Fall 2015

Ammonia Oxygen Demand Determination for the Design of an Oxygenation System in a Water Supply Reservoir

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AMMONIA OXYGEN DEMAND DETERMINATION FOR THE DESIGN OF AN OXYGENATION SYSTEM IN A WATER SUPPLY RESERVOIR

by

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(Under the Direction of Francisco Cubas)

ABSTRACT

The Occoquan Reservoir is a eutrophic reservoir that is part of an indirect potable reuse system. To protect the reservoir water quality, a high quality nitrified product water from a water reclamation facility and an oxygenation system are used during periods of thermal stratification to prevent the onset of anaerobic conditions above the sediments. During the stratified warmest months of the year, oxygen depletion rates exceed nitrate and artificial oxygen supply rates near the dam resulting in ammonia accumulation in the water column. Field observations and laboratory experiments revealed that sediment ammonia release rates ranged from 170-542 $mg/m^2 \cdot day$. At such rates, ammonia concentrations above the sediments reach values as high as 5.6 mg-N/L in the absence of nitrate and oxygen, and values as high as 2 mg-N/L when the oxygenation system is operational. A thorough analysis on ammonia cycling revealed that for the years studied, hypolimnetic ammonia oxygen demand may reach values as high as 77 metric tons of oxygen during a stratification period of 140 days. Furthermore, ammonia oxygen demand represented 20-100%, and in some cases more than 100% of the hypolimnetic oxygen demand estimated from oxygen depletion curves, which are commonly used to design oxygenation systems. Finally, it was determined that to satisfy ammonia oxygen demand in the reservoir, it is necessary to provide three times the oxygen demand estimated from the oxygen depletion curves. These results highlight the importance of estimating benthic fluxes of reduced substances into the water column (e.g. ammonia) when designing oxygenation systems.

INDEX WORDS: Ammonia oxygen demand, Thermal stratification, Eutrophication, Sediment oxygen demand, Hypolimnetic oxygenation

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A Thesis Submitted to the Graduate Faculty of Georgia Southern University in Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE

STATESBORO, GEORGIA

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Electronic Version Approved:

December 2015

DEDICATION

This thesis is dedicated to all of the loved ones who helped get to where I am now. In particular, this thesis is dedicated to Al Edwards and Ron Johnson, thank you for showing me the path to greatness.

ACKNOWLEDGMENTS

I am grateful and privileged to work under Dr. Francisco Cubas. I am thankful for all of the resources, time, and guidance that Dr. Cubas has provided for me. I would like to thank Dr. Mike Jackson, Dr. Peter Rogers, and Melissa Gutierrez for their support, guidance, and energy. I would like to acknowledge my parents, Carla Stewart and Joe Jenkins, and mentors Dr. Femi Adesanya, Marvin Brown, Albert Edwards, Ronald Johnson, Steve Julal, and Jimmy Thomas for their guidance, support, time, and resources. I would like to acknowledge and thank my family, in particular my sister Kimberly Jenkins. I would like to acknowledge and thank all of those who have supported me. In particular, I would like to acknowledge and thank Adatee Okonkwo for her support.

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CHAPTER 1

INTRODUCTION

Background

The Occoquan Reservoir is located in the northern region of Virginia, in the suburbs of Washington D.C. The reservoir is mainly composed of two tributaries, the Occoquan River and Bull Run. The reservoir, which is part of an indirect potable reuse system, is an artificial body of water that is used for potable and recreational purposes and supplies water to approximately two million people. The Occoquan Reservoir is a eutrophic reservoir that experiences thermal stratification and anaerobic conditions within the hypolimnion during the summer months.

Oxygen Demand

The focus of the study was to determine how much of a contributing factor ammonia was to the amount of total oxygen demand present within the hypolimnion of the Occoquan Reservoir. The accumulation of organic matter, reduced nitrogen compounds, and other constituents determine the total oxygen demand. The total oxygen demand within the reservoir is impacted by temperature, aquatic life, and nutrient and pollutant levels. The sediment oxygen demand (SOD) signifies the amount of oxygen consumed in the hypolimnion overlying the sediment water-interface (SWI). The SOD is a major contributing factor to the total oxygen demand in the reservoir, the constant buildup of settled decayed matter released from the sediments increases SOD. The discharge of dissolved compounds released from the sediments above the SWI can result with a negative impact on water quality. A surplus of decomposed biomass will modify the water system by decreasing the amount of available oxygen.

When oxygen demand exceeds the amount of available oxygen the water system becomes anoxic, which may lead to low water quality. Anoxic and anaerobic conditions occur when oxygen is no longer present in the reservoir. The impact of anaerobic conditions can result in an increase release of ammonia, phosphorus, and other soluble constituents within the water system. Aquatic biota is very susceptible to ammonia in anaerobic conditions. The release of ammonia from the sediments triggers the production of algae, toxic water is present when an abundant amount of algae exists in the reservoir. Algal blooms in warm surface waters results in anaerobic conditions in cold bottom waters after algae die, sink into bottom waters, and are biodegraded by oxygen-consuming microorganisms (Beutel, et al. 2008). The abundance of algae increases total oxygen demand within the water system by the respiration of oxygen at night and by the decomposition of decayed matter. When algae perishes, the decomposable matter becomes an available food source for bacteria. The decomposition of decayed matter will require a contribution of the total available dissolved oxygen present.

Anaerobic conditions in the hypolimnion adversely impacts cold-water biodiversity, potable water and recreational uses, and compound release from the sediments. Anaerobic conditions caused by the release of compounds from the sediments and the decomposition of algae degrade water quality causing a repellent taste, smell, and color. A contaminated reservoir will have to be immediately and consistently monitored to ensure toxicity levels are low. Treating degraded water for potable and recreational usage is an expensive process which typically requires the adding of chemical cleaning agents into the water supply.

Treatment Device

The installation and operation of an oxygenation system can prevent some of the effects caused by anaerobic conditions. Hypolimnetic oxygenation devices diminish ammonia and other unwanted compounds released from the sediments. The purpose of hypolimnetic oxygenation is to oxygenate the isothermal hypolimnion to elude perturbation of the thermal-density foundation of the metalimnion (Kortmann et al. 1994). The usage of an oxygenation system oxygenates the hypolimnion while preventing the mixture of cold water with warm water. Oxygenation devices place oxygen into the reservoir while maintaining layer characteristics and preserving stratification. Oxygenation devices must account for sediment turbulence into the design. Turbulence prevention at the bottom layer obviates the mixing of ammonia sediments into the entire reservoir. Hypolimnetic oxygenation systems allow the hypolimnion to remain cool with the input of oxygen. Sampling was performed before and after the installation of an oxygenation system to reveal the levels of DO and ammonia concentrations.

Objectives

The first objective was to determine the total observable oxygen demand within the hypolimnion. The second objective was to determine sediment ammonia release rates. The third objective was to determine the estimated ammonia dissolved oxygen demand. The fourth objective was to determine the total ammonia oxygen demand. The fourth objective determined how much of a significant percentage ammonia contributes to total observable oxygen demand.

CHAPTER 2

LITERATURE REVIEW

Eutrophication

Eutrophication is the excessive supplementation of chemical and biological nutrients within an ecosystem. Eutrophication is a natural enhancement in the rate amount of nutrients released into a reservoir. The significant nutrients that modify a water system include: nitrogen and phosphorus compounds, and organic matter. Natural eutrophication can occur within hundreds to thousands of years, climate changes and geology are two natural occurrences that significantly impact natural eutrophication. An abundant amount of nutrients entered into a reservoir can adversely alter the natural ecosystem. The naturally balanced state of the aquatic ecosystem is disturbed by anthropological actions that artificially supplement water bodies with nitrogen and phosphorus, resulting in extraordinarily high rates of plant production and accumulation of organic matter that can degrade habitat quality (Alvarez-Vázquez et al. 2014).

Cultural Eutrophication

Cultural eutrophication occurs when human activities alter the natural conditions of the reservoir. Cultural eutrophication can completely alter a body of water in less than a decade. The release of nutrients into a water supply from point and nonpoint sources accelerates the eutrophication process. Nutrients can also be released into the reservoir via watershed, soil erosion, sedimentation, and precipitation. A significant proportion of ammonia inflow derives from watershed and a major source of phosphorus derives from soil erosion. The entrance of sewage, runoff, pesticides and other pollutants into a reservoir accelerates the eutrophication process.

Rapid urbanization and agricultural practices are two leading causes of cultural eutrophication. The activities associated with rapid urbanization and agriculture practices can overload surface waters with macronutrients. Rapid urbanization and agricultural intensification have led to extensive nutrient enrichment of surface waters, as evidenced by it being ranked as the third leading source of water quality impairment in streams, lakes and reservoirs of the US

(USEPA 2011). The release of fecal matter from animals contributes to water contamination, the runoff of animal detritus and fertilizers ignite eutrophication. Animal excretions produce a proficient amount of ammonia which fuels algae metabolism and growth. Agricultural intensification is the over usage of fertilizers and overcrowding of animals. Agriculture is the leading source of nonpoint source loadings of nitrogen and phosphorus in the United States (Carpenter et al. 1998; Sharpley et al. 1994). The usage of an abundant amount of fertilizer has the potential to be released into surface waters and groundwater, the compounds derived from fertilizers can seep into soils and eventually leak down into a groundwater source. The compounds released from fertilizers can also become entrapped within the sediments. Once nutrients reach a receiving surface water body, the end result maybe permanent loss, sediment burial, temporary storage in biomass, or they are recycled back into the water column (Harrison et al. 2009; Howarth et al. 1996; Saunders and Kalff 2001).

Eutrophication allows an abundance of consumable nutrients to become easily available to aquatic life. The penalties associated with a reservoir filled with enriched nutrients include: dwindled dissolved oxygen, increased algal production, multiplication of undesirable aquatic plants, tainted water quality, and expensive water treatment costs. Eutrophication affects the recreational and potable usages of water and influences aquatic life, non-aquatic life, fisheries, purveyors, and stakeholders (Cooke et al. 1993). The abundant amount of available nutrients present enhances the metabolic performance of algae. Excessive nutrients and organic matter expedites the development of algal blooms, reduces available oxygen in water causing anaerobic conditions, and ultimately degrades water quality. An algal bloom covers the surface water and prevents aquatic animals from receiving light, thus preventing aquatic plants to photosynthesize. Aquatic plants that are incapable of photosynthesizing decompose, the buildup of decomposed plants enhances the production of bacteria. Anaerobic conditions occur due to an increase in nutrient consumption and biomass released into the reservoir. The consumption of nutrients and the decomposition of aquatic plants and biomass within the reservoir require oxygen. Every reservoir has a limited amount of available oxygen present, bacteria and fungi devour oxygen when decomposing biomass is present. The reduction of oxygen and increased production of algae, bacteria, and fungi hinders the chance of survival for a multitude of aquatic life.

Thermal Stratification

The Occoquan Reservoir experiences periods of hypolimnetic anoxia because of thermal stratification. In a deep reservoir, thermal stratification restricts the atmospheric exchange of oxygen into the hypolimnion. Thermal stratification is the process of dividing the reservoir water into multiple layers. Thermal stratification occurs in both warm and cold water temperatures and is powered by solar radiation. The sun is a power source that permits the rates of various chemical and biological functionalities within the aquatic ecosystem. During the thermal stratification period, the surface water absorbs majority of the sunlight and causes the top layer to segregate from the bottom layer. The heat from the sun reduces the water density at the top layer, the bottom cooler layer of higher density water cannot be replenished with oxygen because the density differential forms an effective barrier to the exchange of dissolved oxygen between the layers (Cubas et al. 2014).

Thermal stratification results in a three layer system. The epilimnion layer is formed at the top of the surface, the hypolimnion is located at the bottom layer, and the metalimnion is the middle layer between the epilimnion and hypolimnion. The metalimnion acts as a barricade that averts exchange between the epilimnion and the hypolimnion (Sahoo and Luketina 2003). The regions within the reservoir that exhibit significant change are labeled thermoclines. The thermocline can range in various temperatures and can be established at various depths. The thermocline depth slowly drops down during the summer and alters during the fall season. Seasonal thermoclines occur in the metalimnion and temporary thermoclines generally take place in the epilimnion.

