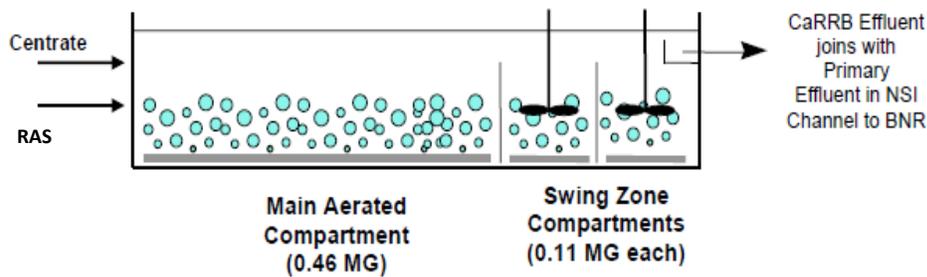


Figure 1. Process Schematic of CaRRB Tank provided by Metro WW

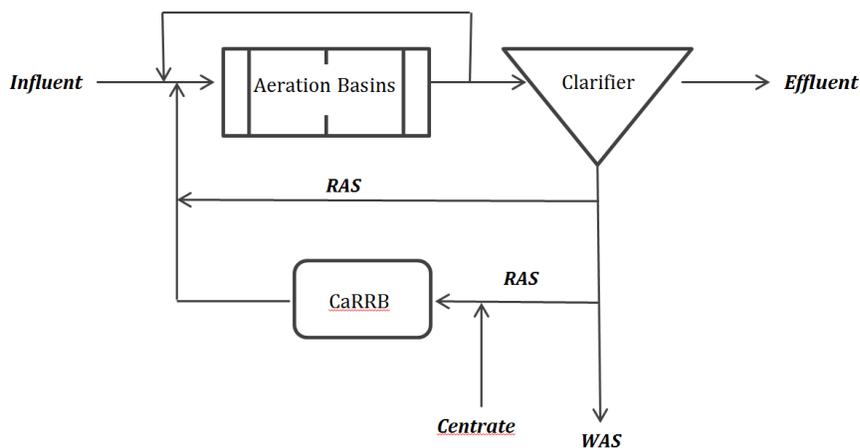


Figure 2. NSEC Aeration Basin and CaRRB Inflow and Outflow Schematic

A unique operational property of CaRRB is the low aerobic solids retention time (ASRT) in which the basins are operated. The lower the ASRT, the lower the air usage which allows for larger aeration energy savings. The District uses an operational factor (OF), which equals the actual ASRT divided by theoretical minimum ASRT, to control the DO concentrations and other operation parameters in the basins. In many other wastewater treatment facilities, the sidestream reactor is operated at an OF greater than or equal to 2 (double the theoretical min ASRT). This provides a safety factor since more than enough time is provided in the reactors. The downside is the larger aeration costs that are associated with increased operating factors. Metro currently operates CaRRB using an OF = 0.9 meaning less than the theoretical minimum ASRT is applied allowing the District to significantly reduce their aeration costs.

Despite a fairly consistent operation of CaRRB (OF used by the operators to regulate DO levels in basin) and 150-200 mg/l alkalinity reported to be leaving the basins, large fluctuations were observed in the nitrification performance which resulted in inconsistent CaRRB effluent ammonia concentrations (Figure 3).

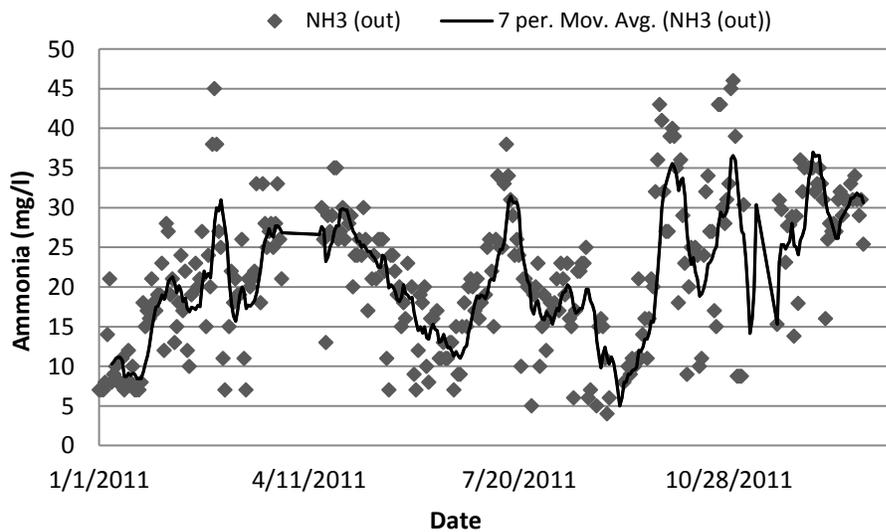


Figure 3. Daily CaRRB Effluent Ammonia Concentrations

Based on similar trends observed in the effluent, it has been hypothesized that the ammonia fluctuations are impacting the main system (Figure 4).

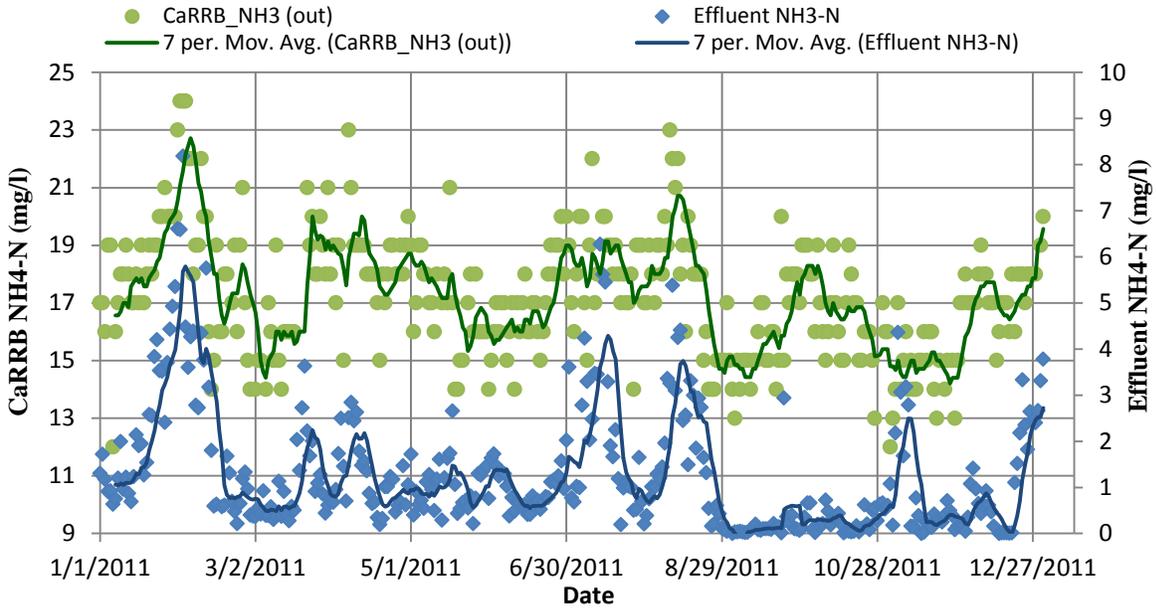


Figure 4. Ammonia Concentration Fluctuations from CaRRB and the NSEC Effluent

This creates a challenge for the plant since consistently low effluent ammonia concentrations are necessary to meet compliance. Dependable effluent concentrations will become increasingly important to the District due to the implementation of more stringent total nitrogen (TN) effluent standards in the near future.

