

2016-01-01

# Analysis Of Nitrogen Speciation And Removal In Direct Potable Reuse In El Paso, Texas

Oluwaseye Michael Owoseni

*University of Texas at El Paso, doubleosima33@gmail.com*

Follow this and additional works at: [https://digitalcommons.utep.edu/open\\_etd](https://digitalcommons.utep.edu/open_etd)



Part of the [Environmental Engineering Commons](#)

---

## Recommended Citation

Owoseni, Oluwaseye Michael, "Analysis Of Nitrogen Speciation And Removal In Direct Potable Reuse In El Paso, Texas" (2016).  
*Open Access Theses & Dissertations*. 918.  
[https://digitalcommons.utep.edu/open\\_etd/918](https://digitalcommons.utep.edu/open_etd/918)

This is brought to you for free and open access by DigitalCommons@UTEP. It has been accepted for inclusion in Open Access Theses & Dissertations by an authorized administrator of DigitalCommons@UTEP. For more information, please contact [lweber@utep.edu](mailto:lweber@utep.edu).

ANALYSIS OF NITROGEN SPECIATION AND REMOVAL IN DIRECT  
POTABLE REUSE TREATMENT IN EL PASO, TX

OLUWASEYE MICHAEL OWOSENI

Master's Program in Environmental Engineering

APPROVED:

---

W. Shane Walker, Ph.D., Chair

---

Ivonne Santiago, Ph.D.

---

Vanessa Lougheed, Ph.D.

---

Charles Ambler, Ph.D.

Dean of the Graduate School

Copyright ©

by

Oluwaseye Michael Owoseni

2016

ANALYSIS OF NITROGEN SPECIATION AND REMOVAL IN DIRECT  
POTABLE REUSE TREATMENT IN EL PASO, TX

by

OLUWASEYE MICHAEL OWOSENI, B.Eng. Mining Engineering

THESIS

Presented to the Faculty of the Graduate School of

The University of Texas at El Paso

in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING

Department of Civil Engineering

THE UNIVERSITY OF TEXAS AT EL PASO

May 2016

## **Acknowledgements**

My sincere appreciation goes to my graduate advisor, Dr. Shane Walker, for his guidance, sincere effort and motivation in making this paper a success. I also acknowledge the support of the El Paso Water Utilities (EPWU) and ARCADIS for giving me a role on this project. I am also grateful to my colleagues that worked on this project; Cesar, Clara, Patricia, Raul, Sucky, Tatiana, and Troy.

My appreciation goes to my thesis committee members and to all my professors for their understanding and support. I sincerely appreciate the members of staff of the Center for Inland Desalination Systems (CIDS) for their assistance and training.

Ultimately, I give all the glory to God for the grace to complete this work and I am also grateful unto Him for giving me the best parents (Olugbenga and Mercy Owoseni) and siblings (Ibiwumi, Olasehinde, and Oluwanifemi) who support me both spiritually and physically.

## **Abstract**

Population growth and increasing demand for potable water is causing a need for additional sources to water portfolios in areas with water scarcity. Direct Potable Reuse (DPR) is gaining recognition in these regions and ensuring appropriate measures for the removal of nitrogen and other contaminants cannot be overemphasized. Two nitrogen species, nitrate and nitrite are known to cause harmful effects on young infants below the age of six months. El Paso Water Utilities conducted a pilot test for DPR to ascertain the viability of DPR as an additional source to the current water portfolio.

Non-chlorinated secondary clarifier effluent from a wastewater treatment plant was treated through several barriers for different contaminants. The effectiveness of the barriers provided in the treatment train for nitrogen species removal was evaluated in this paper. These barriers include the wastewater treatment plants nitrification process, denitrification filters, and nanofiltration /reverse osmosis membranes.

To generate confidence in the results of analyses of the nitrogen species, the accuracy or reliability of the measurements for nitrogen species was evaluated. The inter and intra laboratory comparisons used showed good relationships indicating accuracy. The denitrification filters had challenges with variabilities in influent water nitrogen speciation and was removed from the pilot test. The NF/RO membranes were consistent in nitrogen removal and performed stably during the pilot test. Nitrification inhibition rate tests performed on the wastewater showed low rates in comparison to a standard model. Overall, the pilot test helped in identifying key factors that will enhance nitrogen removal in the DPR facility.

## Table of Contents

Acknowledgements.....	iv
Abstract.....	v
Table of Contents.....	vi
List of Tables .....	vii
List of Figures .....	viii
1. Introduction.....	1
1.1 Background.....	1
1.2 AWPf process overview.....	2
1.3 Goals and Objectives .....	7
2. Methods.....	9
2.1 Analysis of samples from pilot study.....	9
2.2 Chemsan and Eurofins data.....	10
2.3 Nitrification rate test .....	11
3. Results and Discussion .....	16
3.1 Quality assurance of nitrogen analyses.....	16
3.2 Evaluation of the performance of the denitrification filters.....	19
3.3 Evaluation of the performance of NF/RO with respect to nitrogen removal.....	22
3.4 Analysis of nitrification rate in upstream wastewater treatment .....	25
Chapter 4: Conclusions .....	28
References.....	29
Vita.....	31

## **List of Tables**

Table 1.1 Denitrification filter system .....	4
Table 1.2 MF/UF Characteristics.....	5
Table 1.3 NF/RO parameters .....	6
Table 2.1 Ion Chromatograph operation parameters .....	10
Table 3.1 Average MLVSS concentrations .....	26



## List of Figures

Figure 1.1 Effluent concentrations of ammonia and nitrate from the Bustamante WWTP, January, 2012 to September, 2014 (Source: ARCADIS, 2015) .....	2
Figure 1.2 Advanced water purification facility process schematic .....	3
Figure 1.3 Denitrification filters .....	4
Figure 1.4 Ozonation system .....	4
Figure 1.5 Pall and Evoqua filtration units .....	5
Figure 1.6 NF/RO Skids .....	6
Figure 1.7 Online Monitors .....	7
Figure 2.1 Ion Chromatograph System .....	9
Figure 2.2 TOC/TN Analyzer .....	10
Figure 2.3 DR 5000 spectrophotometer .....	12
Figure 2.4 DR 4000 spectrophotometer .....	12
Figure 2.5 Nitrification test set up .....	14
Figure 3.1 Comparison of IC measurements and TN analyzer .....	17
Figure 3.2 Comparison of online measurements and TN analyzer .....	17
Figure 3.3 Comparison of nitrate results (CHEMSCAN/UTEP) .....	18
Figure 3.4 Comparison of nitrate results (UTEP/EUROFINS) .....	19
Figure 3.5 Denitrification filters dissolved nitrogen .....	20
Figure 3.6 Chemsan measurements of nitrogen species: (a) influent and (b) effluent of the denitrification filters .....	21
Figure 3.7 Dissolved nitrogen removal by NF/RO .....	22
Figure 3.8 Ammonia removal by NF/RO .....	23
Figure 3.9 Nitrate removal by NF/RO .....	24
Figure 3.10 Nitrite removal by NF/RO .....	24
Figure 3.11 Nitrification control test one .....	25
Figure 3.12 Effect of recycle ratio, aeration zone and temperature on nitrification rates in wastewater aeration .....	26
Figure 3.13 Effect of industrial wastewater on nitrification .....	27

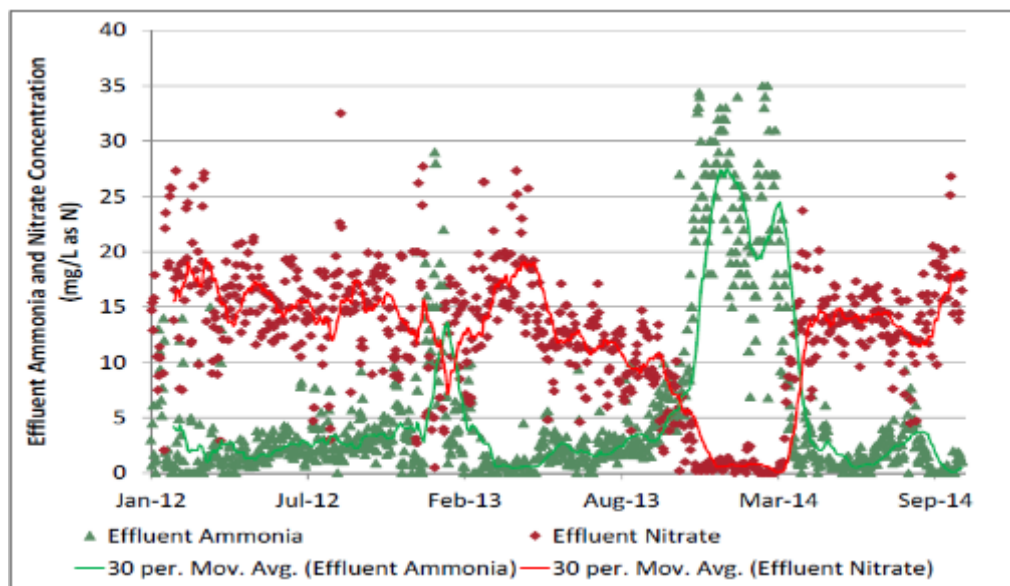
# **1. Introduction**

## **1.1 Background**

Direct potable reuse (DPR) involves the direct introduction of purified water from initial wastewater sources into a drinking water supply system (National Research Council (NRC), 1998). In the case of El Paso, Texas, non-chlorinated secondary clarifier effluent from a wastewater treatment plant was treated in a pilot scale system through: biological denitrification, ozonation, microfiltration and ultrafiltration, nanofiltration and reverse osmosis, ultraviolet advance oxidation process (UV-AOP), and granular activated carbon (GAC). The city of El Paso is planning to add alternative potable municipal water supply sources to its current portfolio. Historically, wastewater treatment for industrial and domestic sources is designed to meet stream discharge and or non-potable water standards. Some wastewater treatment plants have processes for reducing nutrient loads in order to discharge to receiving waters.