Reservoirs go through various trophic stages, oligotrophy being the first stage. Oligotrophy is defined by having clear water and substantial amounts of dissolved oxygen. Oligotrophy reservoirs have low levels of nutrient loading which results in a low amount of aquatic plant development. The second trophic stage is mesotrophy, the mesotrophy stage encounters conservative plant production in fairly clear water. The mesotrophy stage reduces levels of available oxygen in the hypolimnion of the reservoir. The third trophic stage is the eutrophy, the eutrophy encompasses an exuberance of nutrients in the reservoir. The clarity of the reservoir water is reduced, algae becomes present, and oxygen is depleted in the hypolimnion during the summer months. The final trophic stage is hypereutrophy. In the hypereutrophy stage, oxygen is completely unavailable within the hypolimnion, algal blooms dominate the reservoir, and a very limited amount of aquatic life can survive under these conditions.

The process of photosynthesis and atmospheric exchange places oxygen into the reservoir. Thermal stratification fuels algal growth by the prevention of aquatic plant photosynthesis and by the prevention of the hypolimnion receiving oxygen from the surface. The available oxygen within the reservoir is consumed by algae, aerobic microorganisms, and aquatic plants by respiration during the night. Lack of oxygen in the hypolimnion increases the production of algae by the release of ammonia, phosphorous, and other enriched nutrients from the sediments. Anoxia will transpire when enrichment becomes available to deplete all or a significant percentage of the hypolimnetic oxygen reserve prior to autumn destratification (Cooke et al. 1993). Anoxia occurs when oxygen demand surpasses the available amount of oxygen available within the area (Beutel et al. 2007). Anoxic conditions in the hypolimnion of a reservoir can cause adverse effects to water quality. When anoxia occurs chemical and biological reactions occur in the bottom sediments which releases sediment-bound phosphorus into the water column, this surplus of phosphorus prolongs the cycle of more and more plant and algal development and diminished water clarity (Addy and Green 1996).

The amount of phosphorus and nitrogen that enters into a reservoir impacts the amount of microorganisms produced. High loading of phosphorus and nitrogen leads to significant algae biomass, opaque water and often biological variations (Søndergaard et al. 2003). The nutrients released into the water drives the production of accumulated organic materials, the increase in the production of nutrients will generate more microorganism and aquatic plant development which leads to an increase biomass decomposition. The biomass produced sinks into the sediments of the bottom layer and is decomposed by microorganisms. The organic materials excreted by the microorganisms settle into the sediments of the reservoir. The accumulation of decomposed biomass will formulate bacteria and fungi, which will significantly contribute to the depletion of dissolved oxygen. Water filled with an overloaded amount of nutrients will need additional oxidants in order to make the water potable; chlorine is a typical oxidant used to treat contaminated water overwhelmed with nutrients.

Nitrogen/Ammonia Cycle

During the autumn and winter seasons, discharges from sediments, tributary inflows, precipitation, and replenishment from the hypolimnion upsurge nitrate and ammonia concentrations (Horne and Goldman 1994). The nitrogen cycle contains all of the oxidation phases of the nitrogen atom, from +5(NO_3) to -3 (NH_4), and is more complex compared to a multitude of other elements (Horne and Goldman 1994). Nitrogen enters and exists in the reservoir as nitrate, nitrite, ammonia, and organic nitrogen. Ammonia and nitrate are the typical form of nitrogen available to aquatic life in a reservoir. Ammonia is formed by the biological dissimilation of nitrate (Wetzel 2001). Biological nitrification has the capability to increase nitrate and reduce ammonia in an aerobic environment. Under anaerobic conditions, nitrification, the biological oxidation of ammonia to nitrate, is inhibited and ammonia assimilation, the biological uptake of ammonia, is low comparative to aerobic conditions (Beutel et al. 2008).

Ammonia is considered more toxic and reactive compared to nitrate. Ammonium (NH_4^+) is an ion derived from ammonia that is present in reservoirs. Ammonium has a positive charge and bonds with negatively charged soils, the bond allows the soil to retain ammonium. The ammonium is swiftly engulfed by algae and various aquatic plants in the reservoir. The amount of ammonia present in a reservoir depends on the balance of animal waste rates, plant absorption, and bacterial oxidation. Ammonia is a potent toxin to aquatic biota, particularly at an elevated pH (Beutel et al. 2008). The gas ammonia (NH_3) when dissolved in water formulates ammonium hydroxide (NH_4OH). An exceeded amount of ammonium hydroxide is toxic to an aquatic system. Undissociated ammonium hydroxide is hazardous, but the dissociated ion NH_4 is nearly innocuous. High levels of pH in the aquatic system form ammonium hydroxide, ammonium hydroxide toxicity to aquatic species varies with pH, temperature, dissolved oxygen flows, the hardness or salt characteristics of the water, and animal species and age (Horne and Goldman 1994). Ammonia concentrations correlate with pH levels, as algal production increases pH levels rise within the water. Aquatic animals have a greater chance of being poisoned by ammonia whenever oxygen demand is exceeded by available oxygen.

Nitrate is the most highly oxidized form of nitrogen and typically the most copious form inorganic nitrogen in lakes and reservoirs (Horne and Goldman 1994). Nitrate can be removed from the reservoir by denitrification. The process of denitrification, the bacterial reduction of nitrate to nitrite and then to N_2 gas, transpires when a reduced level of oxygen is present in the hypoliminion (Horne and Goldman 1994). Nitrogen gas is nearly inert and consumed by certain algae and bacteria. Nitrification is the transformation of ammonia to nitrate. There is some evidence that nitrate can reduce sediment ammonia release by sustaining an oxidized atmosphere, but the necessary procedures remain uncertain (Cubas et al. 2014). Nitrate reductase transforms nitrate to nitrite, nitrite is produced by the reduction of oxygen from nitrate. Nitrite reductase transforms nitrite to nitrogen gas. Algae absorbs nitrate after the nitrate reductase process. High levels of ammonia blocks the nitrate reductase process. Biological nitrogen removal (BNR), involving the microbiological processes of nitrification and denitrification, is a cost-effective and well-established practice that has been adopted for both municipal and industrial wastewater treatment (Ramanathan et al. 2014).

Autotrophs exist in environments wherever ammonia is present naturally or by human intervention. Autotrophic bacteria are capable of generating a food supply via photosynthesis and heterotrophic bacteria attain food from decayed organic matter. The nitrification process is a two-step procedure composed of autotrophic ammonia-oxidizing bacteria (AOB) and nitrite oxidizing bacteria (NOB). The combination of AOB and NOB functions with the existence of oxygen. The first step within the nitrification process is the oxidation of ammonia (NH_4) to nitrite (NO_2), NH_4 is converted to NO_2 via ammonia-oxidizing bacteria. The second step within the nitrification process oxidizes nitrite (NO_2) to nitrate (NO_3) via nitrite oxidizing bacteria. AOB are chemolithoautotrophs that use ammonia as an electron donor for respiration and cell synthesis and carbon dioxide as the only carbon source (Keluskar et al. 2013). Ammonia-oxidizing bacteria reduce inorganic carbon to form biomass via organic predecessors (Keluskar et al. 2013). AOB are generally found in environments where ammonia is available via mineralization of organic matter, or in wastewater of a fertilizer company (Keluskar et al. 2013).

Nitrosomonas is the most common type of species affiliated with AOB, but other oxidizing autotrophic bacteria include Nitrosococcus, and Nitrosospira (USEPA 2002). The AOB of the genus Nitrosomonas can perform autotrophic denitrification reactions in a reduced-oxygen reaction environment that allow the direct conversion of NH_4^+ and NO_2^- to N_2 (Ramanathan et al. 2014). Nitrobacter is the most common type of species affiliated with NOB, but other species including Nitrospina, Nitrococcus, and Nitrospira are capable of autotrophically oxidizes nitrite (USEPA 2002). The conversion of NO_2 and NO_3 to nitrogen gas N_2 can be completed by heterotrophic denitrification. Heterotrophic denitrification is capable of occurring when an electron donor is present in anoxic conditions. When the hypolimnion of a eutrophic reservoir is in an anoxic state the demand for electron acceptors regularly completely removes nitrate from the system, which is either denitrified or converted to ammonia (Horne and Goldman 1994).

Sediment Oxygen Demand (SOD)

Sedimentary oxygen demand (SOD) is the rate of DO flow from water above a sediment surface to the sediment with possible control of the DO equilibrium in the water column (Higashino and Stefan 2011). Maintaining an oxygenated hypolimnion reduces the sediment release of ammonia, iron, hydrogen sulfide, manganese, sulfide compounds, and various soluble compounds. The reduction in the amount of released compounds will alleviate eutrophication by preventing the overproduction of degradable biomass. A reduction in inside nutrient loading joined with an improved zooplankton habitat, both an outcome of aeration or oxygenation, may cause a reduction in algal biomass or alternate to more beneficial organisms (Beutel and Horne 1999). The release of various compounds in the hypolimnion mixes with other layers of water within the system triggering algal growth. The overproduction of algae contaminates the reservoir and adversely impacts: zooplankton, aquatic life, fisheries, water quality, and any form of life that depends on the reservoir for survival.

Turbulence and oxygen concentration impact sediment oxygen demand. SOD increases after the initiation of hypolimnetic oxygenation or aeration due to a disturbance in the sediments. The flux velocity overlaying the sediment can have a substantial effect on the SOD measurement (Arega and Lee 2005). The SOD element of total oxygen demand is chiefly sensitive to turbulence and DO concentration at the sediment-water interface (Arega and Lee 2005). Elevated water currents tend to reduce or disturb the diffusional boundary layer at the sediment-water interface, thus increasing the flow of oxygen from overlying water into the sediment (Beutel et al. 2007). Elevated DO concentration in the water above sediments also increases the DO flow as it results in a greater diffusional driving force amongst the water column and sediments (Beutel et al. 2007). The elevated DO flow is responsible for causing an increase in the hypolimnetic oxygen demand after the initiation of a hypolimnetic oxygenation or aeration system.

The attribution of the elevated DO flow creates difficulty for calculating the total oxygen demand with the implementation of an oxygenation or aeration system. SOD is typically higher in shallow bottom layers as opposed to deep bottom layers. Organic matter settles and decomposes faster in shallower areas as opposed to deep areas. The SOD represents the amount of oxygen consumed at the bottom layer of the water body overlying the sediments. SOD is a measure of the combined rate of mineralization, diagenesis of particulate organic matter, and biological respiration in the sediment (Arega and Lee 2005). The mineralization of organic matter in the sediments increases oxygen demand and discharges nutrients into the water from the sediment-water interface (Bryant et al. 2010). SOD is commonly measured in situ by installing a chamber device on the sediment surface, a steady water flux is established over the sediment to simulate a natural hydraulic environment (Arega and Lee 2005). The SOD is calculated by either a batch method or continuous method. The batch method determines the amount of DO concentration that has dropped inside the chamber throughout a time period. The continuous method determines the difference of DO concentration between inflow and outflow. The continuous method and batch method typically use cylindrical chambers to house the sediment.

Treatment and Restoration

The installation and operation of an oxygenation system can prevent some of the effects caused by eutrophication. Hypolimnetic oxygenation devices diminish the release of ammonia and other unwanted compounds from the sediments. Before a system can determine the necessary parameters to design a hypolimnetic oxygenation device, an estimate of oxygen demand must be determined. Each hypolimnetic oxygenation system needs an accurate estimate of hypolimnetic oxygen demand in order to build an adequate design for the area in need of treatment. Hypolimnetic oxygen demand is the combination of oxygen demand in the hypolimnion by respiring pelagic species and sediment oxygen demand SOD exerted at the sediment-water interface by microorganisms devouring settled organic matter as well as the oxidation of reduced compounds (e.g., hydrogen sulfide, methane, and iron) diffusing upwards from anoxic sediment below (Beutel et al. 2007).