The dewatering of digested sludge (biosolids) using a centrifuge or belt filter press produces a side stream with very high concentrations of ammonia. Concern that the activated sludge process cannot handle peak inflows of ammonia from dewatering processes has led to the development of biological pretreatment processes to reduce the impact of peak loads. However, inconsistent performance reduces the effectiveness of side stream processes, so an understanding of the factors that cause process upsets may lead to mitigation strategies and improvement of overall plant performance.

The objective of this research project was to identify the causes of the large and frequent variations of nitrification in the CARRB process and to assess the effect of CARRB performance on plant effluent ammonia concentration after the activated sludge process. It is hypothesized that the system is alkalinity limited causing the pH to decrease to levels outside the optimal pH range and repressing

nitrification. The basic factors that impact nitrification such as pH, alkalinity, and DO concentration were assessed using batch test experiments. Online data from the plant was analyzed for trends, similarities to batch test results, and potential limitations of the system. The NSEC facility was also modeled in Biowin by using operational data provided by the District. The model outputs allowed for analysis of rate information of the unit processes and the sensitivity of the system. Possible resolutions for alleviating the fluctuations will also be analyzed by system modeling.

2. Materials and Methods

2.1 Lab Experiments: Batch Tests

Each batch test was run in a 3.0 L glass beaker filled with 0.11 L of centrate and 2.9 L of RAS. The volume of centrate and RAS for each batch test had a 30:1 ratio of RAS:Centrate yielding an initial ammonia concentration range of 40-50 mg/l $\text{NH}_3\text{-N}$. The chosen ratio reflects how the plant currently operates their CaRRB basins. The main source of alkalinity is provided by the centrate which contains ~ 4400 mg/l alkalinity as CaCO_3 . Each beaker contained a fine bubble aeration stone, pH probe (Orion 4 star pH/ISE Benchtop meter with Ross Ultra Combination probe 8102BNUWP), DO probe (Orion 3 Star RDO meter with Thermo RDO probe 087010MD), and a stirrer. Experimental set-up is shown below in Figure 5.

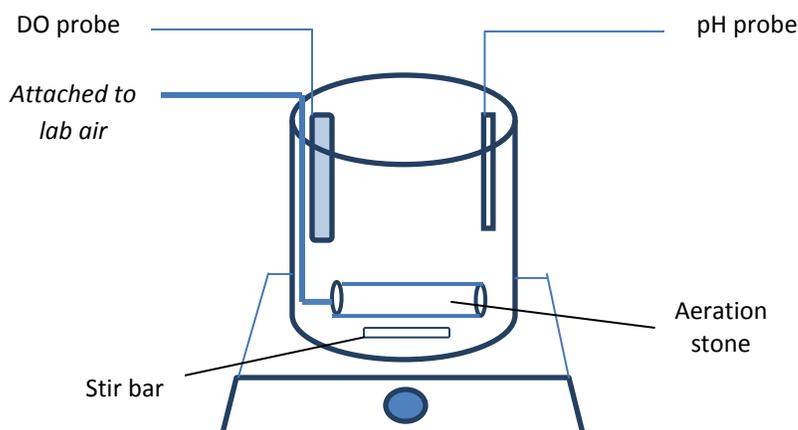


Figure 5. Schematic of Experimental Batch Test Set-Up

The time, pH, temperature and DO range were recorded before each sample was taken. All samples were obtained using a large pipette and immediately filtered to ensure no further reaction took place. Samples were labeled and stored at 4°C.

2.1.1 Addition of Tris Buffer

To observe the effect of pH on the rate of nitrification, the addition of Tris buffer to maintain a pH greater than 7.0 was carried out. In a second beaker, an “unbuffered” solution, meaning no additional alkalinity was added, was aerated for comparison. The “unbuffered” solution represents the contents of CaRRB which contains a large source of alkalinity from the centrate (centrate alkalinity ~ 4400 mg/l CaCO₃). With a RAS:Centrate ratio of 30:1 and an effluent alkalinity of 109 mg/l CaCO₃ approximately 250 mg/l alkalinity as CaCO₃ is contained in the unbuffered solution.

Batch tests were aerated for 180 minutes with DO concentrations greater than 2.0 mg/l to ensure oxygen was not a limiting factor during nitrification. Samples were taken every 30 minutes. The pH was continuously monitored in both beakers. Tris buffer solution was added to the buffered batch once the pH dropped to 7.0. The pH was maintained at a level that was greater than or equal to 7.0 until the end of the test.

2.1.2 Rebound.

Rebound batch tests were carried out to observe the organism’s ability to rebound back to its original oxidation rates once returned to favorable conditions. The hydraulic residence time (HRT) of CaRRB is approximately 1 hour and the pH frequently drops below 6.5 before it reaches the end of the aeration zone, therefore exposure to a pH < 6.5 for a minimum of 30 minutes was chosen to reflect conditions that are occurring in the basins.

The 30:1 RAS to centrate mixture was aerated at a DO > 2.0 mg/l for 120 minutes with samples taken every 30 minutes. At the end of each run, the solution was centrifuged and the liquid was drained. A

mixture composed of primary effluent and centrate (2.9 L of effluent, 0.11 L centrate) was added to the solids until ~ 2.9 L of solution was in the beaker. This was done to “reset” the mixture to similar ammonia and alkalinity concentrations. Note that the beaker was not filled back to 3L since 5 samples at 20 mL each (100 mL total) were removed in the first run. The “reset” mixture was aerated at a similar DO as the original solution and again sampled every 30 minutes during the 120 minute interval.

2.1.3 DO versus Nitrification Rate.

The influence of dissolved oxygen on the rate of nitrification in the CaRRB basins were tested in batch experiments with DO concentrations of 0.5 – 2.5 mg/l. The DO concentrations were increased by increments of 0.5 mg/l with three test runs carried out at each DO concentration. Each batch test was aerated until a pH of 6.5 or less was reached. Samples were taken during the entire length of each run to ensure several samples were taken before and after the pH dropped below 6.8. Due to increases in the nitrification rates with an increase in DO, the sampling times varied between 15 to 30 minutes depending on the rate of decreasing pH.

2.2 Online Plant Data

Online plant data was collected for 2011 and used for Biowin model calibrations and to assess trends that may be occurring in CaRRB along with the plant effluent. The parameters available include DO, pH, NH₃-N, NO₅-N, TSS, and alkalinity. The values were found by either lab analysis by Metro or online probes. The pH probes were located at the end of the aerated zone for CaRRB 1 and the end of the anoxic zone in CaRRB 3. Hach DO probes were located at the end of the aerated zone for both CaRRB 1 and 3. The ChemScan UV6101 received a combined sample from the end of the anoxic zone of CaRRB 1 and 3 and another from 2 and 4 and analyzed for NH₃ and NO₅.

2.3 Sample Collection

2.3.1 Centrate and RAS.

Designated sampling points are located throughout RWHTF. A separate sampling pipeline is in place for the centrate and waste activated sludge (WAS). The WAS was assumed to accurately represent

the RAS. Each sample was collected after allowing the flow from the sample pipelines to run for several minutes to ensure a fresh mixture was obtained since the pipe may contain settled or unmixed WAS or old centrate.

2.3.2 Batch Test Samples.

All batch test samples were collected using a 10 mL pipette. For quality assurance and quality control (QA/QC) purposes, two samples were collected for each time interval and analyzed using two different methods. One set was filtered immediately using a 0.2 um glass fiber filter into a screw-cap vial and then placed in a 4°C refrigerator until analysis. The second set was placed into sampling containers with 2 drops of sulfuric acid (10 M H₂SO₄) to stop any further reactions and then placed in a 4° C refrigerator until analysis.