Nitrogen speciation, as discussed in this research, covers several major forms of inorganic nitrogen compounds remaining in conventional municipal wastewater treatment plant effluents that must be removed to meet drinking water quality standards. Ammonia ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ) are the main nitrogen compounds of concern. The maximum contaminant level (MCL) for nitrate and nitrite according to the U.S. Environmental Protection Agency (USEPA) is 10 mg/L and 1 mg/L as nitrogen respectively (USEPA, 2016). The health effects of nitrate and nitrite in drinking water includes illness in infants below the age of six months and a symptom called the blue baby syndrome or methemoglobinemia (McCasland et al. 2012). This research covers the analysis of water samples collected at each stage in a DPR pilot system and analyzed for nitrogen components.

ARCADIS led the pilot study from May 2015 to January 2016 with 100 gpm from the Roberto R. Bustamante Wastewater Treatment Plant (WWTP) secondary clarifier effluent being treated in a setup with the proposed Advanced Water Purification Facility (AWPF) processes. Figure 1.1 shows the effluent concentrations of ammonia and nitrate from the WWTP from January, 2012 through September, 2014. Ammonia was typically nitrified to nitrate for most of the year. This is to meet the Texas Pollutant Discharge Elimination System (TPDES) limit of 5 mg/L as nitrogen for ammonia on a 30 day average. The WWTP is designed to nitrify between the months of April to October and has an exception of a maintenance during the winter when the limit set by TPDES does not apply.

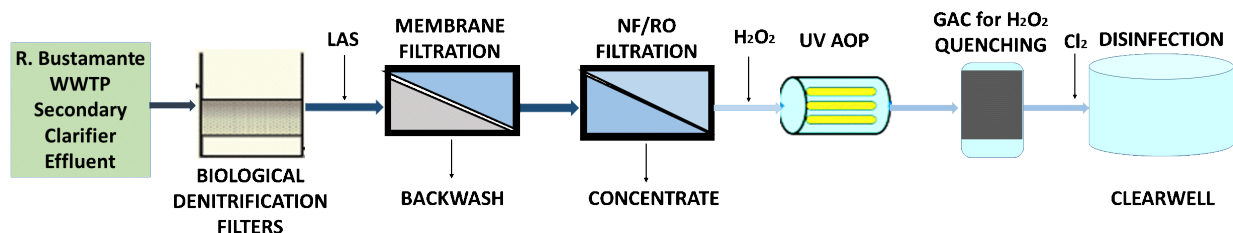


**Figure 1.1 Effluent concentrations of ammonia and nitrate from the Bustamante WWTP, January, 2012 to September, 2014 (Source: ARCADIS, 2015)**

## 1.2 AWPF process overview

Water treatment for potable reuse purposes should include a provision of several barriers for the different kinds of contaminants in wastewater. The system should be reliable, provide redundancy, must be robust and indeed resilient. Reliability of a DPR system simply describes a

system that provides consistent water quality that equals or exceeds current drinking water sources in the safety of public health (Pecson et al., 2015). Redundancy involves the provision of multiple or diverse barriers for different contaminants in wastewater (NRC, 2012). The AWPf comprises of such barriers to ensure all contaminants are removed or reduced to non-harmful concentrations. A schematic of the AWPf pilot is shown in Figure 1.2.



**Figure 1.2 Advanced water purification facility process schematic**

A robust system is one that consists of units that provide removal for several contaminants simultaneously (Gerrity, 2013). Resilience in DPR addresses the need for a treatment system that is able to prevent failure and also respond to failures while ensuring there is no harm to public health (Pecson et al., 2015).

Secondary clarifier effluent from the WWTP is treated through denitrification filters. The denitrification filters were supplied by Severn Trent and filter system information is shown in

Table 1.1. Four of six total filters were used during the pilot test and methanol was used as the food source for the denitrification filters. Figure 1.3 shows the denitrification filters at the pilot facility. Ozonation is used for a period of the pilot test and provides benefits such as disinfection and contribution of dissolved oxygen (Tchobanoglous, 2014). The ozonation unit is shown in Figure 1.4. The addition of liquid ammonium sulfate (LAS) to form chloramines is used as pretreatment for the microfiltration (MF) and ultrafiltration units and helps in the minimization of biological fouling (Nguyen, 2012).

**Table 1.1 Denitrification filter system**

Criteria	Denitrification Filter
Manufacturer	Severn Trent
Model	Modular Deep Bed Filter
Maximum Flow (gpm)	150 gpm
Number of filters	6
Filter diameter (ft)	3.28
Filter surface area (ft <sup>2</sup> )	8.45
Total surface area (ft <sup>2</sup> )	50.7
Media depth (ft)	6



**Figure 1.3 Denitrification filters**



**Figure 1.4 Ozonation system**

The two MF/UF systems tested were provided by Evoqua Water Technologies and Pall Corporation and are shown in Figure 1.5. The MF/UF design characteristics is shown in Table 1.2. MF membranes are designed to remove particles, sediment, algae, protozoa and bacteria while UF membranes can remove small colloids and viruses in addition to that removed by MF membranes (Crittenden, 2012).



**Figure 1.5 Pall and Evoqua filtration units**

**Table 1.2 MF/UF Characteristics**

Criteria	Evoqua	Pall
Module model	L40N/CPII	UNA-620A
Flow pattern	Outside-In	Outside-In
Recovery (%)	92-96	95-98
Nominal pore size ( $\mu\text{m}$ )	0.04	0.1
Membrane material	Polyvinylidene fluoride	Polyvinylidene fluoride
Membrane Surface Area ( $\text{ft}^2$ )	721	538
Number of Modules	2	4
Total Surface Area ( $\text{ft}^2$ )	1442	2152
Anticipated Flux (gfd)	25	25
Pilot System Flow (gpm)	26	37

NF membranes provides additional removal of dissolved organic matter (DOM) and divalent ions. Nonporous RO membranes also provide additional removal of monovalent species



(Crittenden, 2012). The NF/RO membranes that was used in this test were from Hydranautics and Dow. There were three parallel NF/RO systems (provided by Harn R/O) and they were tested to compare performance. The important characteristics of the NF/RO systems are listed in Table 1.3. The three NF/RO systems are shown in Figure 1.6.

**Table 1.3 NF/RO parameters**

Characteristic	Description		
Element Model	<b>ESPA2-LD</b>	<b>NF90-400/34i</b>	<b>ESNA1-LF2-LD</b>
Element Manufacturer	Hydranautics	Dow	Hydranautics
Element Diameter	4-inch	4-inch	4-inch
Element Membrane Area (ft <sup>2</sup> )	80	82	80
TDS Rejection	96-97%	78-84%	43-51%
Array	2:1	2:1	2:1
# of Stages	2	2	2
Total # of Vessels	3	3	3
# of Elements per Vessel	6	6	6
Total # of Elements	18	18	18
Average System Flux	11.7 gfd	11.7 gfd	11.7 gfd
Membrane Area (ft <sup>2</sup> )	80	82	80



**Figure 1.6 NF/RO Skids**

A hydrogen peroxide ( $\text{H}_2\text{O}_2$ )/ ultraviolet (UV) light advanced oxidation process (AOP) is used downstream of the NF/RO membranes for the removal or destruction of toxic synthetic organic compounds (SOCs) (Crittenden, 2012). Granular activated carbon (GAC) filtration was used for quenching residual peroxide from the UV AOP process. Online monitors are put in place and serve as a barrier to monitor the performance of the systems and are shown in Figure 1.7.



**Figure 1.7 Online Monitors**

### **1.3 Goals and Objectives**

A challenge arises with inconsistent water chemistry in the AWPf source water especially with the inorganic nitrogen components. The possibility of diurnal changes in nitrogen speciation is of concern in this research. The overall goal of this paper are as follows:

#### **1. *Quality assurance of nitrogen analyses***

A quality assurance and quality control of analyses of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and dissolved nitrogen is performed to ascertain the precision and or accuracy of the analyzers. This was performed by comparisons of analyses from different analyzers and different laboratory or sources.



## ***2. Evaluate the performance of the denitrification filters***

A comparison of the influent concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  to effluent concentrations in the denitrification filters was performed to observe denitrification performance. A characterization of effect of diurnal concentration variations on the performance of the denitrification filters was also examined.

## ***3. Evaluate nitrogen removal in NF/RO***

The removal of nitrogen by the NF and RO membranes is shown and the effluent concentrations with respect to the MCL of nitrate is discussed.

## ***4. Analyze wastewater nitrification rate and evaluate inhibition.***

Due to variabilities observed in the nitrogen speciation of the secondary clarifier effluent, the nitrification rate of the wastewater was evaluated for potential inhibition. The test involves a simulation of the aeration basin with variations of the physical, biological or chemical composition.