Oxygenation and aeration devices must account for sediment turbulence into the design. Turbulence prevention at the bottom layer avoids the mixing of sediments into the reservoir. The practice of an oxygenation device may cause turbulence and the mixing of sediments in the hypolimnion, which will induce sediment oxygen demand. An increase in the amount of oxygen demand caused by the operation of an oxygenation device must be taken into consideration when calculating total oxygen demand in the hypolimnion. To help avert the undersizing of an oxygenation device, a design "safety factor" is applied to the estimate to account for the increased rate of oxygen demand (Moore et al. 1996). The resuspension of sediment materials caused by the transfer of oxygen from the oxygenation outlet has the potential to increase the release of sediment surface area to the bottom water (Moore 1996).

The currently accepted methodology for attaining an oxygen demand estimate necessitates measuring the reduction in hypolimnetic oxygen content after the onset of spring stratification (Moore et al. 1996). A robust presence of light becomes more available during spring stratification, the sunlight boosts photosynthetic activity and warms the water temperature. The increase in photosynthetic activity will increase algae production, aquatic life development, and nutrient loading within the reservoir. All of these factors are taken into consideration prior to discovering the oxygen demand rate. The oxygen demand rate is viewed as the maximum slope of a plot of depleting total hypolimnetic oxygen content versus time (Moore et al. 1996).

The principle of hypolimnetic aeration is to aerate the isothermal hypolimnion to avoid perturbation of the thermal-density structure of the metalimnion (Kortmann et al. 1994). The usage of an aeration/oxygenation system oxygenates the hypolimnion while preventing the mixture of cold water with warm water. Oxygenation devices place oxygen into the reservoir while maintaining layer characteristics, hypolimnetic oxygenation consists of an engineered system that applies pure oxygen gas to reoxygenate the hypolimnion (Beutel et al. 2007). Hypolimnetic oxygenation and aeration system provide oxygen in the hypolimnion while preserving stratification. Hypolimnetic oxygenation and aeration systems allow the hypolimnion to remain cool with the input of oxygen.

The treatment of a poor water quality source can be costly. There are various systems used to place oxygen in the water system, the amount of oxygen taken up by the sediment significantly directs oxygen depletion in stratified waters with organic-rich sediment (Bryant et al. 2010). The traditional airlift aeration system places air into the reservoir to release oxygen.

The hypolimnetic oxygenation system implements pure oxygen at the bottom of the reservoir. An oxygenated hypolimnion preserves the reservoir while reducing water quality treatment costs. Oxygenation systems typically include oxygen storage or production facilities on shore and submerged in-lake facilities that dissolve oxygen gas into reservoir water (Beutel et al. 2007). Liquid oxygen can be stored on the shore and transferred into the hypolimnion. The transformation of liquid oxygen to gas can be converted by evaporators, oxygen gas naturally dissolves in the hypolimnion.

Hypolimnetic oxygenation can be applied into a reservoir via a bubble plume diffuser array, line diffuser, and submerged contact chamber. There are a variety of systems that apply oxygen into the hypolimnion. The layer aeration system has the ability of obtaining oxygen via algae photosynthesis and atmospheric exchange (Singleton and Little, 2006). The aeration reaches a certain depth in the reservoir and mixes various levels of water. The aerator redistributes dissolved oxygen into the water by mixing aerated water into the reservoir. Partial-lift systems place oxygen into the reservoir by inserting compressed air within the proximity of the hypolimnion. The partial lift system has an air-water mixture travel up a vertical tube to a given depth in the reservoir from which the remaining gas bubbles are expelled to the atmosphere through a pipe to the surface (Singleton and Little, 2006). This process allows oxygenated water to travel to the hypolimnion. The full-lift system is similar to the partial lift system, the air-water mixture travel path is different. The air mixture in a full lift system ascends to the surface prior to the discharge of residual gas bubbles. Side stream pumping is a hypolimnetic oxygenation method that recovers water offshore from a source, combines pure oxygen gas with the collected water, and releases the collected oxygenated water back into the hypolimnion (Singleton and Little 2006; Taggart and McQueen 1981).

Full-lift hypolimnetic aerators normally consist of a vertical riser tube, a diffuser inside the bottom of the riser tube, an air-water separation chamber at the top of the riser, and (4) one or two return pipes, labeled downcomers (Singleton and Little 2006). The aerator is supplied with compressed air, the compressed air formulates bubbles that move free from the diffuser, the water and air mixture formulates a buoyant gas**.** A proportion of compressed air bubbles are released into the atmosphere from the top of the riser, and some bubbles are entrained in the water that come into the downcomers (Singleton and Little 2006). The oxygenated water is transported from the downcomers and placed into the hypolimnion. The Speece Cone is a submerged downflow bubble contactor that has a source of oxygen gas, a conical bubble contact chamber, a submersible pump, and a diffuser that releases heavily oxygenated water into the hypolimnion (Singleton and Little 2006). Water and oxygen gas bubbles are present at the top of the cone. The velocity decreases when water travels down the cone. The purpose of the system is to allow downward water velocity to overpower the upward velocity of released oxygen gas bubbles. The water velocity at the bottom portion of the cone is intended to be slower than the bubble rise velocity.

The bubble-plume diffuser inserts either air or oxygen into the hypolimnion. The air or oxygen flux is released at a low steady rate. The bubble plume diffuser can be identified as a circular plume or linear plume. The bubble plume diffuser is typically used for deep reservoirs. The majority of the bubbles released take place in the hypolimnion. The plume diffuser is placed low enough to avoid substantial erosion of the thermocline. The bubble plume diffuser process involves gas bubbles being inserted into the water column through a porous diffuser establishing a gas/water mixture that rises and builds momentum due to a positive buoyancy flux, which upsurges the water flow rate and cross-sectional area but diminishes the momentum (Singleton and Little 2006).

CHAPTER 3

METHODOLOGY

Study Site

The Occoquan Watershed is located in northern Virginia, southwest of Washington D.C., United States. The watershed has an area of 1530 km^2 and its land use is approximately distributed as 54% forest, 28% urban, and 18% for agricultural and pasture use. Additional physical characteristics of the watershed have been described elsewhere (Cubas et al. 2014). The Occoquan Reservoir is a manmade impoundment built in the 1950s to serve as a water supply source. The reservoir is formed by two main tributaries that drain 4 sub-basins within the watershed. In the southern part of the watershed, Broad Run and Cedar Run drain to the main headwater basins forming the Occoquan River. In the northern part, Cub Run basin drains into Bull Run. Together, the Occoquan River and Bull Run drain into the main body of the reservoir (Figure 1). The Upper Occoquan Service Authority (UOSA) water reclamation plant (WRP) discharges a high quality reclaimed water year round approximately 10 km upstream from the confluence of the Occoquan River and Bull Run. As a consequence, during extended periods of low precipitation, Bull Run contributes to most of the baseflow of the reservoir.

The main body of the reservoir, extending from the dam to the confluence of the two main tributaries, resembles a monomictic lake that experiences thermal stratification during the summer months. As a consequence, hypoxia rapidly develops in the hypolimnion resulting in the release of reduced substances from the sediments that deteriorate the water quality of the reservoir. To improve the water quality, authorities managing the reservoir utilize a highly nitrified product water from the WRP to maintain an oxidized environment above the SWI, thereby preventing or delaying the release of reduced substance from the sediments (Cubas et al. 2014). Additionally, a hypolimnetic oxygenation system was installed in 2012 to maintain an oxidized environment and to prevent the release of reduced substances from the sediments of the downstream area of the reservoir, near the dam. The installed oxygenation system consists of a line diffuser unit capable of releasing fine oxygen bubbles that allow a more effective transfer of oxygen to the water column via diffusion. The oxygenation system has been functional since the summer of 2012 and continuously operates during periods of thermal stratification in the reservoir.

Material and Methods

Field observations and monitoring data

Field sampling was performed in the Occoquan Reservoir at stations RE02, RE05, and RE10 by the Occoquan Watershed Laboratory staff as part of a continuous monitoring program. Water samples were collected from the bottom layers of each station, approximately 30 cm above the SWI, on a biweekly basis. The collected samples were tested for nitrogen species (ammonia and nitrate). Oxidized nitrogen ($NO_3^- + NO_2^-$) (4500-NO_3-F) and ammonia nitrogen (4500-NH_3 G) were analyzed in accordance with Standard Methods (AWWA et al. 2005). Temperature and oxygen profiles were constructed from *in situ* measurements by deploying an YSI 600 XL Sonde and taking readings at 60 cm increments for the first 3 meters and at 1.5 meters thereafter. Water quality analyses and DO profiles taken during the period of study were analyzed to determine the thermal stratification period, DO consumption and depletion rates, ammonia release rates, and ammonia oxygen demand.

Microcosm Studies

Laboratory-scale reactors were operated to determine ammonia release rates under different conditions, emulating the actual conditions observed in the reservoir during the summer months. The Plexiglas cylinders were sealed to the atmosphere to sustain an anaerobic environment or open to the atmosphere and aerated to maintain an aerobic environment. Oxygen was pumped through diffuser stones located at the bottom of each reactor. Mixing in each reactor was achieved by using a paddle connected to a variable speed motor. Vertical baffles were installed to prevent vortex formation and sediment resuspension. Sediment samples used in each reactor were taken from sampling stations RE02, RE05, and RE10 using an Ekman dredge. The sediment samples were placed in glass bottles and stored over ice in insulated coolers until transported to the laboratory. Once in the laboratory, the sediments were stored at 4°C. Glass beakers were used to hold the sediments and to give the desired sediment surface area, which was kept constant during all the experiments. The water used to fill the reactors was collected directly from the reservoir and had low concentrations of ammonium (< 0.3 mg-N/L).

Reactors were operated for a period of 40 days under either an aerobic or anaerobic environment. To measure ammonia release rates under aerobic conditions, the nitrification process was inhibited by using a solution containing Nitrapyrin (2-chloro-6-(Trichloromethyl) pyridine) at a dose of 0.32 gr per 300 ml of water. A HACH® LDO1-01 probe attached to a HACH® HQ40d dual – input multimeter was used to measure and monitor DO concentrations in the microcosms.

Oxygen Depletion Rates and Ammonia Release Rates

Oxygen consumption and total ammonia nitrogen (TAN) rates above the SWI were determined from plotted time series of the available dissolved oxygen and ammonia concentrations during thermal stratification. Linear regression was used to calculate the slope values from each time series plot in order to determine the rate of oxygen consumption and ammonia production. The slope values were needed to determine the ammonia release rates and DO depletion rates. The application of linear regression reveals the rates of total ammonia nitrogen (TAN) concentrations and oxygen consumption during thermal stratification. Calculated negative slope values for the TAN were corrected by the best fit linear regression line.

Estimated Ammonia Released/Year and Estimated DO Deficit/Year (kg)

The ammonia release rates, DO depletion rates, thermal stratification period, and station area were used to determine the estimated ammonia released/year and estimated DO deficit/year. The ammonia release rate estimates the amount of ammonia released from the sediments during the thermal stratification period, the DO depletion rate estimates the amount of depleted DO during the stratification period. The ammonia released/year and estimated DO deficit/year were needed to determine the ammonia oxygen demand.

Stoichiometry/Ammonia Oxygen Demand

The final value obtained for the study is considered to be the total ammonia oxygen demand above the SWI of the reservoir at different stations. The ammonia oxygen demand is the estimated amount of oxygen needed to completely oxidize ammonia present. Ammonia oxygen demand was determined by dividing the estimated ammonia dissolved oxygen demand by the estimated dissolved oxygen deficit/year. From stoichiometric calculations it was determined that 3.56 grams of oxygen are needed to oxidize 1 gram of ammonia. The calculated factor of 3.56 was then used to estimate the total amount of oxygen required to oxidize the estimated ammonia released in a year, ammonia dissolved oxygen demand. The ammonia dissolved oxygen demand is the ammonia release rate multiplied by 3.56.