2.4 Sample Analysis

Two methods of analysis were used for each nitrogen species. A HACH DR 5000 spectrophotometer was used for measuring samples analyzed by the HACH colorimetric method. The values from both tests were compared for each experimental run to ensure accuracy and consistency of results.

2.4.1 Total Ammonia Nitrogen (NH₃-N).

The HACH colorimetric method TNT 832 was used to analyze for NH₃-N. The HACH protocols for the colorimetric method were followed for each sample. EPA method 353.2 was carried out by the laboratory staff at Metro and analyzed by the Lachat QuickChem 8000.

2.4.2 Nitrate (NO₃⁻-N)

The HACH colorimetric method TNT 836 was used for NO₃⁻N analysis. HACH protocols for the colorimetric methods were performed.

2.4.3 Nitrite (NO₂⁻-N)

Nitrite analysis was conducted using the HACH colorimetric method TNT 840. HACH protocols for the colorimetric methods were performed.

2.4.4 NO₅-N

Individual tests for $\text{NO}_3\text{-N}$ and $\text{NO}_2\text{-N}$ were not performed by the laboratory staff at RWHTF. Instead, the staff analyzed for the concentration of $\text{NO}_5\text{-N}$ ($\text{NO}_3\text{-N}+\text{NO}_2\text{-N}$) by using EPA method 353.2 which was analyzed using the Lachat QuickChem 8000. To compare the $\text{NO}_5\text{-N}$ lab results to the concentrations found using HACH, the HACH colorimetric results for $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ were combined and referred to as $\text{NO}_5\text{-N}$ (Hach).

2.4.5 TSS/ VSS

The total suspended solids (TSS) and volatile suspended solids (VSS) in the mixed liquor was analyzed by the RWHTF laboratory staff using USGS TSS Method I-3765-85 and USGS VSS Method I-3753-85. Samples of mixed liquor were collected before each batch experiment was performed and assumed to not change significantly over the course of the experiment.

2.5 System Modeling

Biowin 3.1 by EnviroSim was used to model RWHTF's north secondary treatment train. The model was calibrated using data provided by the District. The basin sizes and flow rates used in the design and calibration of the model can be found in Appendix A. To observe the inhibition effects of low pH, the aerated portion of CaRRB was represented by two basins in series and the nitrification rates for each run were compared between aeration zone 1 and aeration zone 2 (labeled as CaRRB_Air and CaRRB_Air 2 in the model). The CaRRB basin DO concentrations were varied from 0.5 to 2.5 mg/l with intervals of 0.5 mg/l. The pH and ammonia concentration in aerated basin 1 and 2 were recorded for each DO concentration. The ammonia oxidation rates calculated for the model were then compared to experimental results. The model was also used to compare the efficiency of the facility with and without the use of CaRRB.

3. Results and Discussion

3.1 Addition of Tris Buffer

Five sets of batch tests were run to compare the results of a system with pH always greater than or equal to 7.0 versus a system with no chemical addition which allowed the pH to drop as acid was produced during nitrification. For simplicity, the system with Tris buffer addition is referred to as the buffered system (B) while the batch with no addition of Tris is referred to as the unbuffered system (U). Note that the “unbuffered” system still contains alkalinity from centrate and RAS therefore it still contains buffering capacity. Similar results were seen in all five runs. An average of the buffered and unbuffered results normalized to the concentration of volatile suspended solids (VSS) for each batch were calculated and graphed in order to view the data points and trend clearly (Figure 6)

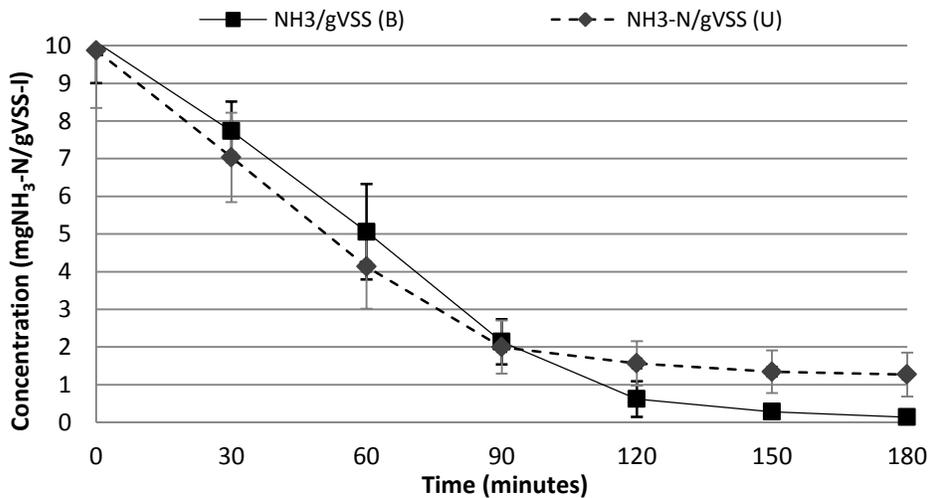


Figure 6. Average $\text{NH}_3\text{-N/gVSS}$ concentrations from buffered (B) vs unbuffered (U) nitrification batch tests

The two systems had a similar rate of ammonia oxidation until $t \sim 90$ mins, at this point the unbuffered batch began to plateau and very little nitrification appeared to be taking place. This point in time ($t = 90$ mins) corresponded to a pH near 6.5 (Figure 7).

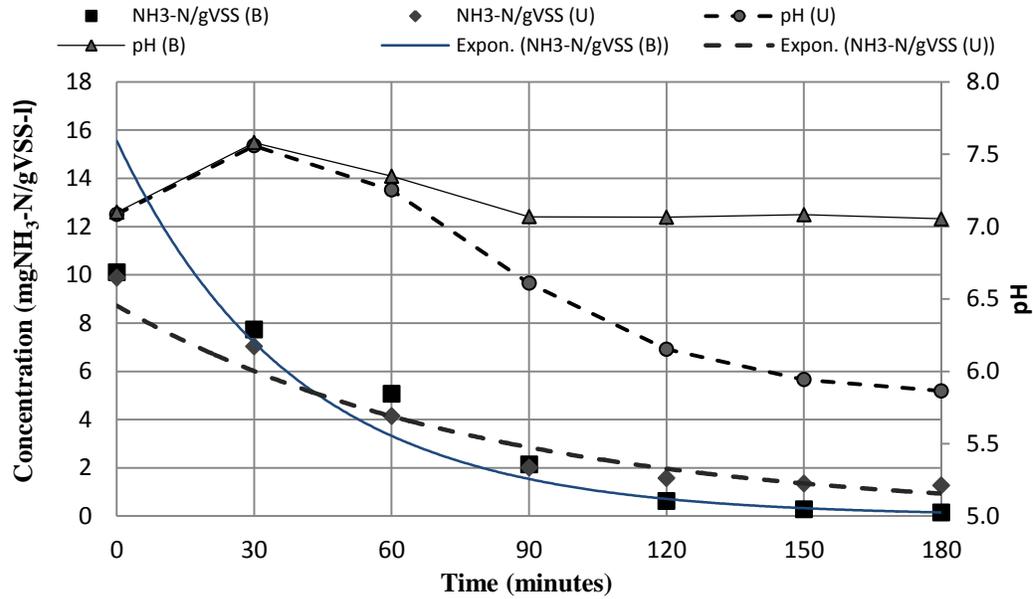


Figure 7. Average NH₃-N/gVSS concentrations of buffered and unbuffered system with pH of unbuffered (U) nitrification batch tests versus time

To analyze the differences in rate between the two systems, a first order equation was fitted to each set and the k values were compared. The first order equation fitted to the data represents the first order integrated rate law shown below in equation (1):

$$N = N_0 e^{-kt} \quad (1)$$

Where N_0 = amount of ammonia originally present, t = time (min), and k = rate decay constant (min^{-1})

The buffered system had a k value that was twice that of the unbuffered system which is shown in Table 1. This suggests a significant difference exists between the rate of nitrification between the two systems. Using a 95% confidence level student t-test, it was found that the k values were significantly different between the buffered and unbuffered system.