## 2. Methods

### 2.1 Analysis of samples from pilot study

Samples from multiple points in the pilot plant were collected either as grab or composite. A simultaneous cation (DIONEX ICS-1100) and anion (DIONEX ICS-2100) ion chromatography system (Figure 2.1) was used for analyzing the concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in a particular sample. The ion chromatography (IC) analyses follows Standard Method 4110 C'' (Rice, 2012) with IC system details listed in Table 2.1. A Shimadzu TOC V<sub>CSH</sub>/TNM1 (Figure 2.2) was used for simultaneous analysis of the total organic carbon (TOC) and total/dissolved nitrogen content of each sample. The total nitrogen (TN) analyzer measures the nitrogen content in a sample by thermal decomposition of TN in the sample. Nitrogen monoxide is generated, cooled and a detection signal from a chemiluminescence gas analyzer generates a peak with which the TN concentration is measured. To prevent damages to the analyzers, all samples collected upstream of the pilot MF/UF unit were filtered in the laboratory with a 0.45  $\mu\text{m}$  filter before analysis.



**Figure 2.1 Ion Chromatograph System**

**Table 2.1 Ion Chromatograph operation parameters**

<b>Ion Chromatograph Parameter</b>	<b>CATION DIONEX ICS-1100</b>	<b>ANION DIONEX ICS-2100</b>
Column model	IonPac CS16	IonPac AS18
Nominal column temperature	40 °C	35 °C
Sample injection volume	20 µL	20 µL
Eluent concentration	30 mM (MSA <sup>1</sup> )	30 mM (KOH <sup>2</sup> )
Eluent flow rate	1 ml/min	1 ml/min
<sup>1</sup> Methylsulfonic acid <sup>2</sup> Potassium Hydroxide		



**Figure 2.2 TOC/TN Analyzer**

## **2.2 Chemscan and Eurofins data**

Results of analyses by online Chemscan monitors and results from Eurofins laboratory (a NELAP-certified laboratory) were obtained from ARCADIS. The online monitors were put in line at the pilot test to have constant monitoring of the concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  at locations such as; the denitrification filters (influent and effluent) and the NF/RO permeates. Samples are also taken and sent to EUROFINS for several analyses including  $\text{NO}_3^-$  by IC. These results were compared with the results from the analyses conducted at the UTEP laboratory. All the points compared were either from split samples or within a close time range.

### 2.3 Nitrification rate test

Compounds such as phenols, cyanides and thiocyanate have been known to cause inhibition in wastewater nitrification. Ammonia in high concentrations could also act as an inhibitor to wastewater nitrification (Kim, 2008). Several methods could be used in determining the presence of potential inhibitors on the rate of nitrification in wastewater. These methods include the use of pure cultures, nitrifying enrichments or activated sludge (Li, 2015). The activated sludge system was used in this test. Aeration basin samples, primary clarifier effluent, return activated sludge, and industrial wastewater were collected for the tests and batch reactors to simulate the aeration basin was setup in the laboratory. The general procedure is explained under Control Test 1.

#### CONTROL TEST 1

A first control test was performed with sample from the WWTP's aeration basin effluent. The pH and temperature of the grab sample was recorded and transported to the laboratory. The initial alkalinity and ammonia concentration of the mixed liquor sample was measured in the laboratory. The alkalinity was measured using Standard Methods 2320 (Rice, 2012). A 2 liter batch continuously stirred reactor was aerated with stone air diffusers to ensure a dissolved oxygen (DO) of at least 2 mg/L. The batch was spiked with ammonium chloride to raise the concentration of ammonia to approximately 30 mg/L (as N), and the batch was spiked with sodium bicarbonate to raise the alkalinity to approximately 200 mg/L as  $\text{CaCO}_3$ . For this control test the mixed liquor volatile suspended solids (MLVSS) concentration is obtained from the WWTP daily analyses. A 50 ml sample was withdrawn every 30 minutes from the batch reactor, filtered and concentrations of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  is recorded.  $\text{NH}_4^+$  and  $\text{NO}_2^-$  concentrations are analyzed on the HACH DR 5000 spectrophotometer (Figure 2.3). Method 10205 Salicylate Method TNTplus™ 832, HR (2 to 47 mg/L  $\text{NH}_3\text{-N}$ ) from the HACH DR5000 procedures manual was used for ammonia tests.

Method 8153 Ferrous Sulfate Method<sup>1</sup> Powder Pillows HR (2 to 250 mg/L  $\text{NO}_2^-$ ) was used for the nitrite test. The nitrate concentrations were measured on the HACH DR 4000 spectrophotometer (Figure 2.4) using Method 8039 Cadmium Reduction Method Powder Pillows or AccuVac® Ampuls HR (0 to 30.0 mg/L  $\text{NO}_3^-$ -N) from the HACH DR4000 procedures manual.



**Figure 2.3 DR 5000 spectrophotometer**



**Figure 2.4 DR 4000 spectrophotometer**

During a test, the temperature, pH, conductivity and DO concentrations are measured every 30 minutes. These parameters were measured with the use of Orion STAR A329 laboratory meter with probes and calibrated daily.

#### TEST 2 – sensitivity to aeration zone

Another control test was performed with mixed liquor samples from three different zones in the aeration basin. Three 2 liter batch reactors, each representing the different zones were assembled in the laboratory and simultaneously analyzed for nitrification rates following the same procedures from control test 1. The MLVSS concentration of the three zones was calculated using the following;

$$MLVSS \left( \frac{mg}{L} \right) = TVS \left( \frac{mg}{L} \right) - DVS \left( \frac{mg}{L} \right)$$

where TVS = total volatile solids concentration  $\left( \frac{mg}{L} \right)$

and DVS = dissolved volatile solids  $\left( \frac{mg}{L} \right)$

TVS was obtained by volatilizing the total solids (TS) and DVS was obtained by volatilizing the total dissolved solids (TDS). All tests follow standard methods for solids analysis (Method 2540) (Rice, 2012)

The laboratory setup of the batch reactors for the tests is shown in Figure 2.5.



**Figure 2.5 Nitrification test set up**

#### TEST 3 – sensitivity to recycle ratio

A control test was performed with multiple return activated sludge (RAS) recycle ratios of 60%, 85% and 100%. RAS and primary clarifier effluent were sampled and a 2 liter batch reactor was prepared for each recycle ratio. All initial analyses and experimental procedure as in control test 1 is used. The MLVSS concentration is also determined with the same approach as discussed under control test 2.

#### TEST 4 – sensitivity to temperature

For this test, three reactors were prepared each at 85% RAS recycle ratios but with multiple temperature conditions of ambient temperature (20 °C for that day), 30 °C and 35 °C. RAS and primary clarifier effluent are sampled and a 2 liter batch reactor is prepared for each temperature condition.

#### INDUSTRIAL WASTEWATER SOURCE TEST – sensitivity

A final test was performed with the addition of industrial wastewater from an industry that is known to use chemicals that might inhibit nitrification. Three reactors are prepared; the first

reactor has an 85% recycle ratio of RAS, a second reactor is prepared with 95 % recycle ratio (85 % RAS and 10 % industrial wastewater) and the third reactor had 105 % recycle ratio (85 % RAS and 20 % industrial wastewater. All procedures as discussed in the previous control tests were used.

The Monod model equation is commonly used in the description of nitrification kinetics. The Monod equation is

$$\mu = \frac{\mu_m S}{K_s + S}$$

where  $\mu$  = specific growth rate constant due to synthesis,  $d^{-1}$

$\mu_m$  = maximum specific growth rate,  $d^{-1}$

S = concentration of rate limiting substrate, mg/L

$K_s$  = half saturation constant, mg/L

= concentration of limiting substrate when  $\mu = \mu_m/2$  (Davis, 2013)

The specific substrate utilization rate for ammonia was calculated as:

$$\text{Specific ammonia utilization rate} \left( \frac{mg}{g \text{ VSS } hr} \right) = \frac{NH_4 - N \text{ decay rate} \left( \frac{mg}{L \text{ hr}} \right)}{MLVSS \left( \frac{g}{L} \right)}$$

The nitrification rate was calculated as:

$$\text{Nitrification rate} \left( \frac{mg}{g \text{ VSS } hr} \right) = \frac{NO_x - N \text{ production rate} \left( \frac{mg}{L \text{ hr}} \right)}{MLVSS \left( \frac{g}{L} \right)}$$

where  $NO_x - N$  is the sum of  $NO_3^-$  and  $NO_2^-$



### 3. Results and Discussion

#### 3.1 Quality assurance of nitrogen analyses

Quality assurance methods were performed through inter- and intra-laboratory comparisons (Rice, 2012). This was to confirm confidence in the analyses for nitrogen species from the different analyzers. Comparison plots were made for either split samples analyzed on multiple analyzers or samples collected at relatively close times. A comparison was made between the sum of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$  measured by ion chromatography (IC) at the UTEP laboratory and dissolved nitrogen (DN) by the total nitrogen (TN) analyzer at the same laboratory (Figure 3.1). (The pilot samples collected upstream of the MF/UF units were filtered in the laboratory before analyzing). Analyses of these samples and samples downstream of the MF/UF units by the TN analyzer are in turn referred to as DN. The plot is shown in a log-log scale and a trend line fit to the data set showed an  $R^2$  value of 0.97 for 36 points with different symbolic representations for different sample points. This relationship indicates accuracy in measurements by both the IC and TN analyzers. The plot shows that the DN results are mostly greater than the sum of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$  occurring 71 % of the 31 points plotted. The difference between TN and the sum of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$  can be used to estimate dissolved organic nitrogen (DON) concentrations (Pagilla, 2008).