Determining Thermal Stratification

The number of days when thermal stratification occurred for each year studied was determined by DO and temperature profiles. The applied methodology revealed that thermal stratification began in the spring or early summer and ended in the fall. The DO profiles reveal an estimated amount of DO present throughout the layers, the amount of DO present throughout the reservoir depths help determine when thermal stratification began and ended. The stratification period began when the bottom layers became depleted of DO and the period ended when a uniformity of DO was present throughout the layers. The methodology revealed that DO levels in the bottom layer declined as the temperature rose and the DO levels ascended when the temperature dropped. The temperature profile reveals water temperatures from the surface to the bottom layer of the reservoir. With the application of the temperature profile, stratification is proven by the correlation of temperature and depth. The stratification period begins when an uneven water temperature distribution is present throughout the layers and the period ends when the layers consist of a uniform temperature.

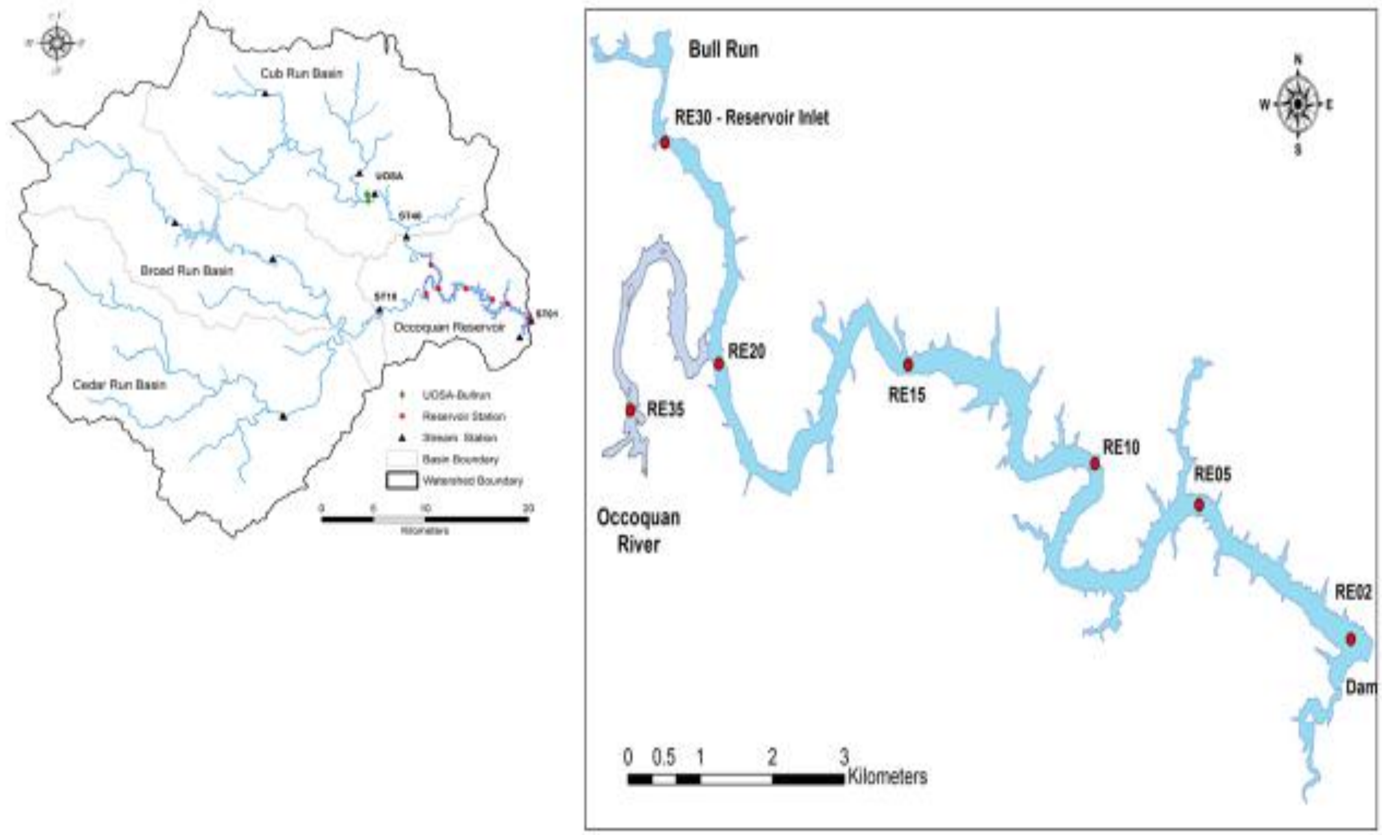


Figure 1: Occoquan Reservoir- Watershed and Station Criteria

CHAPTER 4

RESULTS AND DISCUSSION

The continuous sediment ammonia production, release and depletion cycle in the Occoquan Reservoir has been studied to determine the impact of ammonia on the total oxygen demand of the reservoir. Data from samples collected at three different stations downstream the reservoir near the dam revealed that high ammonia production and subsequent release contributes significantly to the total oxygen demand in the deeper layers of the reservoir during periods of thermal stratification.

Ammonia Accumulation in the Reservoir

Sediment ammonia production and release occur year round in the reservoir, but it only accumulates in the water column after the onset of thermal stratification. When hypolimnetic dissolved oxygen concentrations decrease to less than 1 mg/L during the summer months, ammonia concentrations steadily increase until the hypolimnion is replenished with oxygen after the fall overturn. Ammonia concentrations in the bottom waters of the reservoir may reach values as high as 5.6 mg-N/L, 4.2 mg-N/L and 3 mg-N/L in stations RE02, RE05, and RE10 respectively (Figure 2).

Ammonia mean concentrations were calculated for each station during the period of thermal stratification to observe how ammonia accumulation varies each summer during the period of record. For station RE02, the highest mean ammonia concentration was 2.32 mg-N/L, measured in 2010 (Figure 2a). In this station, an increase in the annual mean ammonia concentration was observed from 2001 to 2011. From 2001 – 2005, mean ammonia concentrations ranged from 0.5 – 1.4 mg-N/L, while from 2006 – 2011, it ranged from 1.5 – 2.2 mg-N/L and the peak values measured after 2005 were higher than 3.2 mg-N/L. The highest mean ammonia concentration for station RE05 and RE10 were 2.1 and 1.5 mg-N/L respectively (Figure 2). In station RE05, mean ammonia concentrations ranged from 0.7 – 2.1 mg-N/L and no increasing trend was observed during the study (Figure 2b). In station RE10, mean ammonia concentrations ranged from 0.5 – 1.5 mg-N/L and there was an increasing trend in mean ammonia concentration observed from 2007 -2011 (Figure 2c). During the period of record, hypolimnetic ammonia concentrations increased in two of the stations studied and remained constant in RE05. These results suggest that ammonia release is a recurring issue in the reservoir during the summer when there is not enough DO available in the hypolimnion to oxidize ammonia to nitrate. The variability observed in the annual mean ammonia concentration may be the result of having inconstant stratification periods at each sampling stations (Table 1). For example, in station RE02 the highest values for the mean ammonia concentration were observed during the years when the stratification periods were longer (i.e. 2006, 2007, 2010 and 2011). The same trend was observed in the other two sampling stations (Table 1).

In the Occoquan Reservoir, hypolimnetic ammonia accumulation is the result of ammonia being released from the sediments and not the result of ammonia being directly imported from the watershed as demonstrated in previous studies (Cubas et al. 2014). Additional data have also shown that ammonia released from the sediments is mainly due to organic nitrogen mineralization within the sediments. Organic nitrogen mineralization and subsequent ammonia production is an ongoing process that occurs year-round, however, ammonia accumulates in the water column after the onset of thermal stratification. Ammonia accumulates because during the warmest months of the year the hypolimnetic waters of the reservoir lack enough dissolved oxygen that is necessary to oxidize ammonia to nitrate, therefore ammonia accumulates until the bottom waters are replenished with oxygen (Wetzel 2001).

High concentrations of ammonia have a negative effect on the water quality of lakes, streams, and reservoirs. For instance, ammonia increases the oxygen demand of freshwater systems exacerbating anoxic conditions in those systems that cannot replenish oxygen at high rates. Additionally, ammonia becomes toxic to certain aquatic species when temperature and pH ranges favor the dominance of the NH_3 species (Beutel et al. 2008, Horne and Goldman 1994). High concentrations of ammonia in water supply reservoirs may result in problems associated with taste and odor, low pH values, and disinfection byproduct formation resulting in higher costs for drinking water treatment.

Figure 2: Total Ammonia Nitrogen maximum concentrations and summer averages for a) RE02, b) RE05, and c) RE10. Error bars represent one standard deviation.

To prevent the release of undesirable substances from the sediments, such as ammonia, iron, manganese and other constituents, authorities managing the reservoir installed an oxygenation system in 2012. This oxygenation system is operated continuously during periods of thermal stratification to maintain an oxidized environment above the SWI that will prevent the release of the aforementioned substances from the sediments. To determine if the installed oxygenation system has the capacity to oxidize ammonia produced within the sediments, a comparison was made between calculated ammonia flux rates and oxygen depletion rates, which are typically used to design oxygenation systems. These comparisons will help to determine if the amount of oxygen calculated from the common methods used to size the oxygenation system accounts for the total ammonia oxygen demand. Water quality parameters measured *in situ*, were used to determine sediment ammonia release rates, DO depletion rates, and to estimate ammonia oxygen demand in the deepest layer of stations RE02, RE05, and RE10 during periods of thermal stratification.

Sediment Ammonia Release Rates:

Ammonia release rates were used to determine the overall ammonia oxygen demand in the reservoir. Sediment ammonia release rates are the determining factor used to estimate the total ammonia oxygen demand during the stratification period. From 2001 – 2005, in station RE02, ammonia release rates ranged from 170 $mg/m^2{\cdot}day$ – 542 $mg/m^2{\cdot}day$, while from 2006 – 2011, ammonia release rates ranged from 46 $mg/m^2{\cdot}day$ – 540 $mg/m^2{\cdot}day$ (Table 1). Ammonia release rates resulted in values as high as 542 $mg/m^2{\cdot}day$, 226 $mg/m^2{\cdot}day$, and 185 $mg/m^2{\cdot}day$ in stations RE02, RE05, and RE10 respectively (Table 1). Stations RE02 and RE05 reveal an increase in the amount of sediment ammonia released into the reservoir from the respected beginning year compared to the end year of the study.

Results reveal that station RE02 has the highest sediment ammonia release rates compared to station RE05 and RE10. Ammonia flux rates at station RE02 were the highest because the stratification period, which is the time period in which the rates were calculated, was longer compared to stations RE05 and RE10. The results reveal that the highest sediment ammonia release rates correspond to a stratification period of over 110 days, while the lowest release rates correspond to stratification periods lower than 110 days (Table 1). Results also show that the highest sediment ammonia release rate (542 $mg/m^2{\cdot}day$) occurred at station RE02 during a stratification period of 112 days and the lowest ammonia release rate (46 $mg/m^2 \cdot day$) occurred at station RE10 during a stratification period of 78 days. Additionally, the mean stratification period from 2007 to 2011 was 159, 134, and 112 days for RE02, RE05, and RE10 respectively. Another reason for the difference in ammonia release rates is related to the spatial location of each station. Sediment fluxes are typically affected by the ratio of water volume that flows over a specific sediment area. For the study, ammonia release rates are normalized by the volume and the sediment area so that ammonia fluxes can be compared in all stations. However, it is possible that having a higher volume of water at station RE02, compared to the other stations, retards the flux of oxygen from the atmosphere to the bottom of the reservoir after the fall overturn. Therefore, ammonia accumulates for a longer period at station RE02 even after the stratification disappears in the reservoir. Ammonia release rates are used to calculate the actual ammonia oxygen demand. By performing stoichiometric calculations on the amount of ammonia released it becomes possible to estimate the total ammonia oxygen demand in the reservoir.

DO Depletion Rates:

The DO depletion rates for each station were used to estimate how much DO is consumed in the hypolimnion of the reservoir. DO depletion rates are estimated from oxygen depletion curves that are obtained during the days following the onset of thermal stratification in the reservoir. It is during this period of time that oxygen is depleted in the hypolimnion and it is not replenished until the fall overturn in a monomictic and dimictic lake. DO depletion rates are further used to determine an areal hypolimnetic oxygen demand which is then used to size oxygenation systems based on the duration of each stratification period (Cooke et al. 2005, Wetzel 2001).