Table 1. Tris addition batch test rate constant and correlation value from first order fit equations

Batch Type	K (min^{-1})	K (hr^{-1})	R ²	95 % Confidence Interval
Tris Addition	0.026	1.56	0.9691	(0.0313, 0.0207)
No Tris Addition	0.012	0.72	0.9255	(0.0161, 0.0080)

A decrease in the rate of nitrification at a pH less than or equal to 6.5 is consistent with the literature discussed previously. These results are beneficial to the District because it gives an idea of how sensitive their nitrifying populations are to low pH conditions. Although it is common for facilities to nitrify efficiently at pH 6.5-7.0, the data shows that once pH drops below 6.5, nitrification rates are severely slowed. This is relevant to the District since hourly online probe data located in CaRRB basin 1 has recorded pH values dropping below 6.5 on a regular basis (Figure 8).

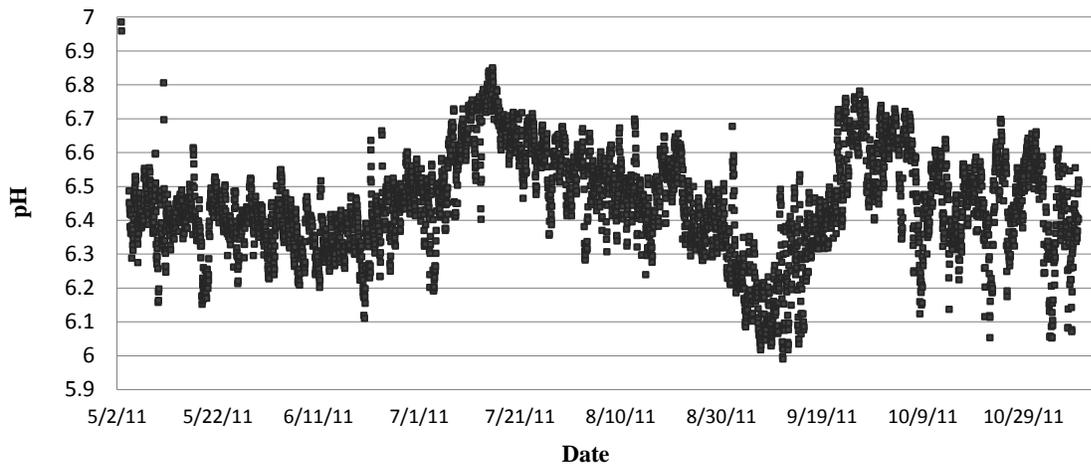


Figure 8. Hourly pH values found in CaRRB Basin 1 during May through November

As shown in Figure 6 and 7, the buffered system continued to nitrify until very little ammonia was left in the system. Although the rate of nitrification slowed for the buffered system as well, its reduction is most likely associated with low substrate (ammonia) concentration versus pH. This is suspected since a decrease in the rate of ammonia oxidation in the buffered system consistently occurred once the ammonia concentration dropped to 10-12 mg/l. Since the microorganisms reside in an environment that does not commonly lack substrate, it is possible that the nitrifier population is acclimated to optimal performance at higher ammonia concentrations and unaccustomed to scavenging for substrate.

3.2 Rebound Tests

The rate of ammonia oxidized for the initial run versus the rebound run generated similar results (Figure 9). A first order equation was fitted to each set of data and the k values were compared (Table 2).

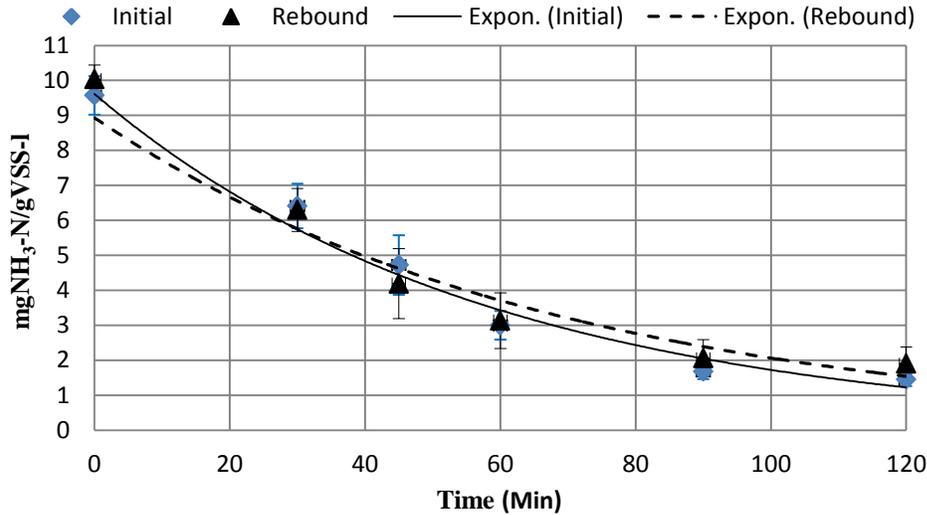


Figure 9. Initial versus Rebound Nitrification Rate

Table 2. Rebound batch test rate constant and correlation value from first order fit equation

Batch Type	K (min ⁻¹)	K (hr ⁻¹)	R ²	95 % Confidence Interval
Initial	0.017	1.02	0.9641	(0.0124, 0.0216)
Rebound	0.015	0.9	0.9395	(0.0098, 0.0202)

A 95% confidence level student t-test was applied to the rate constants and the k values were found to not be significantly different. These results suggest the organisms were able to rebound and were not permanently inhibited when exposed to low pH conditions for short periods of time.

The nitrifiers were exposed to low pH conditions (less than pH 6.5) for 30-60 minutes which showed the effects of low pH inhibition on nitrification but did not allow for the study of how low pH can impact growth. Exposure to low pH conditions for extended periods of time is assumed to have a larger impact on the system since growth inhibition can occur. When the organisms are suppressed due to an

unfavorable environment (in this case, outside the desirable pH range) less “food” is taken up and metabolized by the cells and therefore a reduction of growth occurs.

3.3 DO versus Nitrification Rate

The impact of DO on the rate of nitrification was analyzed by graphing the data and comparing the k values for each increment of dissolved oxygen concentration. The results are displayed in Figure 10. A noticeable increase in the rate of ammonia oxidized for DO= 0.5, 1.0, and 1.5 mg/l is reflected by the larger spacing difference between their fitted lines while for DO = 1.5, 2.0, and 2.5 mg/l the difference is much smaller. This trend suggests oxygen concentrations at 2.0 or higher may result in wasted aeration energy. The decreased amount of variation occurring at the higher DO values is also reflected by the k values listed in Table 1.