A comparison study of the sum of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{NO}_2^-$  measured by the Chemscan online monitors against the DN results from the TN analyzer is shown in Figure 3.2. An  $R^2$  value of 0.90 was observed indicating lesser relationship as against the comparison of the IC and TN analyzers. This is because analyses by the online monitors for lower concentrations below the 10 mg/L MCL for nitrate were higher than the respective DN measurements. The comparison showed that the DN were mostly greater than those of the online monitors for 62 % of the 63 points plotted.

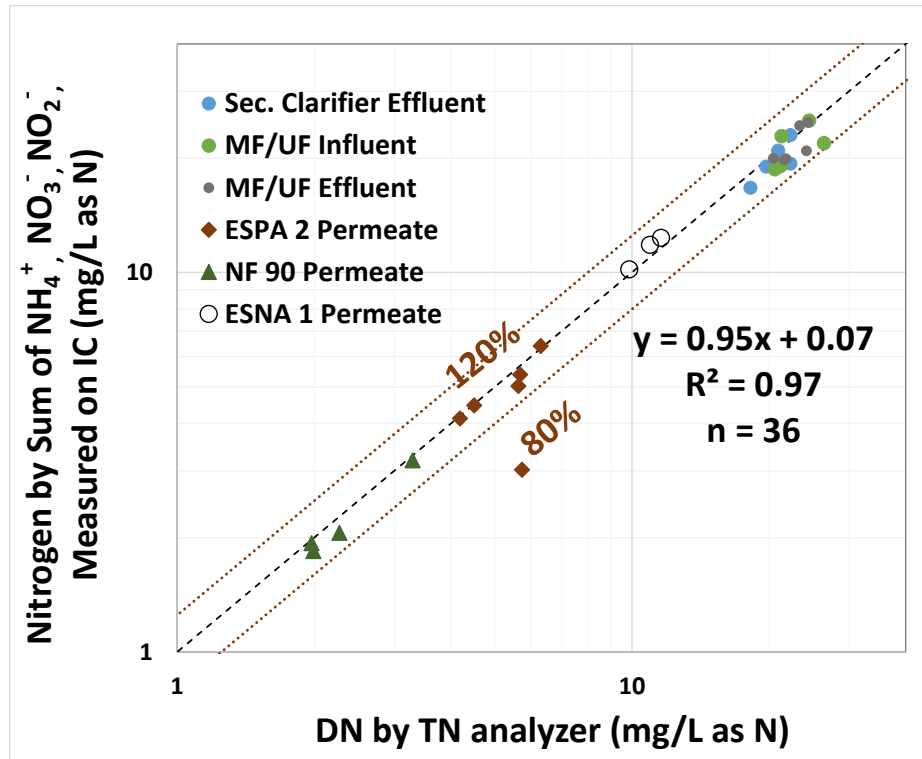


Figure 3.1 Comparison of IC measurements and TN analyzer

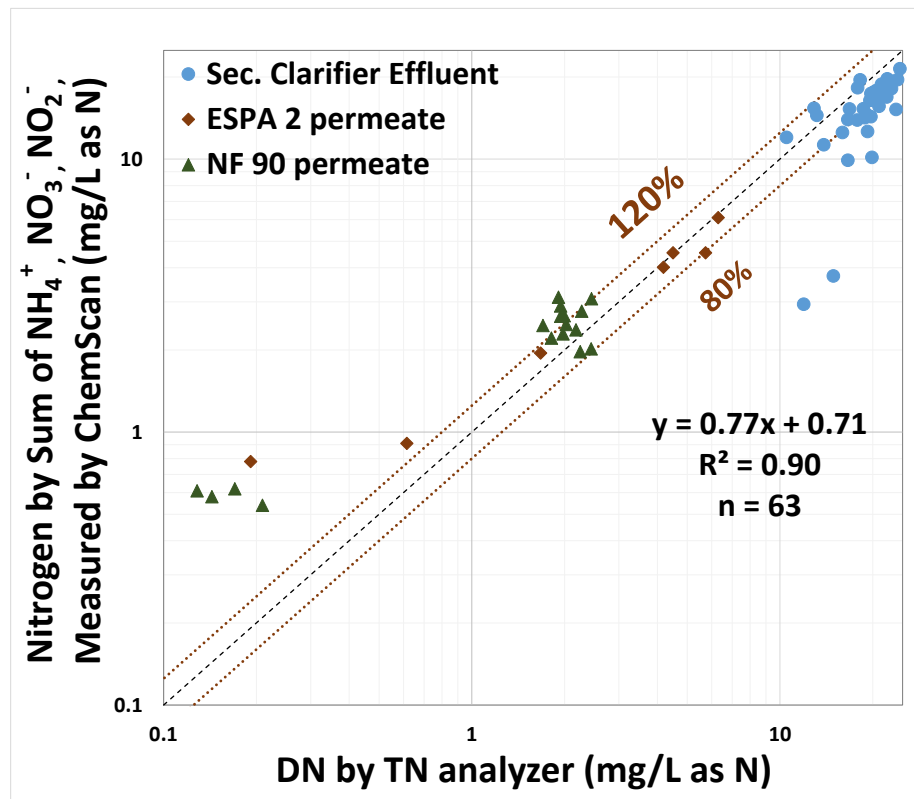
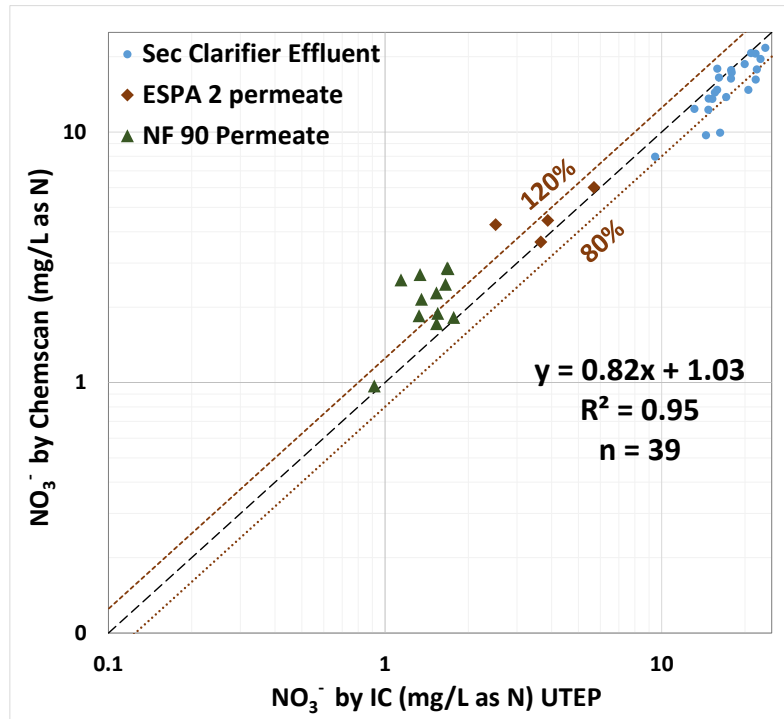
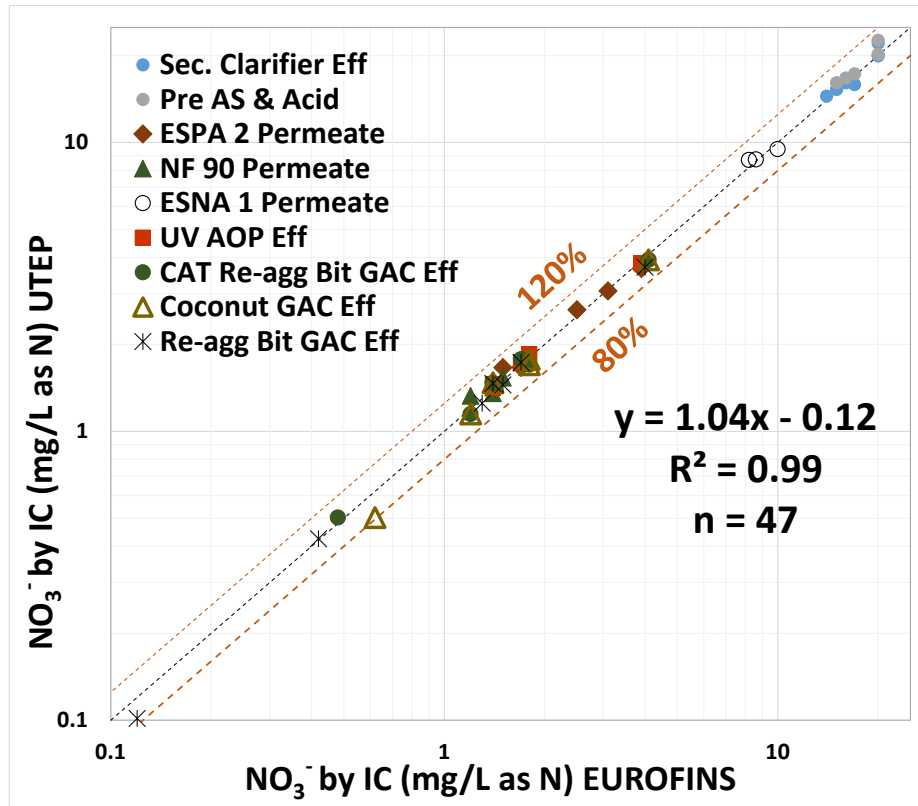


Figure 3.2 Comparison of online measurements and TN analyzer

A comparison of nitrate in mg/L as nitrogen of the measurements by the online monitor and by the IC at the UTEP laboratory is shown in Figure 3.3. With an  $R^2$  value of 95 % the results show a good correlation. It was also observed from this plot that the online monitors have higher concentration values for the NF/RO permeates (15 of 16 points) than the UTEP IC measurements. This can be a “fail-safe” in the DPR facility, providing resilience with faster response time in the case of a failure in the system (Pecson et. al., 2015). Laboratory test results from EUROFINS laboratory, a certified laboratory was also compared with results from the UTEP laboratory. Figure 3.4 shows a comparison of nitrate results in mg/L as nitrogen between UTEP laboratory and EUROFINS laboratory. An  $R^2$  value of 0.99 was observed and indicates good correlation and also establishes confidence in the measurements of nitrate by the two sources. Based on a paired t-test, there is no statistical difference between the UTEP data and the EUROFINS data (P two-tail = 0.065).