DO depletion rates reached values as high as 3,615 $mg/m^2 \cdot day$, 1,279 $mg/m^2 \cdot day$, 903 $mg/m^2 \cdot day$ in stations RE02, RE05, and RE10 respectively (Table 1). From 2001 – 2005, DO depletion rates ranged from 1,093 $mg/m^2 \cdot day$ – 3,615 $mg/m^2 \cdot day$, while from 2006 – 2011, DO depletion rates ranged from 370 $mg/m^2 \cdot day$ – 2,222 $mg/m^2 \cdot day$ (Table 1). The highest DO depletion rate value reveals that the installation of the oxygenation system should account for 3,615 $mg/m^2 \cdot day$ of DO. Station RE02 contains the highest DO depletion rates and station RE10 contains the lowest DO depletion rates. DO depletion rates measured at station RE02 are all greater than 1,000 $mg/m^2 \cdot day$ and all of the DO depletion rates for station RE10 are less than

1,000 mg/m^2·day. The 2010 results for each station reveal a higher DO depletion rate compared to the initial year of each respected station (Table 1). The highest DO depletion rates for station RE05 and RE10 occurred in 2010, the second highest DO depletion rate for station RE02 occurred in 2010 (Table 1). DO depletion rates vary due to different factors, some of which are similar to the ones that affect the ammonia release rates. In the case of DO, depletion rates are higher at station RE02 because the stratification period begins earlier at this station than in RE05 and RE10. Additionally, at RE02 the stratification is not easily disrupted so DO is not easily reintroduced during the days following the onset of thermal stratification.

DO depletion rates provide a good approximation of how much oxygen is used by microorganisms to mineralize organic matter and other components and to oxidize reduced compound species in the sediment and the water column (Cubas et al. 2014)). DO depletion rates are generally used to design and size oxygenation systems because the DO data used to estimate the rates is commonly available. Although DO depletion rates are commonly used for the design of aeration and oxygenation systems, there are a series of limitations that need to be considered when designing these types of systems. One of the limitations is that in most cases the estimated DO depletion rate is not a good representation of the total oxygen demand. Therefore, it usually underestimates the actual amount of oxygen that is needed to keep a concentration greater than 4 mg/L in the hypolimnion which is required by existing regulations. To avoid under sizing an oxygenation system, designers utilize safety factors to better estimate the total oxygen demand. Another disadvantage of using the oxygen depletion curves to estimate an oxygen demand is that the oxygen depletion rate does not provide any information about the constituents that are contributing to the total oxygen demand. To determine which constituents (e.g. organic matter, ammonia, iron, manganese, etc.) contribute the most to the total oxygen demand it is necessary to perform long and costly laboratory and *in-situ* studies, which in most cases are not feasible for utilities managing freshwater bodies.

Table 1: Ammonia DO Demand for a) RE02, b) RE05, and c) RE10

Year	DO Depletion Rate (mg/m²·day)	Ammonia Release Rate (mg/m²·day)	Stratification period (days)	Estimated DO Deficit/Year (kg)	Estimated Ammonia Released/Year (kg)	Estimated Ammonia DO Demand (kg)
2001	1823	197	119	62654	6759	24032
2002	1093	380	113	35656	12392	44060
2003	3615	170	70	73090	3437	12222
2004	1875	170	126	68218	6178	21967
2005	1211	542	112	39169	17540	62365
2006	1756	540	140	71007	21846	77674
2007	1572	351	174	79020	17651	62758
2008	1788	352	119	61458	12092	42994
2009	1763	376	126	64160	13688	48669
2010	2222	315	194	124506	17644	62734
2011	1285	231	181	67172	12067	42904

Year	DO Depletion Rate (mg/m²·day)	Ammonia Release Rate (mg/m²·day)	Stratification period (days)	Estimated DO Deficit/Year (kg)	Estimated Ammonia Released/Year (kg)	Estimated Ammonia DO Demand (kg)
2007	1266	216	146	91572	19344	68780
2008	869	141	105	44864	9058	32205
2009	1083	142	118	76223	10269	36511
2010	1279	197	161	128238	19437	69111
2011	854	226	140	82783	19347	68789

Year	DO Depletion Rate (mg/m²·day)	Ammonia Release Rate (mg/m²·day)	Stratification period (days)	Estimated DO Deficit/Year (kg)	Estimated Ammonia Released/Year (kg)	Estimated Ammonia DO Demand (kg)
2007	696	185	133	61465	16318	58019
2008	370	48	105	25791	3352	11920
2009	619	46	78	32050	2368	8420
2010	903	117	147	88166	11426	40624
2011	625	102	98	40694	6636	23595

Yearly DO Deficit and Ammonia Release:

The estimated annual DO deficit is the mass of DO needed to support the oxygen depletion rate during the period of thermal stratification. These values were obtained by multiplying the oxygen depletion rate times the influence area of each sampling station times the stratification period duration for each corresponding year. The estimated DO deficit/year in the reservoir resulted in values as high as 124,506 kg, 128,238 kg, and 88,166 kg for stations RE02, RE05, and RE10 respectively (Table 1). The lowest estimated DO deficit/year for each station was 35,656 kg, 44,864 kg, 25,791 kg in RE02, RE05, and RE10 respectively (Table 1). Results show that constituents within the reservoir have increased the demand for oxygen throughout time. From 2001 – 2005, estimated DO deficit/year ranged from 35,656 kg – 73,090 kg, while from 2006 – 2011, estimated DO deficit/year ranged from 25,791 kg – 128,238 kg. The highest estimated DO deficit/year results for stations RE02, RE05, and RE10 occurred in 2010. The study reveals that the estimated DO deficit/year is impacted by the thermal stratification period, the highest values calculated correlate with the longest stratification periods. The longest stratification period for stations RE02, RE05, and RE10 are 194, 161, and 147 days respectively (Table 1). Results also show a tremendous increase in the amount of DO deficit throughout the studied years for station RE02. From station RE02, the 2010 DO deficit (124,506 kg) is nearly twice the amount of the initial 2001 year DO deficit (62,654 kg).

The estimated DO deficit is a value that represents an approximate amount of oxygen that is needed to sustain an aerobic environment in the hypolimnion of the reservoir during the summer months based on the calculated oxygen depletion rates. In other words, the oxygen deficit results from the oxidation of organic matter and other reduced compounds during the period of thermal stratification. If an oxygenation system were to be designed using the data provided in this study, it should at least satisfy the oxygen deficit (total mass) for each year. In this study, the estimated DO deficit is compared against the ammonia oxygen demand which is determined from the measured ammonia release rates.

For the case of ammonia, the values under the estimated ammonia released/year column represent an estimate of the mass of ammonia released during the period of thermal stratification for each year. These values were obtained based on the ammonia release rates calculated from the field data. The highest ammonia mass observed for stations RE02, RE05, and RE10 were

21,846 kg, 19,437 kg, and 16,318 kg respectively (Table 1). The estimated ammonia released/year for station RE02 have values above 12,000 kg in the years 2002 and 2005 – 2011 (Table 1). The results reveal that stations RE02, RE05, and RE10 all exceed an estimated ammonia mass of 10,000 kg in the year 2010 (Table 1). The results also reveal that in the years 2007 and 2009 – 2011 station RE05 exceed an estimated ammonia mass amount of 10,000 kg.

Ammonia is produced year round as microorganisms mineralize nitrogen rich organic matter. In some cases, excess ammonia is produced during the mineralization process resulting in the release of ammonia into the water column. Once ammonia becomes soluble it may be consumed by microorganisms that use ammonia as their preferred form of nitrogen, it may be sorbed into sediments depending on the sediment ability to sorb cations, it may be rapidly oxidized to nitrate in the presence of oxygen or it may accumulate in the water column with the absence of oxygen. Additionally, ammonia production and release rates may vary throughout the year depending on the environment conditions. It is expected that under anaerobic conditions, typical of the summer months, ammonia production rates are lower under aerobic conditions with similar temperature values (Beutel et al. 2008). In this study, ammonia release rates were obtained during anoxic periods, therefore it is possible that ammonia production rates may be higher during warm aerobic periods in the reservoir. The mass of ammonia released is used to determine the total ammonia oxygen demand in the reservoir during periods of thermal stratification.

Ammonia Oxygen Demand:

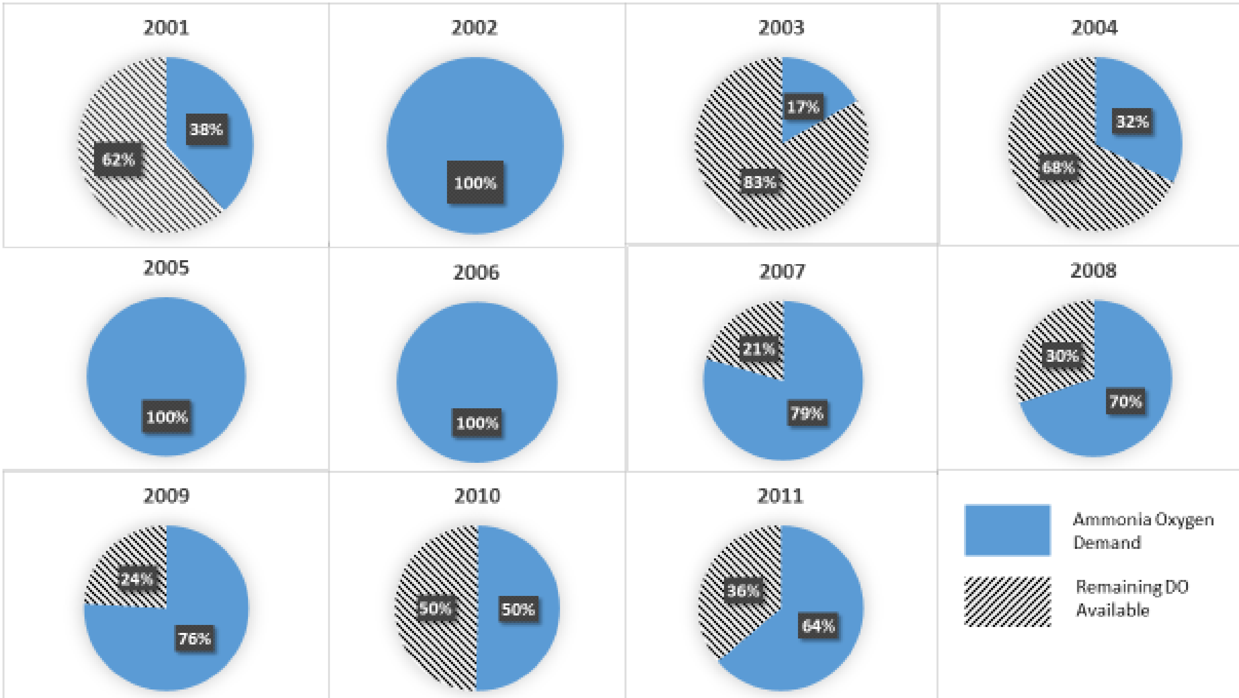
The ammonia oxygen demand was calculated based on the mass of ammonia produced during the period of thermal stratification. Using the stoichiometric relationship between ammonia and oxygen that results from the nitrification process, it was possible to estimate the mass of oxygen needed to oxidize the mass of ammonia estimated from the sediment release rates. The overall nitrification reaction was used to determine the amount of oxygen required to oxidize ammonia using the microorganisms as a catalyst. Nitrification is the process that oxidizes ammonia to nitrite and then to nitrate. The nitrification reaction $NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$ reveals a 2:1 ratio of oxygen to ammonia, thus 2 moles of oxygen (3.56 gr of O_2 for 1 gr of NH_4^+) are needed to oxidize 1 mole of ammonia (Wetzel 2001). The estimated ammonia DO demand, which disclose how much DO was necessary to oxidize the ammonia present, was determined by the estimated ammonia released/year multiplied by the nitrification factor of 3.56.