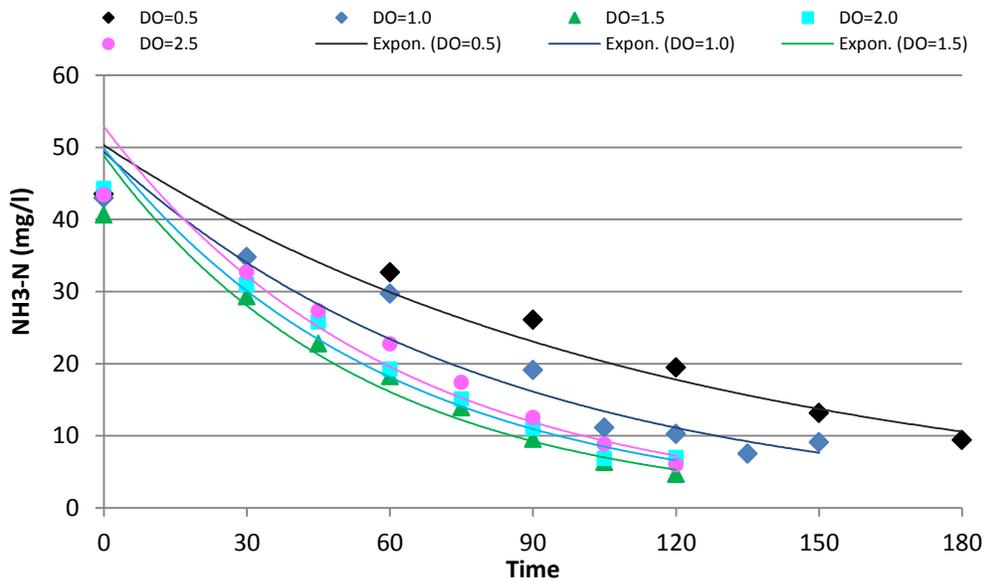


Figure 10. Ammonia oxidation versus time with first order equation fit for DO = 0.5 to 2.5 mg/l

Table 3. Average oxidation rate for DO concentrations of 0.5 - 2.5 mg/l

DO (mg/l)	K (min ⁻¹)	K (hr ⁻¹)	R ²	95 % Confidence Interval
0	0.0	0.0	0	0
0.5	0.009	0.54	0.9587	(0.0065,0.0115)

1	0.013	0.78	0.9372	(0.0090,0.0170)
1.5	0.018	1.08	0.9749	(0.0150,0.0210)
2	0.017	1.02	0.9684	(0.0137,0.0203)
2.5	0.017	1.02	0.9604	(0.0136,0.0204)

An increase in k is observed for DO values 0 to 1.5 mg/l, once the oxygen concentration reached 1.5 mg/l, the k values began to plateau with a max $k \sim 1.0 \text{ hr}^{-1}$. The data displayed in Figure 10 and Table 3 proposes that no significant increase in nitrification rate will occur if DO is increased to values greater than 1.5 mg/l. A student t-test was performed for the k values of DO=1.5 and 2.0 mg/l ($k= 1.08$ and 1.02 hr^{-1}) and with DO= 1.5 and 2.5 mg/l ($k=1.08$ and 1.02 hr^{-1}). No significant difference between the rate constants were found at the 95 % confidence level. This information infers that the District could reduce their DO set-point from 1.8 to 1.5 mg/l to reduce their aeration costs while still achieving the same amount of nitrification.

The concentration of ammonia was also graphed against pH to assess any trends that may exist (Figure 11).

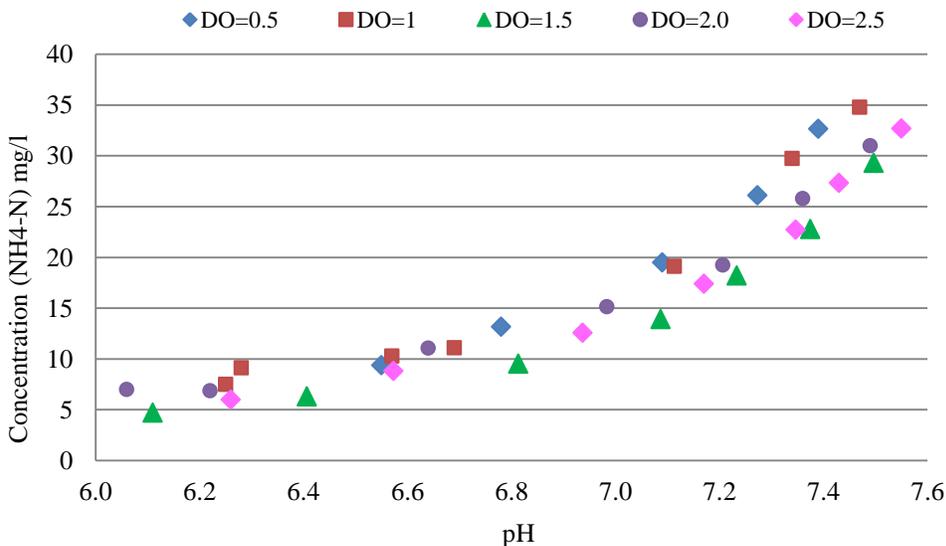


Figure 11. Ammonia concentration versus pH at various DO concentrations

Consistent with the pH trend observed in the “unbuffered” tests, a decrease in the nitrification performance occurred once pH dropped below 6.5. At the higher pH values a steady decline in the ammonia concentration can be observed with slight variations in rate depending on the DO. It should be noted that once the pH drops below 6.6, the difference in rates become less defined with a tendency to overlap. Although this may be the result of low substrate concentrations, the trend proposes that pH inhibition may overpower the effect of increased nitrification rates at increased DO values. The impact of pH over aeration is further supported by the k value of the Tris buffered system (Table 1) which is greater than the largest k value obtained from the DO rate tests (Table 3).

3.4 Online Plant Data

Based on the alkalinity in the centrate and plant effluent, CaRRB has an estimated alkalinity of ~ 250 mg/l CaCO_3 (discussed in more detail in materials and methods). If CaRRB has an initial $\text{NH}_4^+\text{-N}$ concentration of 45 mg/l and two-thirds of it is oxidized then 213 mg of CaCO_3 will be required based on the consumption of 7.1 mg of CaCO_3 for every mg of ammonium oxidized. These calculations suggest sufficient alkalinity is available to buffer the system during nitrification but the batch test results suggest otherwise.

A potential explanation is the form of carbonate species in the system. At a pH of 6.5 - 7 alkalinity is mostly in the bicarbonate form which can only take up one proton versus carbonate which can take up two. This species does not provide a strong enough buffering capacity which is reflected in the declining pH which further reduces the buffering capacity of the system. Also, CaRRB may have a natural inclination to equilibrate towards the bicarbonate/carbonic acid pKa (pH ~ 6.3) since it is an open system. Once pH values drop to 6.3 only half of the alkalinity in the system will be able to provide buffering since the other half will be in the form of carbonic acid which does not take up any protons. These factors make maintaining a pH greater than 6.5 a challenge unless chemical addition is used.

Based on the batch test results it is likely that CaRRB effluent ammonia fluctuations are associated with fluctuating pH trends. The daily values of the two parameters were plotted against time to assess their trends and support this hypothesis (Figure 12).