**Figure 3.3 Comparison of nitrate results (CHEMSCAN/UTEP)**

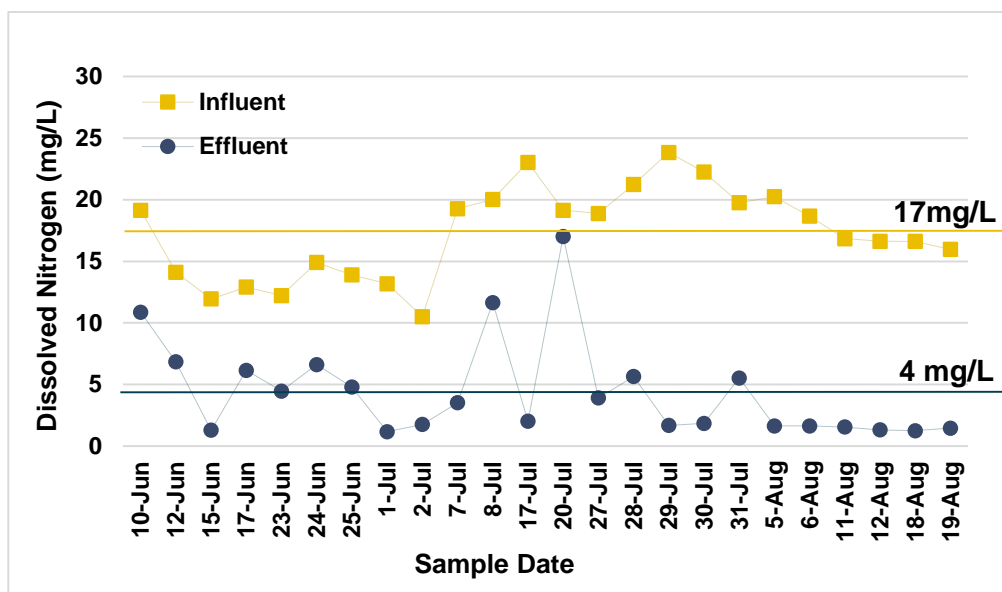


**Figure 3.4 Comparison of nitrate results (UTEP/EUROFINS)**

The relationship observed in all these comparisons therefore indicate reliability and confidence in the analyses of nitrogen species.

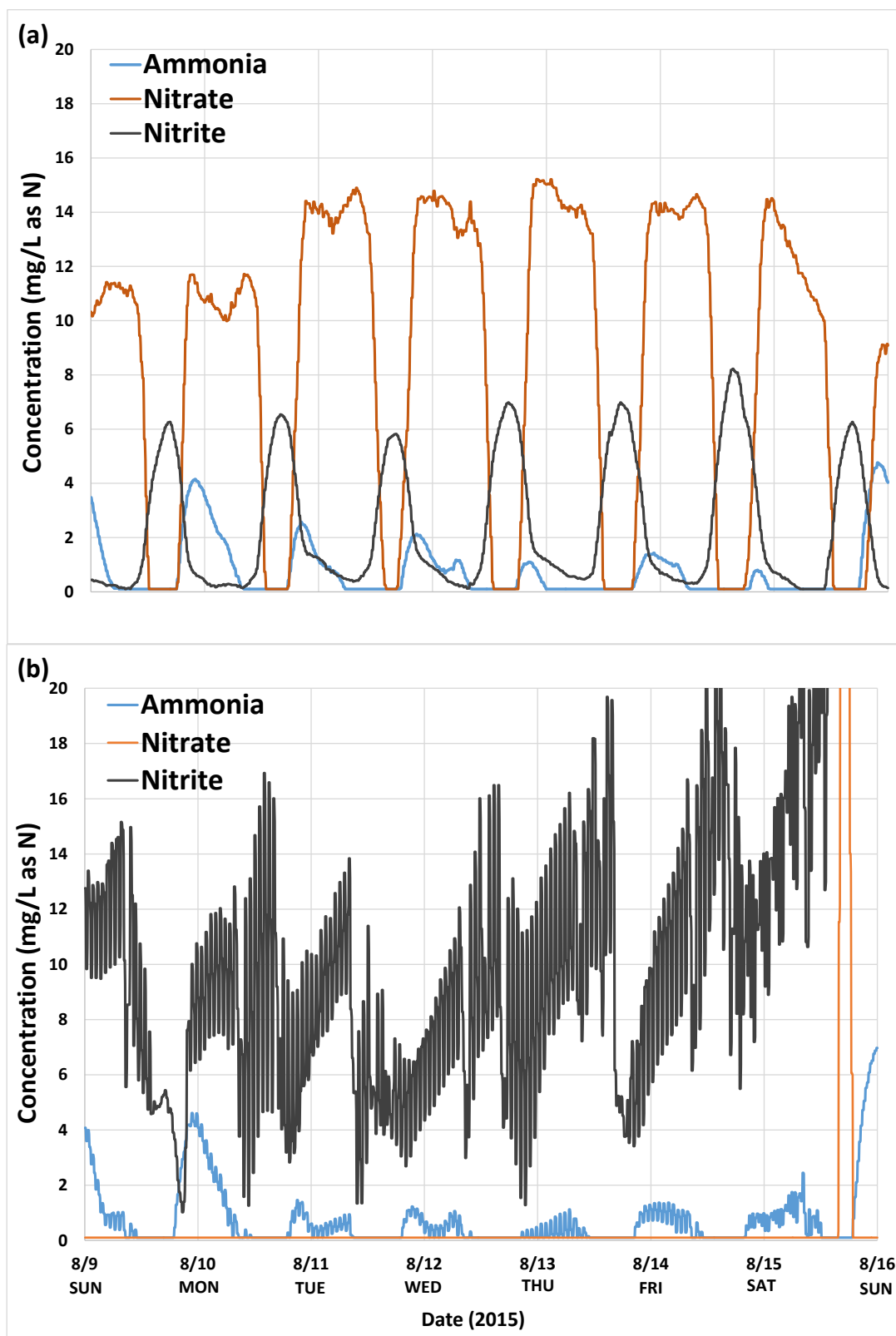
### 3.2 Evaluation of the performance of the denitrification filters

The removal of dissolved nitrogen for samples collected and analyzed by the UTEP team is shown in Figure 3.5. The denitrification filters provided an average removal of 74% of dissolved nitrogen over the sampling period with an average influent concentration of 17 mg/L and an average effluent concentration of 4 mg/L of dissolved nitrogen.



**Figure 3.5 Denitrification filters dissolved nitrogen**

These samples were typically taken in the morning on the respective days by the UTEP team. However, significant diurnal variations were observed in the online monitors, as shown in **Error! Reference source not found.** (near the end of the period shown in Figure 3.5). For most of the day (evening and morning), the upstream wastewater treatment plant achieved significant nitrification (Figure 3.6(a), periods of high nitrate), but during the afternoon, the plant was only achieving nitrification without nitrification (periods of relatively high nitrite). This significant variation undermined the performance of the filters in effective denitrification and produced significant effluent nitrite concentrations, as shown in **Error! Reference source not found.**(b). Furthermore, the denitrification filters were suspected to contribute to biofouling of the downstream membrane filtration units, which ultimately led to the decision to remove the biological denitrification filters from the treatment system.



**Figure 3.6 Chemscan measurements of nitrogen species:**  
**(a) influent and (b) effluent of the denitrification filters**

### 3.3 Evaluation of the performance of NF/RO with respect to nitrogen removal

The performance of the NF/RO membrane skids in dissolved nitrogen removal is shown in Figure 3.7.