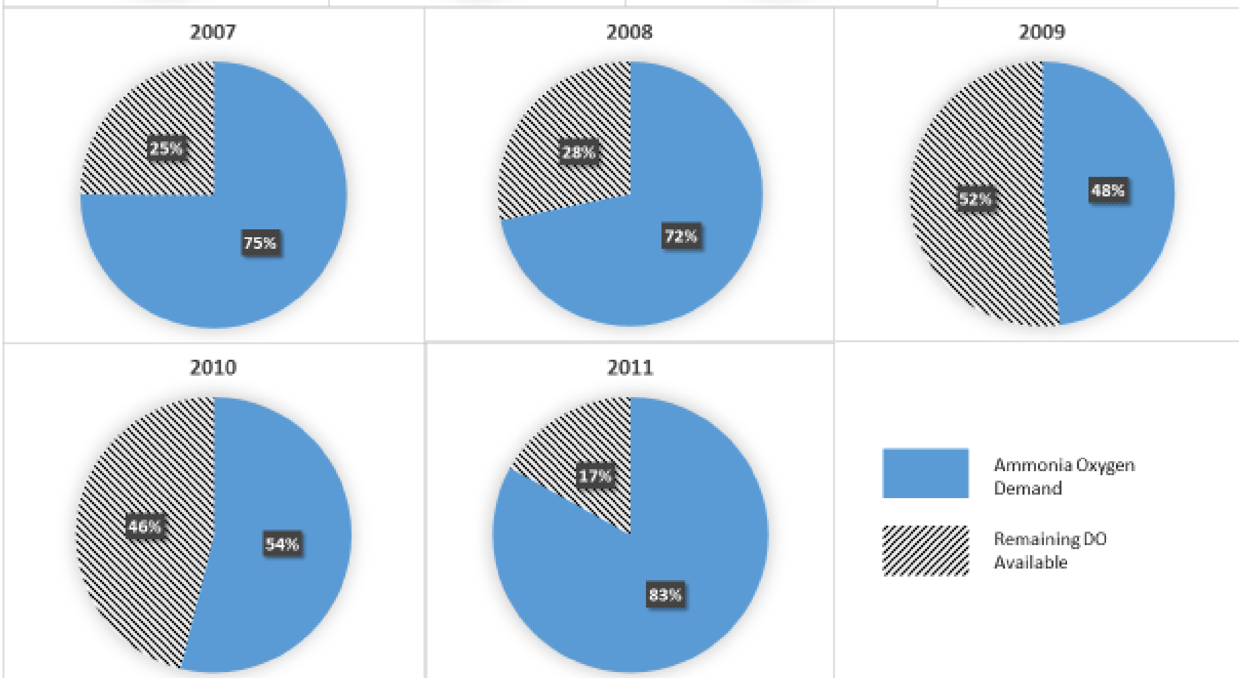
For the majority of the years in stations RE02, RE05, and RE10 the estimated ammonia DO demand was above 40,000 kg (Table 1). Estimated ammonia DO in the reservoir resulted in values as high as 77,674, 69,111, and 58,019 kg in stations RE02, RE05, and RE10 respectively (Table 1). From 2001 – 2005, estimated ammonia DO ranged from 12,222 kg – 62,365 kg, while from 2006 – 2011, estimated ammonia DO ranged from 8,420 kg – 77,674 kg.

The calculated ammonia oxygen demand was compared to the estimated DO deficit in an attempt to determine if the DO depletion rate is a good approximation of the total oxygen demand. Generally, oxygenation systems are designed mainly to oxidize organic matter with the assumption that less amount of oxygen is needed to oxidize other reduced compounds such as ammonia. It was expected that if the estimated ammonia demand was a small fraction (e.g. < 20%) of the total DO deficit then the DO depletion rate may be a good approximation for the total oxygen demand in the reservoir. Conversely, if the estimated ammonia demand was greater than 40%, then it is possible that using the DO depletion rates as a design parameter may underestimate the total oxygen demand of the system.

Results show how much of a major contributing factor ammonia was on the observed oxygen demand. The percentage of ammonia attributed to the oxygen demand for stations RE02, RE05, RE10 were found in this study (Figure 3). When comparing ammonia oxygen demand and DO deficit it was shown that ammonia alone was not capable of being fully oxidized in stations RE02 in 2002, 2005, and 2006. For these years, the ammonia oxygen demand exceeded the amount of oxygen required to keep an aerobic environment calculated from the DO depletion rates (Figure 3a). This result suggests that the projected amount of DO needed for the stratification period in 2002, 2005, and 2006 of the reservoir is not enough to solely oxidize ammonia, which is one of the compounds expected to contribute less to the total oxygen demand.

A different scenario was observed in those years where the stratification period was the shortest. In 2003, at station RE02, a lower ammonia oxygen demand was observed. During this year, ammonia demand represented only 17% of the DO deficit estimated at RE02 (Figure 3a). This was the lowest ammonia oxygen demand measured in station RE02 for the period of record. In 2011, 83% of the DO deficit in station RE05 would have to be contributed to ammonia in order to fully oxidize the amount of ammonia present (Figure 3b). The year 2009 reveals the lowest concentration ratio of ammonia to DO at 48% for station RE05 (Figure 3b). In 2007, 94% of the available DO present in station RE10 would have to be contributed to ammonia in order to fully oxidize the amount of ammonia present (Figure 3c). The year 2009 reveals the lowest concentration ratio of ammonia to DO at 26% for station RE10 (Figure 3c).


2001
38%
62%
2002
100%
2003
17%
83%
2004
32%
68%
2005
100%
2006
100%
2007
21%
79%
2008
30%
70%
2009
24%
76%
2010
50%
50%
2011
36%
64%
Ammonia Oxygen Demand
Remaining DO Available


2007
25%
75%
2008
28%
72%
2009
52%
48%
2010
46%
54%
2011
17%
83%
Ammonia Oxygen Demand
Remaining DO Available

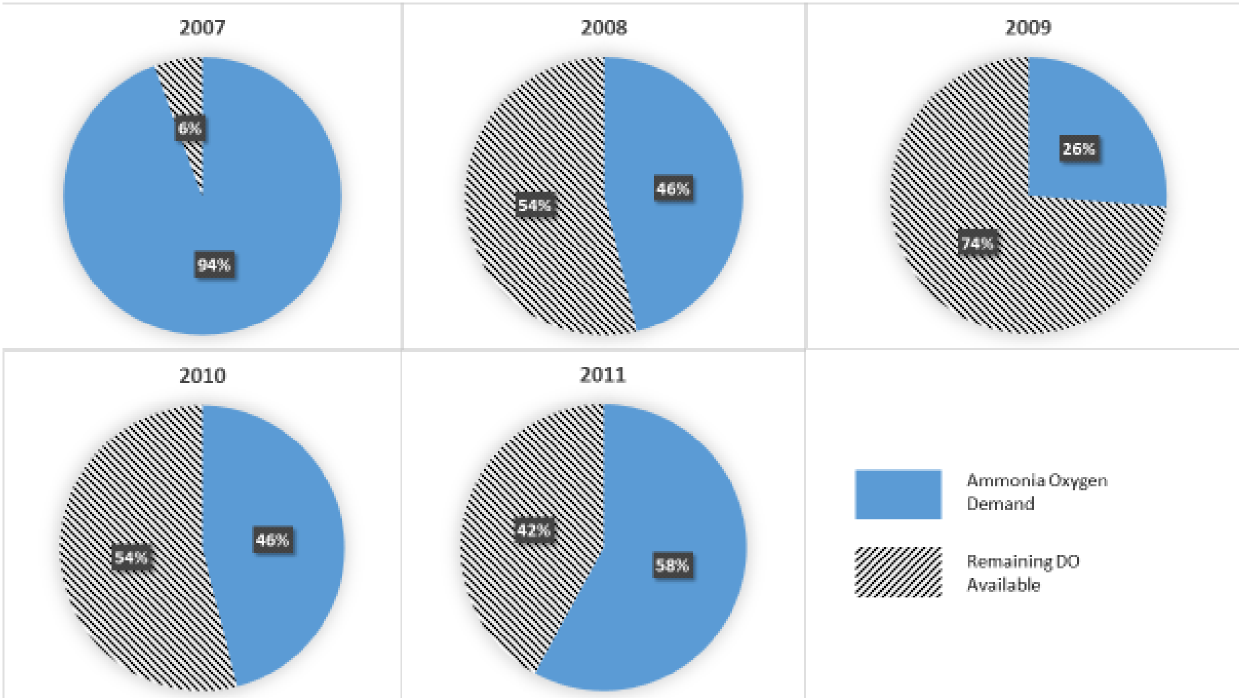


Figure 3: Ammonia Oxygen Demand/Available Dissolved Oxygen Concentration

In surface waters, oxygen demand is exerted mainly by the mineralization of organic matter and the oxidation of reduced species such as ammonia, iron, manganese, sulfide, methane, etc. In this study, only the contribution of ammonia to the dissolved oxygen demand was analyzed in an effort to provide estimates of the true ammonia demand based on sediment fluxes from a nitrogen rich environment. Originally, it was expected that ammonia would represent a low fraction of the overall oxygen demand in the reservoir, but results suggest otherwise. Results reveal that in nitrogen rich systems that experience periods of hypolimnetic anoxia during the summer months, ammonia is an important contributor to the overall oxygen demand. Therefore, when designing an oxygenation system of this type, special attention to the flux of reduced substances from the sediments should be taken into consideration. In most cases, to account for lack of data regarding the flux of reduced substances, safety factors are applied to design oxygenation systems. However, misuse of these factors can result in high operational costs.

A further analysis was done using the collected data to determine which conditions in the reservoir would result in the highest ammonia oxygen demand. These results were compared to the DO deficit to test how reliable the data obtained from the DO depletion rates is when designing oxygenation systems. Four ammonia oxygen demand/dissolved oxygen deficit scenarios were conducted with the given station data. Each scenario reveals how much of an impact ammonia has on the available observable DO. Each scenario tested is described in Table 2, the scenarios were chosen to reveal what would happen if all of the contributing components occurred during one period. The scenarios were developed to expose the significance of each contributing factor would have on ammonia oxygen demand, the most detrimental results were selected. The scenarios were also developed to assist with potential future design changes to the oxygenation system.

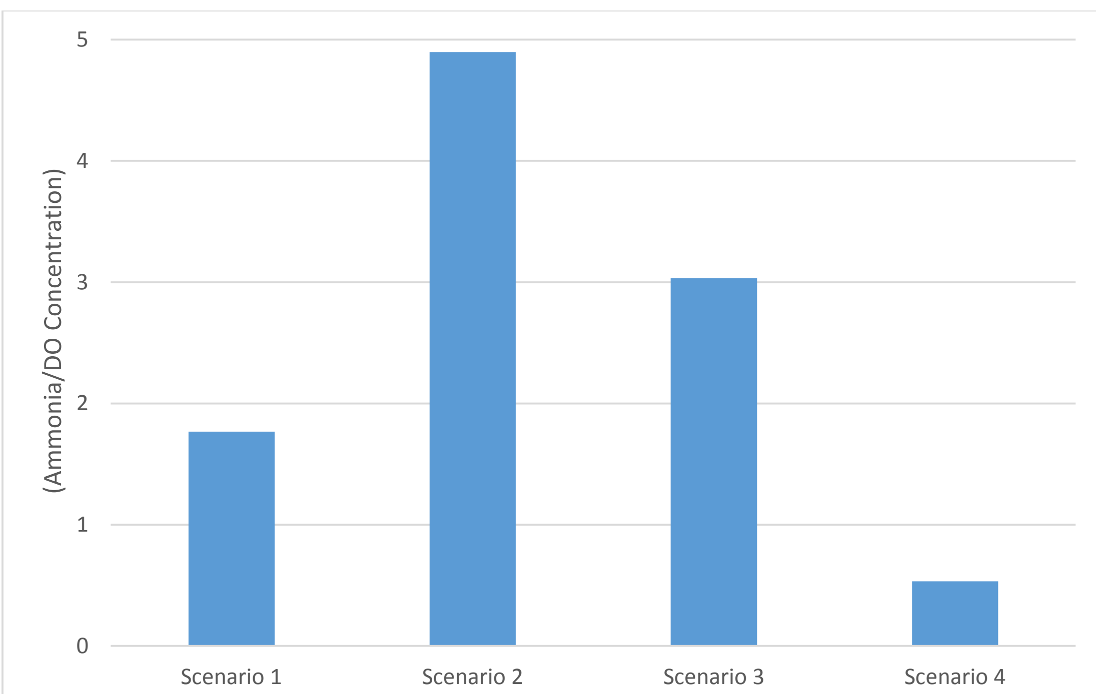
The development of the case scenarios data helped determine a worst case scenario. Out of the case scenarios, the scenario with the highest ammonia oxygen demand was determined to be the worst case. The worst case scenario with the given data for stations RE02, RE05, and RE10 was Scenario 2. Scenario 2 is composed of the following station data calculations: lowest DO depletion rate, highest ammonia release rate, longest stratification period for ammonia, and shortest stratification period for DO (Table 2). The case scenario with the lowest ammonia oxygen demand for stations RE02, RE05, and RE10 was Scenario 4. Scenario 4 is composed of the following station data: highest DO depletion rate, highest ammonia production rate, and longest stratification period for ammonia and DO (Table 2).