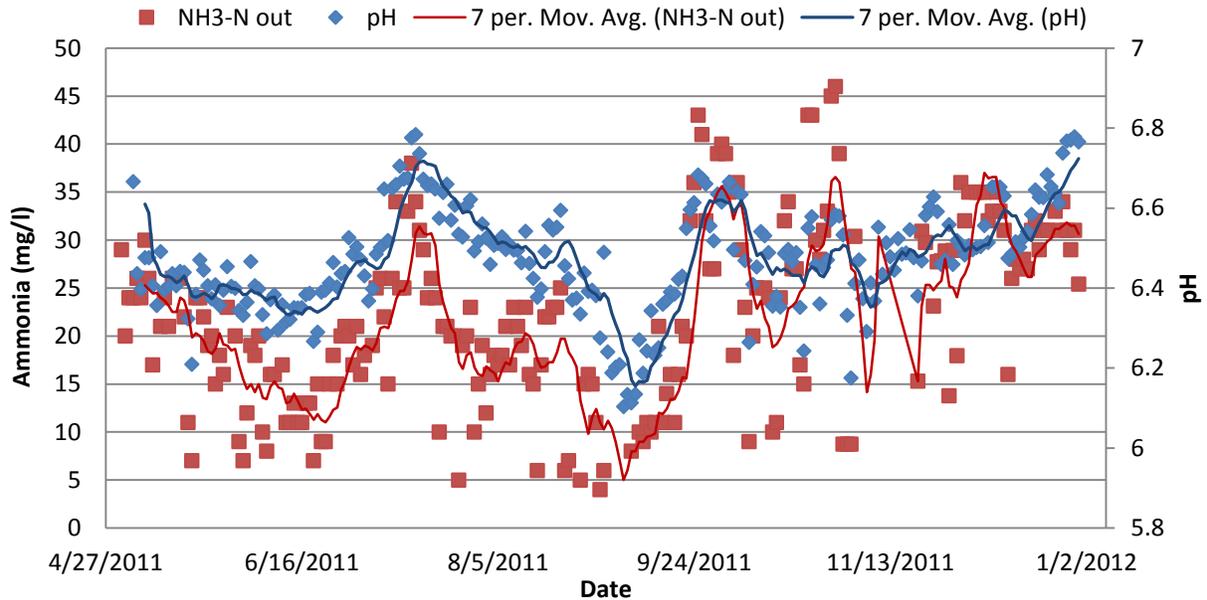


Figure 12. Online CaRRB Effluent Ammonia and pH data

Assumptions for why these fluctuations are occurring are based on the main factors of nitrification and the experimental results. As nitrification takes place, acid production and alkalinity consumption causes the pH to decrease. This is reflected by the decreasing effluent ammonia concentration and pH values in the graph. The decreasing pH is known to slow both the nitrification performance and potentially inhibit the growth of the organism. The centrate that flows into CaRRB at a steady state carries a high alkalinity and a desirable nitrification pH (7-7.2). Once nitrification in the system becomes inhibited, little to no acid will be generated and the pH will begin to rise due to the chemistry of the centrate and RAS flowing into CaRRB. The ammonia concentration in CaRRB will also increase from the incoming centrate since little to no nitrification is occurring in the system. These occurrences are reflected in the figure by the increasing pH and ammonia values. Once favorable conditions return to the basins (increased pH and alkalinity) the nitrifiers will rebound and begin

nitrifying again until the entire cycle repeats itself. Based on the time series data it appears that it takes several weeks for the system to rebound. This may imply that nitrifier growth is inhibited during low pH conditions and the rebound occurs once proper conditions are restored and the organisms have replenished in numbers to provide strong nitrification performance.

The fluctuations of ammonia exiting the NSEC follow a similar trend to the CaRRB effluent ammonia (Figure 4) inferring CaRRB may be impacting the main system. During the time period where CaRRB experiences inhibited growth of nitrifiers, a “bad batch” of CaRRB effluent, referring to a lower nitrifier population in the stream, is recycled into the aeration basins in the main system. With decreased numbers of nitrifying organisms, the aeration basins cannot oxidize the same quantity of ammonia resulting in higher effluent ammonia concentrations. In the opposite direction, during periods of high pH and strong nitrification, the nitrifiers are growing and a “good batch” of CaRRB effluent, meaning a high concentration of organisms, is sent to the aeration basin resulting in increased rates of ammonia removal and therefore a lower effluent ammonia concentration.

3.5 Biowin Modeling

A Biowin model was generated to evaluate the impact of pH on the rate of nitrification (Figure 13).

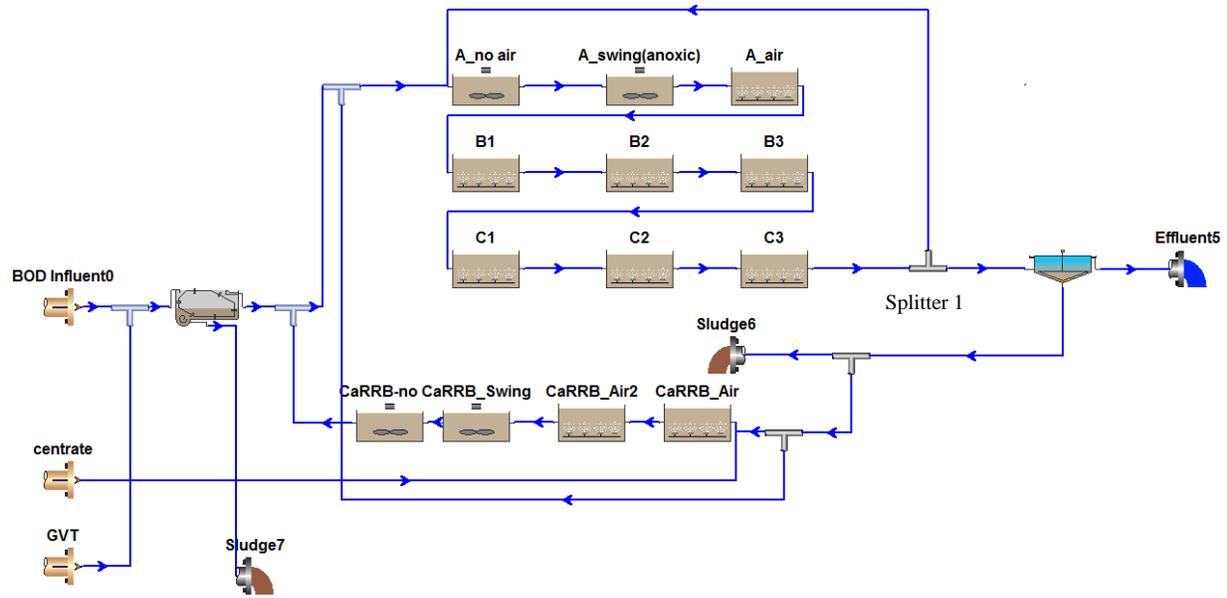


Figure 13. Biowin model configuration of the NSEC Treatment Facility

The basin sizes used to design the model are displayed in Table 2. These volumes were based on the number of units in use at Metro during 2011 and the size of each unit (volumes and number of units were provided by Metro).

Table 4. Biowin Basin and Unit Sizing

Unit	# (in use)	V _{each} (MG)	V _{Total} (MG)	V _{Total} (m ³)
CaRRB_Air1	1.5	0.46	0.69	1.0
CaRRB_Air2	1.5	0.46	0.69	1.0
CaRRB_Swing	3	0.11	416.4	1249.1
CaRRB_Anoxic	3	0.11	416.4	1249.1
A Pass_no air	12	0.225	851.6	10219.5
A_swing(anoxic)	12	0.225	851.6	10219.5
A_air	12	0.23	870.6	10446.6
B1	12	0.23	858.0	10296.0
B2	12	0.23	858.0	10296.0
B3	12	0.23	858.0	10296.0
C1	12	0.23	858.0	10296.0
C2	12	0.23	858.0	10296.0
C3	12	0.23	858.0	10296.0
Unit	# (in use)	Area (m ²)	Depth(m)	V _{Total} (m ³)

Clarifier	12	14802	3	44406
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The District also provided flow rate and parameter values that were used to calibrate the model. The influent, centrate, and gravity thickener overflow data were directly input into the Biowin model as inflows. Calibration data comparing the NSEC and Biowin inputs and outputs are listed in Appendix B. All output values of the model are within a 10% difference of the facility concentrations. The exceptions include alkalinity and effluent ammonia concentration. An overestimation by Biowin on the amount of ammonia removed from the system caused the ammonia concentration to be lower than the plant's reported values.