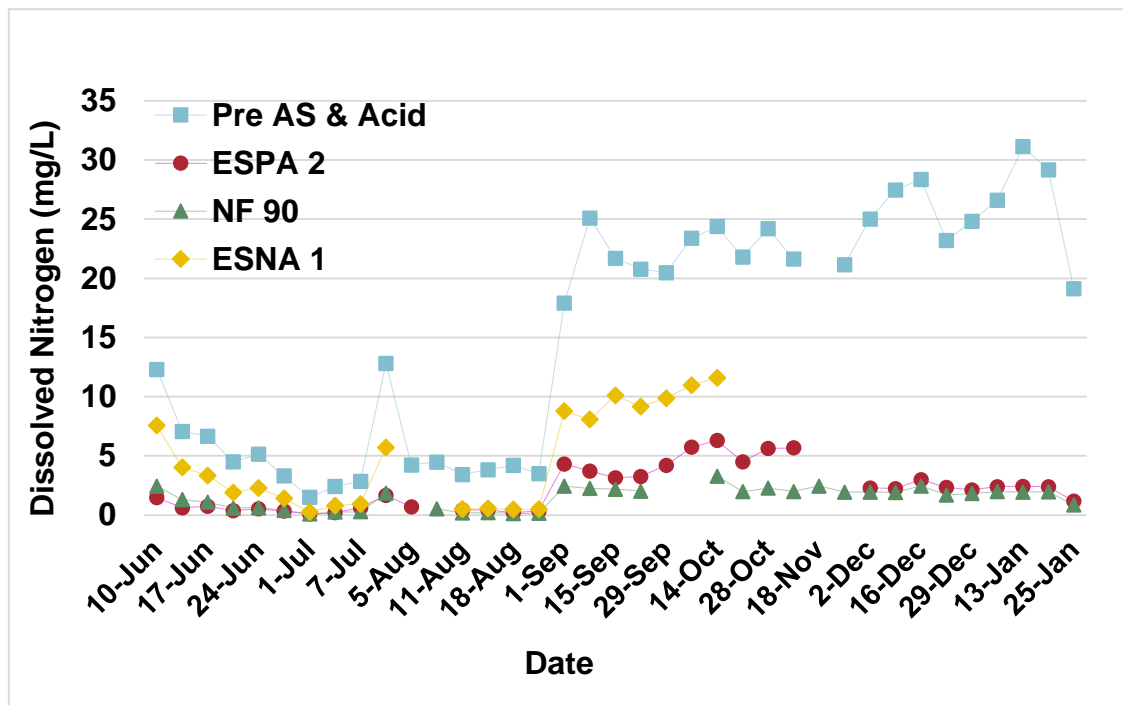
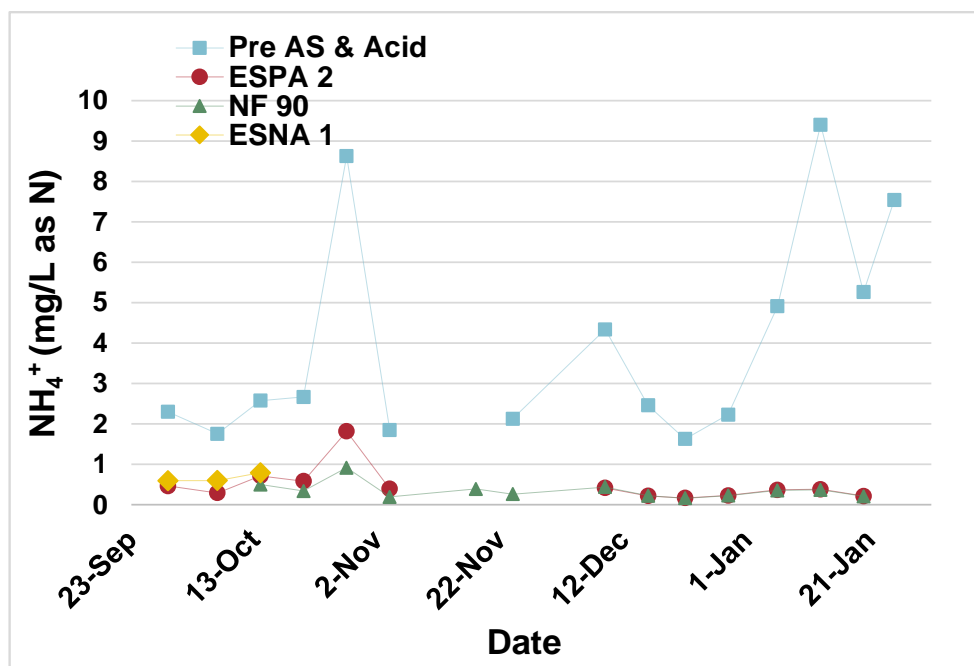


Figure 3.7 Dissolved nitrogen removal by NF/RO

Pre AS & Acid represents the feed water to the three NF/RO skids before the addition of antiscalant (AS) and acid. The NF 90 membranes showed better removal with a 90 % average removal over the pilot test period as against 87 % by the ESPA 2 membranes and 62% by the ESNA 1 membranes. The average feed water dissolved nitrogen concentrations for the sample times shown before addition of AS and acid was 5 mg/L when the denitrification filters were running and 24 mg/L after the denitrification filters were removed. The test of the ESNA 1 membranes was discontinued due to its performance in October, 2015. The removal of ammonia by the three NF/RO membrane skids is shown in Figure 3.8. The average ammonia concentration in the feed water (Pre AS and Acid) was calculated as 4 mg/L as N for the duration shown.



**Figure 3.8 Ammonia removal by NF/RO**

The ESPA 2 membranes showed an 86 % removal for ammonia while the NF 90 and ESNA 1 membranes showed 90 % and 70 % removal respectively. A nitrate trend after the removal of denitrification filters for samples collected by the UTEP team is shown in Figure 3.9. The NF 90 membranes also showed better removal with a 92 % average removal for nitrate for the trend shown. ESPA 2 had an average removal of 85% and the ESNA 1 membranes showed an average of 47 %. The NF 90 and ESPA 2 membranes performed consistently in nitrate removal with no points over the MCL for nitrate. The average Pre AS & Acid concentration for the period shown was 18 mg/L as N. The performance of the NF/RO membranes in terms of nitrite removal is also observed and shown in Figure 3.10. The nitrite results were mostly non-detects with an average of 0.6 mg/L for the Pre AS & Acid sample. The removal of nitrite by the ESPA 2, NF 90 and ESNA 1 membranes were 74 %, 73% and 79% respectively.



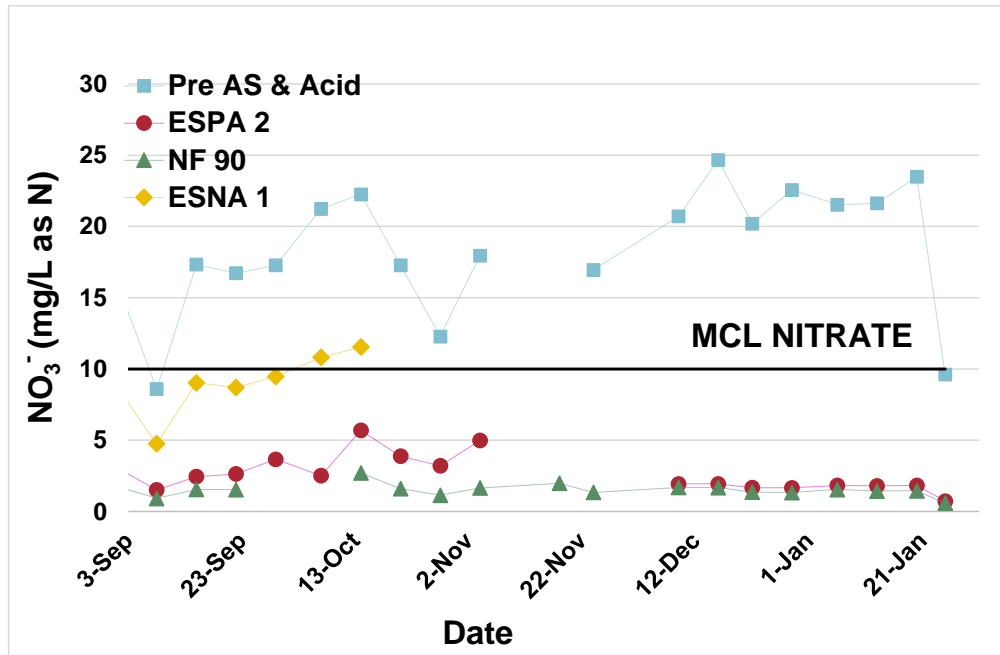


Figure 3.9 Nitrate removal by NF/RO

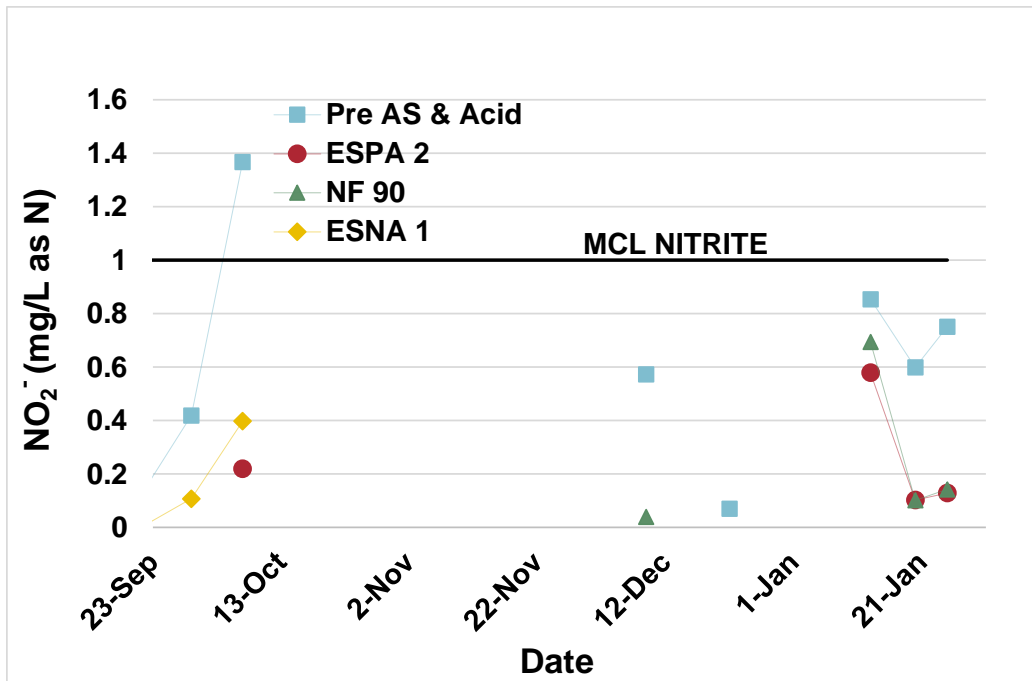


Figure 3.10 Nitrite removal by NF/RO

### 3.4 Analysis of nitrification rate in upstream wastewater treatment

The specific ammonia (substrate) utilization rate from the first control test was observed as 1.44 mg NH<sub>4</sub>-N/g VSS/hr, and the nitrification rate was observed as 1.26 mg NH<sub>4</sub>-N/g VSS/hr. This was obtained by normalizing the linear regression of ammonia decay (6.43 mg/L/hr) and production rate of nitrate and nitrite (5.67 mg/L/hr) by the average MLVSS (4477 mg/L VSS). Figure 3.11 shows the concentration scatter plot from the first control test.