Case Scenarios:

Table 2: Ammonia Oxygen Demand Case Scenarios

Ammonia Oxygen Demand Scenarios
Scenario 1: Lowest DO Depletion Rate, Highest Ammonia Release Rate, Longest Stratification Period for Ammonia and DO
Scenario 2: Lowest DO Depletion Rate, Highest Ammonia Release Rate, Longest Stratification Period for Ammonia, Shortest Stratification Period for DO
Scenario 3: Lowest DO Depletion Rate, Highest Ammonia Release Rate, Longest Stratification Period for Ammonia, DO Stratification Period for Lowest DO Depletion Rate
Scenario 4: Highest DO Depletion Rate, Highest Ammonia Release Rate, Longest Stratification Period for Ammonia and DO

The case scenarios reveal the significance of the thermal stratification duration, ammonia release rates, and DO depletion rates. The worst case scenario for stations RE02, RE05, and RE10 resulted with ammonia /estimated DO concentrations of 4.9, 1.4, and 3.4 respectively (Figure 4). From Figure 4, the x-axis identifies the case scenario and the y-axis reveals the amount of oxygen needed to oxidize ammonia present for that scenario. Stations RE02, RE05, and RE10 Scenario 2 reveals that the amount of oxygen required to fully oxidize ammonia would require 4.9 times, 1.4 times, and 3.4 times the amount of oxygen compared to ammonia respectively. Stations RE02, RE05, and RE10 Scenario 4 ammonia/available dissolved oxygen concentrations were 0.53, 0.63, and 0.73 (Figure 4). Scenario 4 for stations RE02, RE05, and RE10 reveals that 53%, 63%, and 73% of the available DO present would have to be contributed to ammonia in order to fully oxidize the amount of ammonia present respectively.



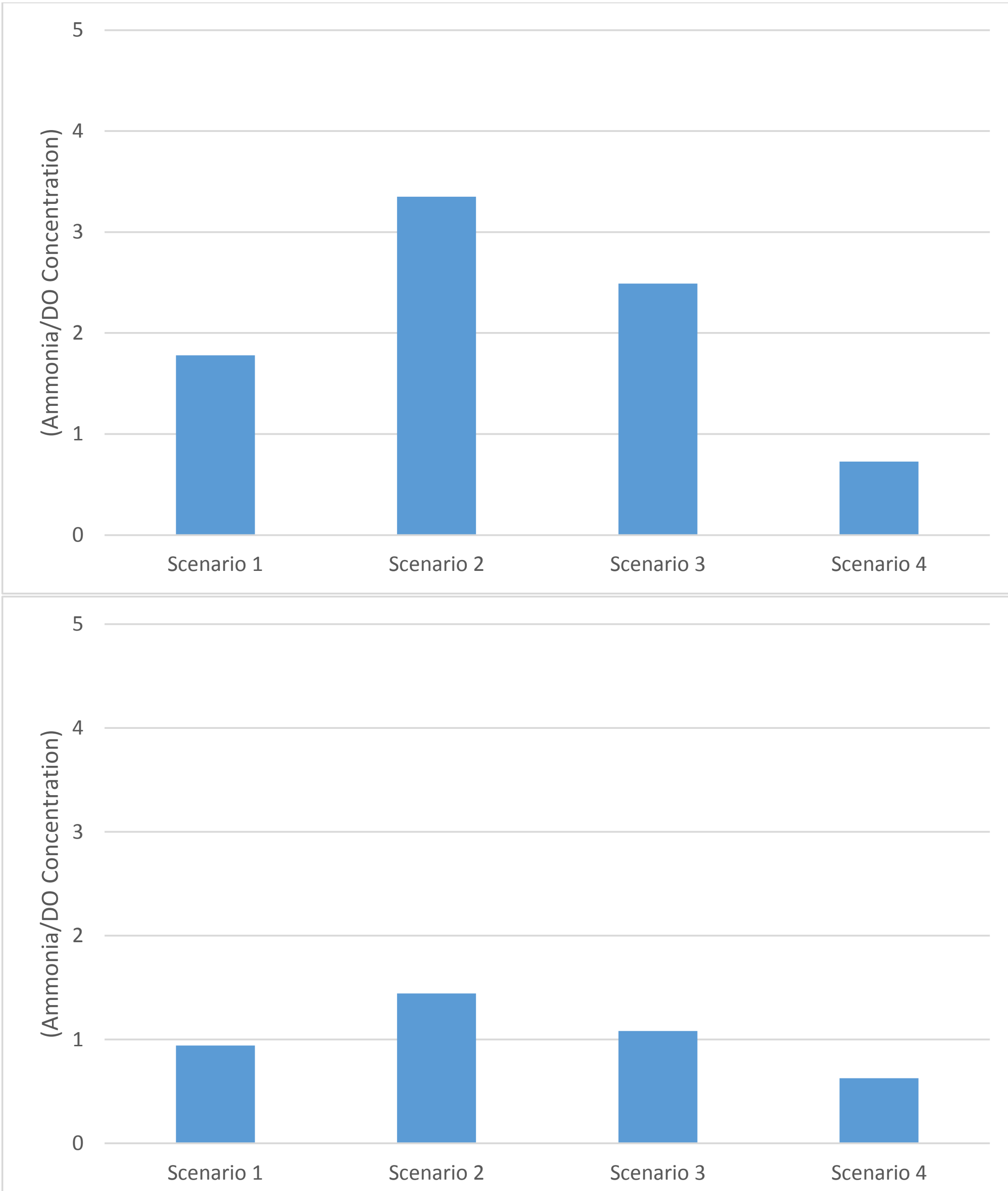


Figure 4: Ammonia/DO Concentration Case Scenarios

A line diffuser oxygenation system was installed in the Occoquan Reservoir in 2012 to prevent the onset of anaerobic conditions in the bottom waters of the reservoir during the summer months. The hypolimnetic oxygenation system has operated since 2012 at a flowrate of 65 cfs, which is close to the maximum operating capacity. DO and TAN time series during the stratification period for station RE02 for the years 2012, 2013, and 2014 were plotted to determine the effects of the oxygenation systems on ammonia accumulation in the reservoir

(Figure 5). Results reveal that the additional oxygen from the hypolimnetic device was not fully effective during the stratification period of 2012, 2013, and 2014 for station RE02 as evidenced by ammonia accumulating in the water column after the oxygenation system was fully operational. Ammonia concentrations peaked at values higher than 2 mg-N/L at RE02 and at values close to 1 mg-N/L at RE05 and RE10 (Figure 5). Maximum concentrations of ammonia measured between 2012 and 2014 were lower than the concentrations observed before the oxygen system installation and operation. Although the ammonia concentrations after the oxygenation system was operational were approximately 25% of the concentrations observed prior to 2012, it was expected that no ammonia accumulation would develop during the summer months. Time series further revealed that ammonia concentrations tend to increase toward the end of the stratification period, around the month of August and September.

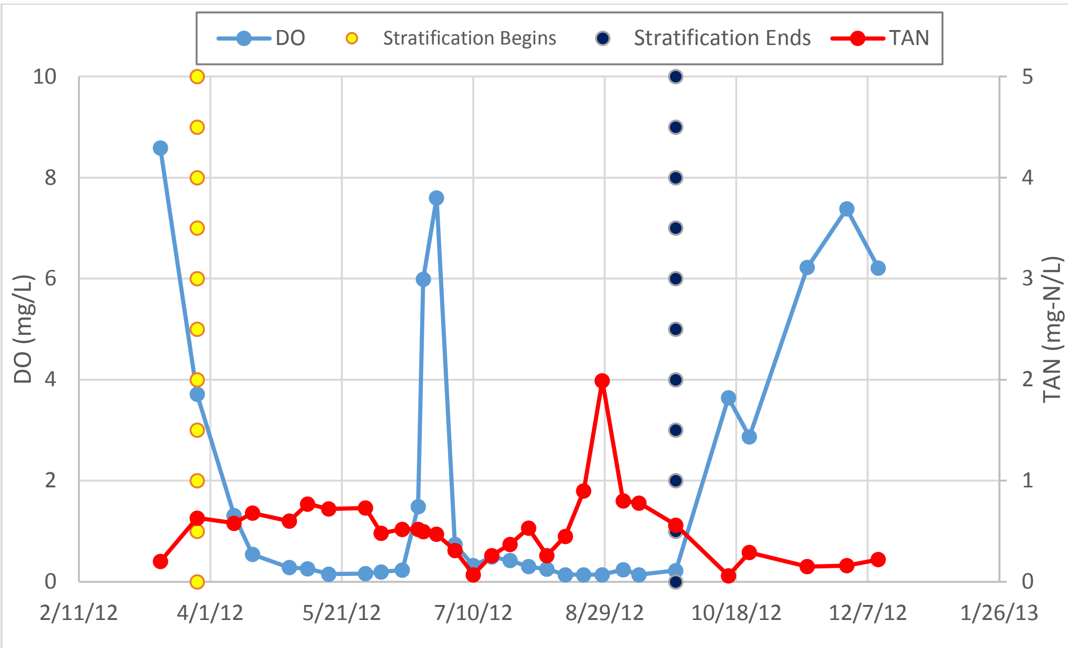
In 2012, the stratification period in the reservoir began early April and ended in late September. Stratification was revealed by the epilimnion having a water temperature of 15.2 °C and the bottom layers having a temperature of 8 °C. At the end of the stratification period, September 25, 2012, a temperature uniformity between the layers ranging from 21.7 to 22.6 °C was displayed. Immediately after the onset of the thermal stratification, DO concentration in the hypolimnion abruptly decreased from values higher than 10 mg/L in late March to values close to 0 mg/L by the end of April. Operation of the oxygenation system began shortly after DO depletion in the reservoir. The oxygenation system was initially operated at normal design capacity (≈ 35 cfs) from late April to late May, but by the early June, the oxygen flow was increased to values close to the maximum design capacity (≈ 65 cfs). Authorities managing the reservoir decided to increase the oxygen delivery because oxygen was not accumulating in the water column after the system was initialized. The spike in DO concentration (increase from 0.23 – 7.6 mg/L) observed from June 29 – July 3 was the result of the sudden increase in oxygen flow to the reservoir (Figure 5a). Results revealed that the increase in oxygen flow did not have an impact in the overall DO concentration because oxygen values remained low (0.4 mg/L) for the remainder of the summer until the fall overturn. Additionally, ammonia accumulation increased toward the end of the summer until reaching a concentration value of 2 mg/L. Ammonia accumulated because there was not enough DO available to oxidize ammonia despite the oxygenation system working at maximum design capacity.