The variation in alkalinity may be due to how Biowin calculates alkalinity. CaRRB is an open system therefore it is constantly in contact with the atmosphere and exchanging CO₂. Biowin may be calculating alkalinity based on a closed system therefore nothing is being replenished which results in an output concentration much lower than reality.

3.5.1 Sensitivity to pH

Decreasing pH occurring along the length of CaRRB results in a reducing rates of nitrification along the basin. The model's aerated portion of CaRRB was split into two zones (CaRRB_Air1 and CaRRB_Air2) to better represent what is occurring on site. DO concentrations of 0.5 to 2.5 mg/l were input into the model and output values were recorded. To compare the differences in the rate of ammonia oxidized the results were graphed for CaRRB_Air1 and CaRRB_Air2 for each DO concentrations used (Figure 14).

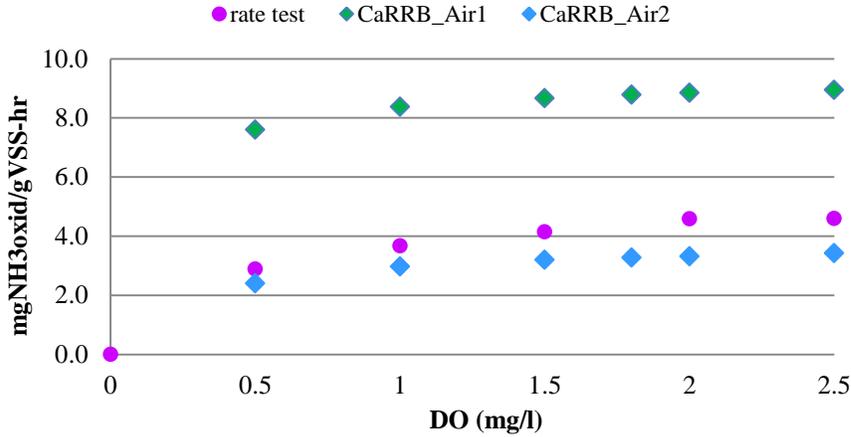


Figure 14. Comparison of the rate of ammonia oxidized at each DO from Biowin CaRRB results and DO rate test results

The rate of ammonia oxidized was found using equation (2):

$$\text{Ammonia Oxidation Rate} = \frac{N_t - N_{(t-1)}}{VSS \times \Delta t} \quad (2)$$

As shown in Figure 14 and Table 5, noticeably lower oxidation rates were calculated in CaRRB_Air2 in comparison to CaRRB_Air1. CaRRB_Air1 reflects nitrification occurring at the higher incoming pH (~7.0- 7.2) while CaRRB_Air2 is the nitrification rate at a lower starting pH (initial pH of CaRRB_Air2 = output pH of CaRRB_Air1). Both sets of data show a plateau in the oxidation rate at DO =1.5 mg/l which is consistent with the findings in the DO rate tests.

Table 5. Biowin CaRRB effluent pH and ammonia concentration versus DO concentration

	DO (mg/l)	0.5	1.0	1.5	1.8	2.0	2.5
CaRRB Air 1	NH ₃ -N	26.6	24.8	24	23.7	23.55	23.3
	pH	6.81	6.78	6.77	6.77	6.77	6.77
	mgNH ₃ ox/hr-VSS	7.60	8.38	8.66	8.78	8.84	8.95
CaRRB Air 2	NH ₃ -N	20.7	17.5	16.15	15.65	15.4	14.9
	pH	6.65	6.55	6.5	6.5	6.49	6.48
	mgNH ₃ ox/hr-VSS	2.40	2.97	3.20	3.28	3.32	3.42

Figure 12 shows frequent drops of pH to values below 6.4 despite the maintenance of DO concentrations between 1.5-2.0 mg/l. With this information, it seems Biowin under predicts the decrease

in pH that occurs in CaRRB, particularly for the higher DO values (2.0 and 2.5 mg/l) therefore the calculated oxidation rates may be slightly higher than what occurs on site. Since the DO versus nitrification rate tests encompass the decreasing pH effect, the oxidation rate values should fall within the model's CaRRB Air 1 and Air 2 results. Once graphed, it can be seen from Figure 14 that the experimental oxidation rates did lie between the two aerated portions and was more similar to the inhibited CaRRB Air 2 rate. The nitrification rates of the experimental batch tests correspond to the facility's CaRRB basins which suggests the basins are experiencing reduced nitrification performance due to pH inhibition. These results enhance the importance of a proper pH range in the system.

One possible solution to maintaining a pH above 6.5 is to monitor the NH₄-N leaving CaRRB along with the pH and DO in the basins. By setting the initial DO to 1.3-1.5 mg/l, the operator can maintain or adjust the oxygen concentration in CaRRB depending on the pH and effluent ammonia concentrations at the end of the basin. If the pH at the end of the basin is approaching 6.5, the DO can be slightly reduced to decrease the rate of nitrification and refrain the system from dropping outside the desired pH range. If the ammonia concentration leaving CaRRB is too high and pH is still in the desired range, the DO can be slightly increased to increase the nitrification rate and reduce the effluent ammonia concentration. This will allow the system to remain relatively stable while operating at a minimum ASRT.

3.5.2 Potential System Modifications

Due to the high number of upsets the CaRRB experiences and the potential impact on the entire plant, the bypass of CaRRB was analyzed using the Biowin model. By removing CaRRB, the system becomes reliant on the nitrification and denitrification capabilities of the aeration basins. It was predicted that the concern over high ammonia loads stressing the main system should be resolved by the large dilution of centrate upon entrance into the aeration basins. Effluent output values were compared to the reported concentrations provided by Metro along with the baseline model (with CaRRB) results (Table 4).

Table 6. Comparison of Metro WW and Biowin plant effluent results

	Metro	With	No CaRRB	Increased	Increased
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	WW	CaRRB		Q _{recirculation}	Q _{recirculation}
Q _{recirculation} (mgd)	---	151.7	151.7	246.5	379.2
S/M Ratio	---	0.8	0.8	1.3	2.0
NH ₃ -N (mg/l)	1.15	0.04	0.1	0.08	0.12
NO ₅ -N (mg/l)	8.4	8.4	10.4	8.15	6.35
TKN (mg/l)	3.8	2.5	2.5	2.6	2.6
TN (mg/l)	12.2	11.7	13.7	11.5	9.75
Alkalinity (mg/l)	109	3.1	3.0	3.1	3.3

Due to the higher total nitrogen (TN) concentration generated when CaRRB is not in use, it is recommended that the aeration basin recirculation rate is increased. The larger recirculation rate will increase the amount of denitrification occurring in the system which will lower the effluent NO₅ (NO₃ + NO₂) and decrease the TN concentration leaving the plant. The results from increasing the recirculation rate are displayed in Table 6. The recirculation rate was increased by increasing the ratio of the side flow and the main pipe flow (S/M) on splitter 1 on Figure 13. The original S/M = 0.80 which corresponds to a recirculation flow of 151.7 mgd. The S/M ratio was increased to 1.3 and 2.0 and compared to the baseline model results.