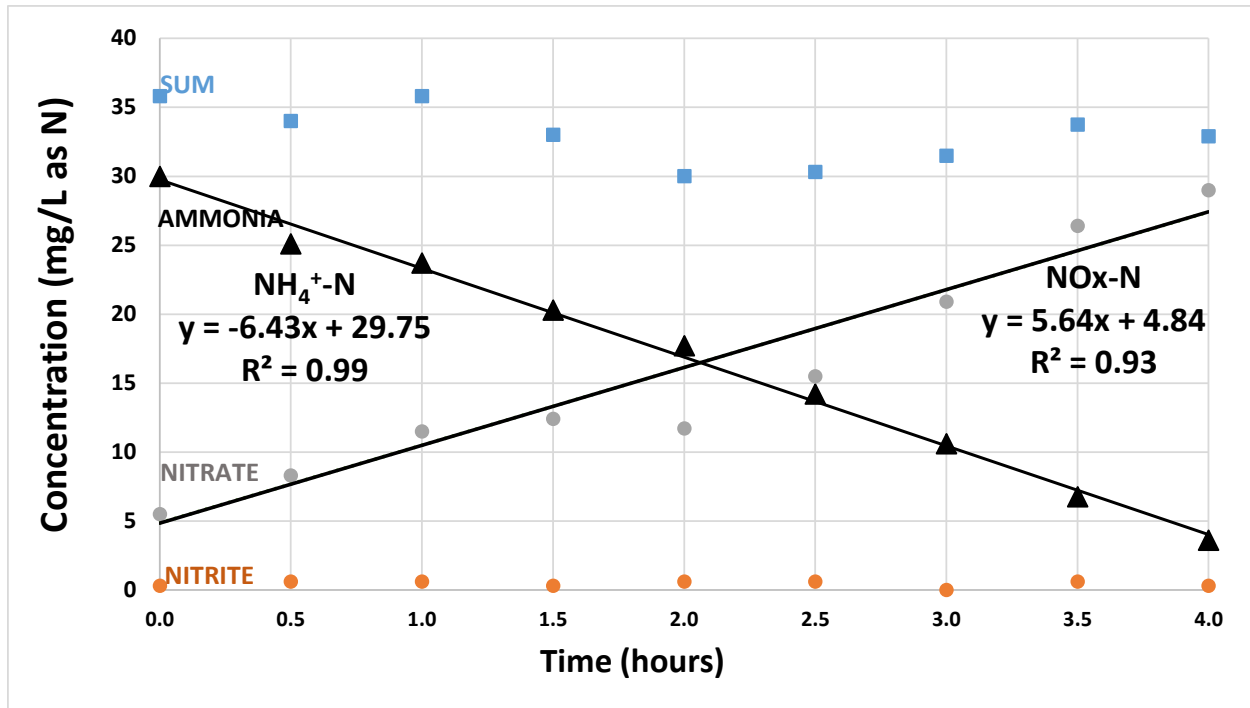
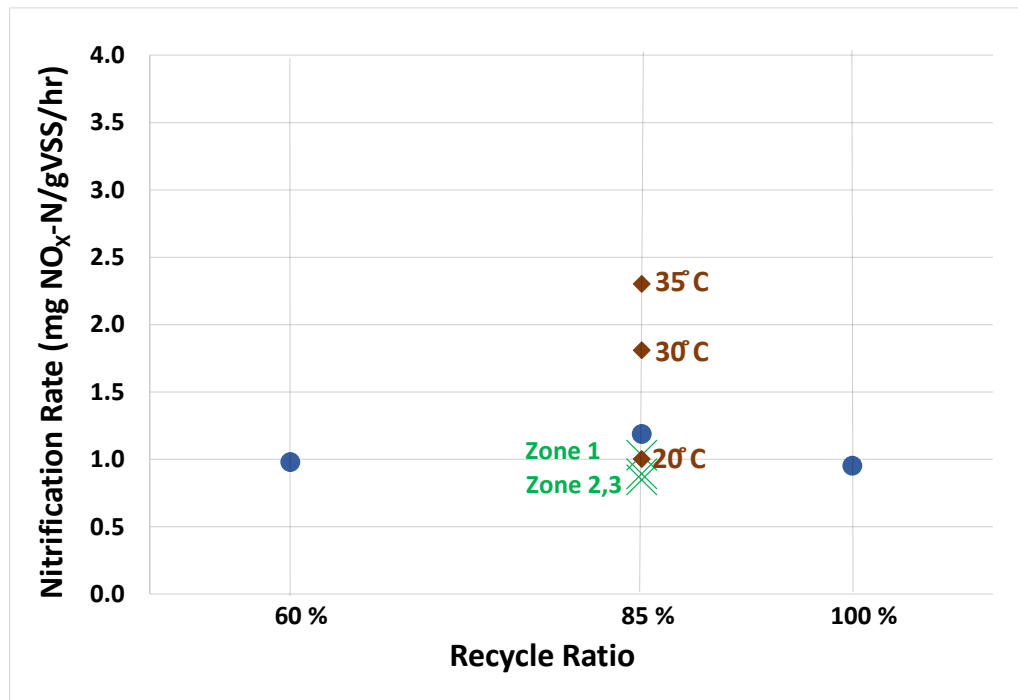


Figure 3.11 Nitrification control test one

#### *Nitrification rate sensitivity to aeration zone, RAS recycle ratio and temperature.*

The utilization rate of ammonia as impacted by the three zones of the aeration basin (test two) is shown in Figure 3.12. Zone 1 represents the beginning of the aeration basin and Zone 3 being the basin end. Also shown is a comparison of nitrification rates at recycle ratios of 60%, 85% and 100% (control test three). The measured RAS and PE MLVSS concentrations for control test three were 7,784 mg/L and 126.2 mg/L respectively. This was used to calculate stoichiometric

MLVSS concentrations for the three recycle ratios with a 20 % average MLVSS increase. The plot also shows the effect of temperature on nitrification rate (test four).



**Figure 3.12 Effect of recycle ratio, aeration zone and temperature on nitrification rates in wastewater aeration**

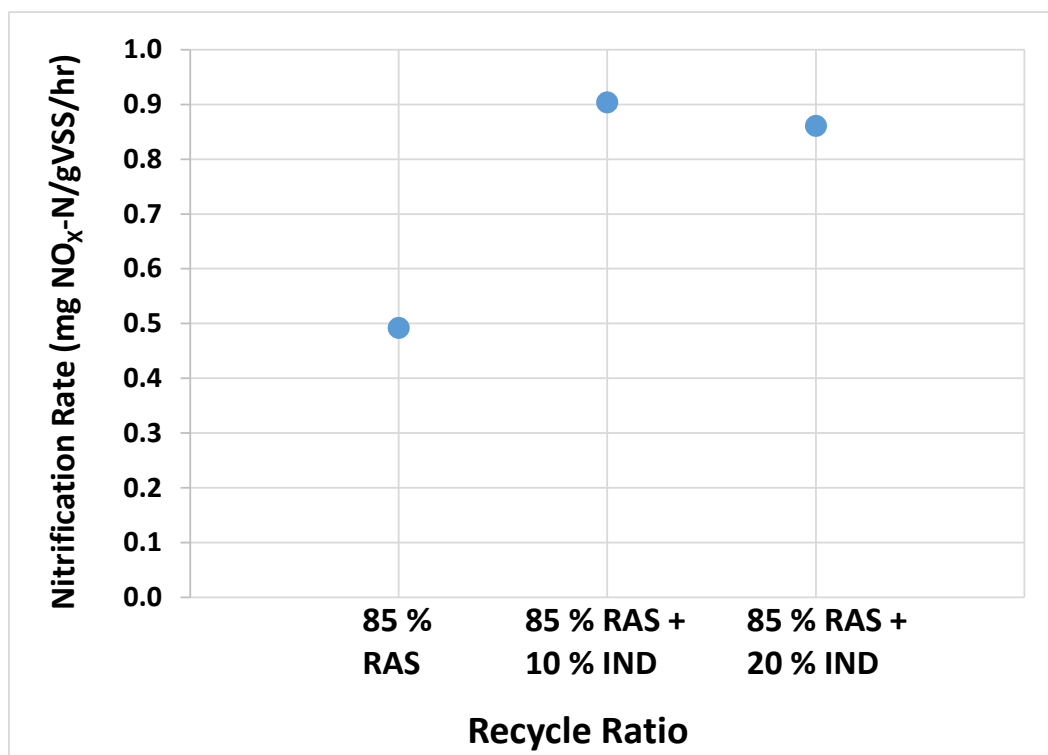
The ammonia utilization rate, nitrification rate and average MLVSS for the respective tests is shown in Table 3.1.