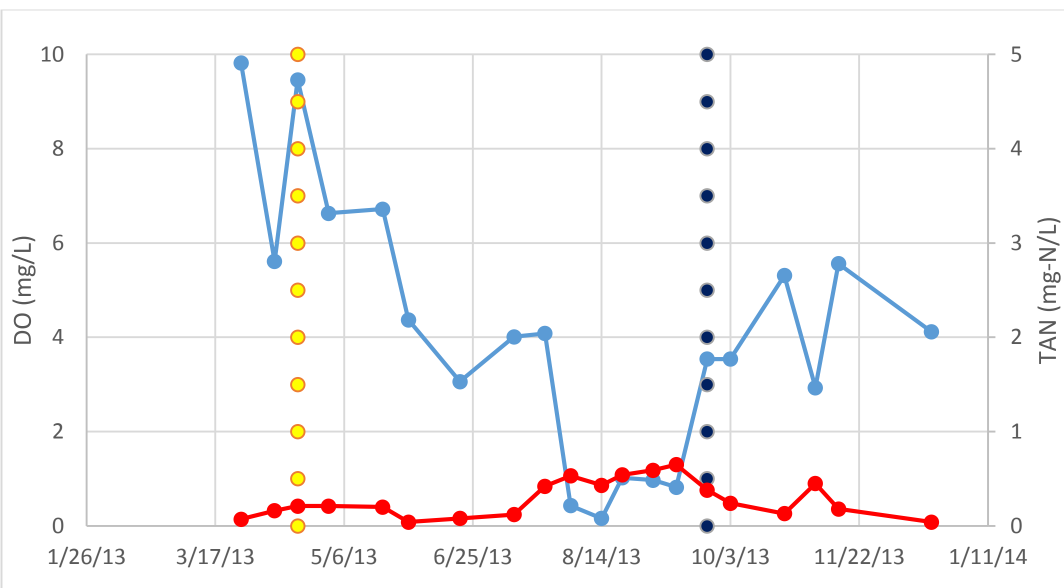
The stratification period for the year 2013 began on April 18 and ended September 24 (Figure 5b). Temperature profiles for April 18 (data not shown) revealed a dispersion in temperature within the reservoir layers ranging from 8.7 to 17.6 °C. At the end of the stratification period, September 24, 2013, there was a temperature uniformity between the layers ranging from 22.6 to 22.7 °C. After the onset of thermal stratification, DO concentrations gradually decreased from April to July following a different trend from the one observed the previous year. Before the beginning of the stratification period in 2013 the DO concentration was 9.82 mg/L on late March, then it decreased to 6.7 mg/L in late May until finally reaching a value of 0.16 mg/L in August 14.

During the 2013 year, the oxygenation system was operational before the onset of thermal stratification. The additional oxygen supplied by the system contributed to the overall oxygen concentration causing it to gradually decrease as the summer progressed and water temperatures increased. The sharp decrease in oxygen following the onset of thermal stratification that was typically observed before the installation of the oxygenation system was not observed in 2013. It was expected that a minimum amount of oxygen was maintained throughout the summer, but results show that oxygen was depleted by mid-August. Environmental regulations stipulate that a minimum concentration of 4 mg/L should be maintained in the hypolimnetic waters of lakes and reservoirs to preserve aquatic biota (VLIS 2010). Oxygen depletion resulted in ammonia accumulation by the end of August. Ammonia concentration increased from 0.1 – 0.7 mg-N/L by late August until it was completely oxidized after atmospheric oxygen was reintroduced to the hypolimnion shortly after the fall overturn.

The stratification period for the year 2014 began on April 22 and ended September 30 (Figure 5c). The temperature profile for April 22 revealed a dispersion in temperature within the reservoir layers ranging from 7.6 to 15 °C. The temperature profile for September 30, 2014 revealed a temperature uniformity around 21.1 to 21.9 °C. Towards the beginning of the stratification period in 2014 the DO concentration was 8.7 mg/L and decreased to 0.72 mg/L by late May. The oxygenation system was fully operational during the period of thermal stratification and it was able to increase DO levels to a maximum of 2.3 mg/L in June, but was not capable of sustaining this concentration until the end of the summer.

By the end of August, DO decreased to a minimum of 0.18 mg/L and stayed low until the fall overturn. Results further revealed that when DO levels decreased below 1.3 mg/L ammonia began to accumulate until reaching a maximum concentration of 0.7 mg-N/L.





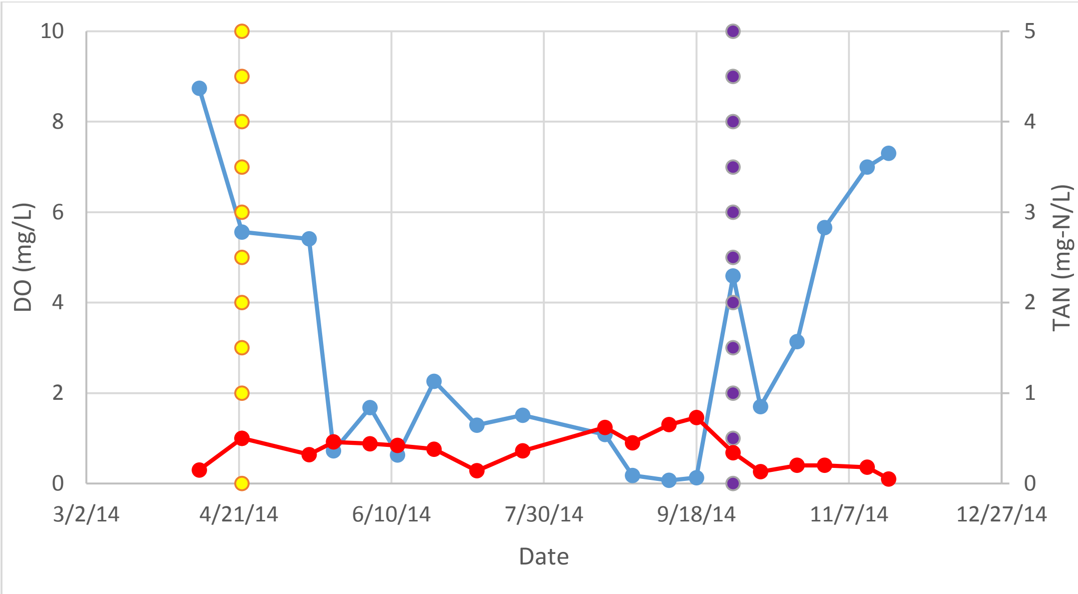


Figure 5: DO and TAN Time Series for Station RE02

Results suggests that it is possible that the installed oxygenation system could not fulfill the actual hypolimentic oxygen demand in the reservoir allowing the flux and accumulation of reduced substances, including ammonia, from the deeper layers of the sediments into the water column. Organic matter and a variety of reduced compound species contribute to the oxygen demand within the reservoir. From these compounds, ammonia released from the sediments requires a certain percentage of the available oxygen in order to fully oxidize to nitrate. During the thermal stratification period the Occoquan Reservoir experiences significant DO depletion and ammonia production. Ammonia production within the reservoir may reach values as high as 542 $mg/m^2 \cdot day$. The installed oxygenation system could not maintain a constant DO concentration in the reservoir during the summer. The expectation of the hypolimnetic oxygenation device was to oxygenate the hypolimnion at a consistent DO level during the stratification period. Results revealed that there were peaks of high levels of DO during the stratification period, but ultimately for each year DO levels declined towards the end of the summer resulting in sediment ammonia release.

Findings show that for the years studied, the amount of oxygen required to oxidize ammonia represents 20-100% and in some cases more than 100% of the amount of oxygen needed to satisfy the overall oxygen demand in the reservoir calculated from the oxygen depletion rates. The findings further indicate that in the years 2002, 2005, 2006 station RE02 exceeded the available amount of dissolved oxygen needed to solely oxidize ammonia. On the contrary, results show that in the year with the lowest contribution of ammonia to the total oxygen demand nearly required 20% of the available dissolved oxygen present in order to oxidize ammonia. The oxidation of organic matter and reduced compounds is generally achieved by microorganisms within the sediments. These organisms adapted to live in aerobic environments and compete for the available oxygen. From these microorganisms, the ammonia oxidizers (Nitrosomonas and Nitrobacter) will be in most cases outcompeted by organic matter oxidizers. Therefore, high amounts of oxygen capable of sustaining an aerobic environment are required to oxidize ammonia within the sediments.

DO depletion rates, which were calculated in this study, are typically used to design oxygenation systems. They are used because the required data is relatively easy to collect and is readily available for most systems. However, the DO depletion rates do not provide any kind of information related to the different compounds that exert an oxygen demand. Additionally, in most cases and as it was demonstrated in this study, the DO depletion rates may underestimate the actual oxygen demand of a system. Accurately estimating the DO depletion rate is critical when determining what additional amount of oxygen needs to be placed into the reservoir during the stratification period regardless of the method that is going to be used to deliver oxygen into the system. An alternative method for estimating the overall oxygen demand is to perform a thorough study on sediment oxygen demand in every system. However, from an engineering point of view, it is unfeasible to perform such studies when installing an oxygenation system and in most cases this data is not available. This study provides a good estimate of the ammonia contribution to the overall oxygen demand within a water supply reservoir. Additionally, the results have proven that ammonia contribution to the total oxygen demand must be taken into consideration with the design of oxygenation systems. It is expected that providing information on the flux of reduced substances from the sediments and estimating their oxygen demand will help improve the process used to design oxygenation and/or aeration systems.

CHAPTER 5

CONCLUSION AND RECCOMENDATION

The consumption of water with a significant portion of ammonia can be poisonous and lead to illness or death. The negative impacts associated with a reservoir filled with an ample supply of ammonia and other nutrients can lead to a hypereutrophy stage, which will lead to serious water quality contamination. The research conducted proves how much of a significant contributing compound ammonia is to the total hypolimnetic oxygen demand of the Occoquan Reservoir. At multiple reservoir stations, the study revealed that ammonia oxygen demand solely accounted for the majority and in some cases the entirety of the total oxygen demand in the hypolimnion during thermal stratification for multiple years.

The implementation of the line diffuser is a water quality strategy intended to diminish the release of ammonia and other constituents from the sediments of the reservoir. The purpose of the oxygenation device is to preserve stratification, oxygenate the hypolimnion while maintaining a cool temperature, reduce sediment release, oxidize compounds, allow cold water fish and aquatic life to respire, and maintain an adequate water quality standard. The research conducted shows that a hypolimnetic oxygenation system should only be used during periods of thermal stratification for the Occoquan Reservoir. The oxygenation system was incapable of completely oxidizing ammonia accumulation, but did reveal reduction in TAN values compared to the TAN values prior to installation. For each year studied after the installation total ammonia nitrogen remained in the hypolimnion, the TAN mean values after the installation of the oxygenation system were lower compared to the TAN mean values prior to the installation.

After the installation of the oxygenation device, peak levels of dissolved oxygen were shown during the thermal stratification periods, thus revealing that DO was present with the operation of the oxygenation device. However, the study reveals that after the installation of the line diffuser there were occurrences of DO depletion during the thermal stratification periods. Environmental regulations require that the reservoir maintain a DO concentration level of 4 mg/L, the analysis shows that the operation of the current line diffuser could not fully oxidize the hypolimnion throughout the entirety of the thermal stratification period. The results reveal during the stratification period for each year studied after the installation of the device multiple occasions with a DO concentration level of less than l mg/L, the lowest DO concentration reached in the study was 0.07 mg/L.

The practice and usage of a hypolimnetic oxygenation system during thermal stratification is recommended for the eutrophic reservoir. An oxygenation system is recommended because the device has potential to protect water quality and aquatic life. The line diffuser could completely oxidize ammonia present, but did reveal a reduction in TAN. The practice of a hypolimnetic oxygenation system is more economical compared to the treatment and cleanup of a contaminated reservoir, the operation of an oxygenation system can prevent water quality contamination. Further testing and sampling at the site should continue to be conducted to help enhance the efficiency of the line diffuser. The placement and calibration of the line diffuser maybe an issue that may needs to be revaluated. The installation of another type of oxygenation device is an option that could also be taken into in consideration to help compare ammonia concentrations and DO results.

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