Although Biowin over predicts the amount of ammonia removed, the TN concentrations are within 10% of the District's values. The removal of CaRRB resulted in a slight increase in TN (2 mg/l) due to increases in both NH₃-N and NO₅-N. By increasing the recirculation flow rate by 60%, the increase in ammonia is offset by the reduction of NO₅-N due to increased denitrification occurring in the system. The TN values from increased recirculation are then equal to the TN concentration with CaRRB. When the recirculation rate was increased to 250% of the original flow, further reduction of NO₅-N occurred yielding a TN concentration that is less than the TN output of the original model (with CaRRB). These results indicate the District could reduce their aeration costs by omitting the use of CaRRB while still maintaining a low TN effluent concentration.

Due to the high number of solids retained in the winter months the secondary clarifier may become overloaded if CaRRB is removed from the system, therefore this suggestion may only be feasible during the summer months.

4.0 Recommendations & Conclusions

Alkalinity and pH play a large role in consistent nitrification performance. The ability to uptake protons generated during nitrification will vary depending on the carbonate species in the system. Insufficient alkalinity due to its speciation results in declining pH values which exacerbates the situation by further reducing the buffering capacity. Ammonia fluctuations occurring in CaRRB is a result of pH declines to 6.5 and lower causing the nitrification to become inhibited. This leads to increased ammonia concentrations leaving the basin. The steady flow of centrate entering CaRRB restores the alkalinity and pH to favorable conditions resulting in the removal of inhibition on the organisms and continued nitrification.

Fluctuations in the ammonia concentrations leaving the NSEC may be associated with growth rate inhibitions taking place in CaRRB. The reduced growth of nitrifiers in CaRRB results in a decreased nitrifier population that is carried into the main system as the CaRRB effluent is cycled into the aeration basins. This results in decreased nitrification performance in the aeration basins which is conveyed by the increased ammonia concentrations in the effluent.

Possible solutions to reducing or removing CaRRB ammonia fluctuations are by pH and DO control along with omitting the use of CaRRB entirely. The District maintains an average DO concentration of 1.5 to 2.0 mg/l in CaRRB and monitors the effluent ammonia and TSS in the system. As the pH decreases to values below 6.5, little to no nitrification occurs in the basins and aeration energy is being wasted. When the DO is increased, the rate of ammonia oxidation increases causing a more rapid drop in pH. By monitoring pH and adjusting the DO concentrations if the pH begins dropping too low

(below 6.6) or the rate of nitrification becomes too slow (effluent ammonia values are too high) the amount of aeration energy used could be reduced along with the system fluctuations.

Omitting CaRRB will also result in aeration energy savings. Modeling analysis shows a small increase in ammonia and NO_5 concentrations occur when CaRRB is removed but this can be offset by increasing the recirculation flowrate in the aeration basins (increased RAS flow for aeration basins). The increased flow results in increased NO_5 removal by denitrification; this offsets the increase in ammonia resulting in an equal or lower TN concentration leaving the plant. Due to the high amount of solids required during the colder winter months, this solution is only recommended for the summer to reduce the potential of clarifier overloading.

Reducing the fluctuations occurring in CaRRB by either monitoring or bypassing the basins can provide the District with aeration energy savings along with a more consistent effluent ammonia concentration. This also allows Metro to continue operation at very low ASRTs. The low effluent ammonia concentrations output by the Biowin model after CaRRB removal indicates the aeration basins are capable of receiving centrate directly without being stressed by the increased ammonia load. It is recommended that the District implement a new strategy to control CaRRB to reduce the ammonia fluctuations occurring in the plant. Steady TN concentrations will be increasingly important to Metro due to the implementation of more stringent nutrient standards in the near future.

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Appendix:

Appendix A. Biowin Basin Sizing based on Size of Unit and Number in Use

Unit	# (in use)	V_{each} (MG)	V_{Total} (MG)	V_{Total} (m3)
CaRRB_Air1	1.5	0.46	0.69	1.0
CaRRB_Air2	1.5	0.46	0.69	1.0
CaRRB_Swing	3	0.11	416.4	1249.1
CaRRB_Anoxic	3	0.11	416.4	1249.1
A Pass_no air	12	0.225	851.6	10219.5
A_swing(anoxic)	12	0.225	851.6	10219.5
A_air	12	0.23	870.6	10446.6
B1	12	0.23	858.0	10296.0
B2	12	0.23	858.0	10296.0
B3	12	0.23	858.0	10296.0
C1	12	0.23	858.0	10296.0
C2	12	0.23	858.0	10296.0
C3	12	0.23	858.0	10296.0
Unit	# (in use)	Area (m2)	Depth(m)	V_{Total} (m3)
Clarifier	12	14802	3	44406

Appendix B: Metro versus Biowin Inputs and Outputs

Influent	Metro	Biowin	Units
Flow	86	86	mgd
BOD	324	324	mg/l
TSS	298	298	mg/l
VSS	267	267	mg/l
TKN	46.5	46.5	mg/l
Centrate			
Total Q	1.06	1	mgd
Alkalinity	4420	4500	mg/l
Ammonia_N	1340	1340	mg/l
BOD5	216.4	n/a	mg/l
TSS	1260	1300	mg/l
RAS			
Flow to CaRRB	30.6	33.1	mgd
Total Flow	91.2	99.4	mgd
TSS	6053	6180	mg/l
RAS:Cent	31.5	33.1	
CaRRB			
NH3_in	40.2		mg/l
MLSS	5500-6200	6024	mg/l
VSS	4680-5270	4880	mg/l
DO	1.3-1.9	1.8	mg/l
NH3_out	15-20	14.2	mg/l
Alk_out	275	2 - 3	mg/l
Aer Basin			
MLSS	3600	3343	mg/l
MLVSS	3100	2713	mg/l
Effluent			
NH3-N	1.15	0.04	mg/l
TKN=	3.8	2.47	mg/l
NO5-N	8.4	8.4	mg/l
TOT-N	12.2	11.7	mg/l
Alk	109	3.1	mg/l
Plant SRT	~ 5	5.53	day

Appendix C. Comparison of Ammonia species results from Biowin Aerated Zone 1 and 2 at DO = 0.5 to 2.5 mg/l

	DO (mg/l)	0.5	1.0	1.5	1.8	2.0	2.5
CaRRB Air	NH ₃ -N	26.6	24.8	24	23.7	23.55	23.3
	NO ₃ -N	15.24	17	17.8	18.17	18.35	18.7
	NO ₂ -N	4.36	4.5	4.4	4.33	4.3	4.2
	Tot N	46.2	46.3	46.2	46.2	46.2	46.2
	pH	6.81	6.78	6.77	6.77	6.77	6.77
	mgNH ₃ ox/hr-VSS	7.60	8.38	8.66	8.78	8.84	8.95
CaRRB Air 2	NH ₃ -N	20.7	17.5	16.15	15.65	15.4	14.9
	NO ₃ -N	19.8	23.4	25.2	25.9	26.3	27
	NO ₂ -N	8.0	8.0	7.69	7.5	7.4	7.24
	Tot N	48.5	48.9	49.04	49.05	49.1	49.14
	pH	6.65	6.55	6.5	6.5	6.49	6.48
	mgNH ₃ ox/hr-VSS	2.40	2.97	3.20	3.28	3.32	3.42