**Table 3.1 Average MLVSS concentrations**

Description		Ammonia Utilization Rate	Nitrification Rate	AVERAGE MLVSS
		mg NH <sub>4</sub> <sup>+</sup> -N/g VSS/hr	mg NO <sub>x</sub> -N/g VSS/hr	(mg/L)
Zone	1	1.62	0.89	3860
	2	1.63	0.85	3697
	3	1.58	1.03	3863
Recycle Ratio	60%	1.70	0.98	3298
	85%	1.59	1.19	4009
	100%	1.52	0.95	4351
Temperature	Ambient	2.15	1.00	3509
	30 °C	3.04	1.81	3475
	35 °C	2.65	2.30	3626

### ***Effect of industrial wastewater on nitrification rate***

The industrial wastewater source that was tested contributed to an increase in the rate of substrate utilization and nitrification rate. The observed rates were 1.54, 1.89, and 2.12 mg NH<sub>4</sub>-N/g VSS/hr and 0.49, 0.90, 0.86 mg NO<sub>x</sub>-N/g VSS/hr for 85% recycle ratio of RAS, 95 % recycle ratio (85 % RAS and 10 % industrial wastewater) and 105 % recycle ratio (85 % RAS and 20 % industrial wastewater) respectively is shown in Figure 3.13. The average MLVSS concentrations were 3509, 3475 and 3626 mg/L respectively.



**Figure 3.13 Effect of industrial wastewater on nitrification**

Although the rates observed in the industrial waste water test showed no additional inhibition to the wastewater, the rates observed for the different tests were low (1.44 – 3.04 mg NH<sub>4</sub>-N/ g VSS/ hr) in comparison to the range (4.1 – 7.8 mg NO<sub>x</sub>-N/ g VSS/ hr) obtained from ARCADIS and generated with “BioWin”, a wastewater process simulator software.

## **Chapter 4: Conclusions**

The inter and intra laboratory comparisons performed showed good correlations and helped to establish confidence in the results produced. The pilot study carried out revealed the variabilities in the concentrations of nitrogen compounds in the secondary clarifier effluent from the WWTP. This is as a result of incomplete nitrification at some time of the day in the WWTP. The nitrification inhibition study conducted showed low nitrification rates but the industrial source tested did not show considerable inhibition to the nitrification process. Other industrial wastewater contributors will need to be tested to ascertain the source of inhibition. This variabilities were also determined to cause problems in the denitrification filters performance. A stable performance of the AWWPF was observed after the denitrification filters had been removed.

The performance of the three NF/RO membrane types for nitrogen removal showed stability with or without the denitrification filters. The NF 90 showed the best nitrogen removal percentage followed by ESPA 2. The test of the ESNA 1 membranes was discontinued since it performed below the required removal necessary to meet the MCL for nitrate at some points in the test. The other barrier in the process for nitrogen removal was the online monitors and will require proper maintenance to ensure optimum performance. The online monitors are important as they could help prevent breakthrough of nitrogen species above the MCL.

Overall, the proposed DPR AWWPF based on the results shown in this paper is able to provide required nitrogen removal with the appropriate systems in place.

## References

- Asano, T., Burton, F. L., Leverenz, H. L., Tsuchihashi, R., & Tchobanoglous, G. (2007). *Water reuse: Issues technologies, and applications*. New York: McGraw-Hill. Retrieved from <http://0-accessengineeringlibrary.com.lib.utep.edu/browse/water-reuse-issues-technologies-and-applications>
- Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J., & Tchobanoglous, G. (2012). Advanced oxidation. *Water treatment: Principles and design* (3rd Edition ed., pp. 1415-1484). New Jersey: John Wiley and Sons, Inc. doi:10.1002/9781118131473
- Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J., & Tchobanoglous, G. (2012). Membrane filtration. *Water treatment: Principles and design* (3rd Edition ed., pp. 819-890). New Jersey: John Wiley and Sons, Inc. doi:10.1002/9781118131473
- Davis, M. L. (2013). *Water and wastewater engineering*. New York: McGraw-Hill. Retrieved from <http://0-accessengineeringlibrary.com.lib.utep.edu/browse/water-and-wastewater-engineering-design-principles-and-practice>
- Gerrity, D., Pecson, B., Trussell, R. S., & Trussell, R. R. (2013). Potable reuse treatment trains throughout the world. *Journal of Water Supply: Research and Technology-AQUA*, 62(6), 321-338.
- Kim, Y. M., Park, D., Lee, D. S., & Park, J. M. (2008). Inhibitory effects of toxic compounds on nitrification process for cokes wastewater treatment. *Journal of Hazardous Materials*, 152(3), 915-921. doi:<http://dx.doi.org/10.1016/j.jhazmat.2007.07.065>
- Leverenz, H. L., Tchobanoglous, G., & Asano, T. (2011). Direct potable reuse: A future imperative. *Journal of Water Reuse and Desalination*, 1(1), 2-10. Retrieved from <http://0-search.ebscohost.com.lib.utep.edu/login.aspx?direct=true&db=boh&AN=BACD201300527765&site=eds-live&scope=site; http://www.iwaponline.com/jwrd/default.htm>
- Li, X., Kapoor, V., Impellitteri, C., Chandran, K., & Santo Domingo, J. W. (2015). Measuring nitrification inhibition by metals in wastewater treatment systems: Current state of science and fundamental research needs. *Critical Reviews in Environmental Science and Technology*, 46(3), 249-289. doi:10.1080/10643389.2015.1085234
- McCasland, M., Trautmann, N. M., Porter, K. S., Center for Environmental Research Wagenet, Robert J. & Dept. of Agronomy Cornell University. (2012). **Nitrate: Health effects in drinking water**. Retrieved from <http://psep.cce.cornell.edu/facts-slides-self/facts/nit-heef-grw85.aspx>
- National Research Council. (1998). *Issues in potable reuse*. Washington, D.C.: National Academy Press. Retrieved from <http://0-search.ebscohost.com.lib.utep.edu/login.aspx?direct=true&scope=site&db=nlebk&AN=987>

- National Research Council (U.S.).Committee on the Assessment of Water Reuse as an Approach for Meeting Future Water Supply Needs, & National Research Council. (2012). *Water reuse :Potential for expanding the nation's water supply through reuse of municipal wastewater*. Washington, D.C.: National Academies Press.
- Nguyen, T., Roddick, F. A., & Fan, L. (2012). Biofouling of water treatment membranes: A review of the underlying causes, monitoring techniques and control measures. *Membranes*, 2, 804-840. doi:10.3390/membranes2040804
- Pagilla, K. R., Czerwionka, K., Urgan-Demirtas, M., & Makinia, J. (2008). Nitrogen speciation in wastewater treatment plant influents and effluents--the US and polish case studies. *Water Science & Technology*, 57(10), 1511-1517. doi:10.2166/wst.2008.213
- Pecson, B. M., Trussell, R. S., Pisarenko, A. N., & Trussell, R. R. (2015). Achieving reliability in potable reuse: The four rs. *Journal - American Water Works Association*, 107, Number 3, 48-58. doi:<http://dx.doi.org/10.5942/jawwa.2015.107.0047>
- Rice, E. W., Baird, R. B., Eaton, A. D., Clesceri, L. S., & editors. (2012). 1020 quality assurance. *Standard methods for the examination of water and wastewater* (22nd Edition ed., pp. 1-15-1-15). Washington, DC: American Public Health Association, American Water Works Association, Water Environment Federation.
- Rice, E. W., Baird, R. B., Eaton, A. D., Clesceri, L. S., & editors. (2012). Physical and aggregate properties. *Standard methods for the examination of water and wastewater* (22nd Edition ed., pp. 2-52-54-2-62-69). Washington, DC: American Public Health Association, American Water Works Association, Water Environment Federation.
- Tchobanoglous, G., Stensel, H. D., Tsuchihashi, R., & Burton, F. (2014). *Wastewater engineering: Treatment and resource recovery* (5th Edition ed.). New York, NY: McGraw-Hill Education.
- USEPA. (2016). **Table of regulated drinking water contaminants**. Retrieved from <https://www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants>

## **Vita**

Oluwaseye Michael Owoseni obtained his Bachelor of Engineering degree in Mining Engineering at the Federal University of Technology, Akure, Nigeria in September, 2011. His academic research works include; a senior capstone project on “Optimization of Drilling and Blasting Operations in Quarries and Mines” and his masters thesis research work on “Analysis of Nitrogen Speciation in Direct Potable Reuse”. His enthusiasm for water treatment led him to obtain a Masters of Science degree in Environmental Engineering and will is pursuing a PhD degree where he will be working on nanotechnology enabled water treatment. Seye as fondly known acquired relevant experiences with Archbode Engineering Limited, ENL Consortium Quarry, and the El Paso water utilities during his bachelors and masters degree programs. Eventually, he hopes to work closely with scientists and other engineers in leading processes that efficiently transform nature’s raw materials into beneficial products, and helping to solve industrial problems with adequate knowledge in the preservation of the environment.

Permanent address: No. 10 Olorunbe Street Iyange Quarters  
Akure, Ondo State, Nigeria

This thesis/dissertation was typed by Oluwaseye Michael Owoseni