An Investigation into the Effects of an External Electron Acceptor on Nutrient Cycling at the Sediment-Water Interface of the Occoquan Reservoir

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Abstract

Water supply reservoirs are often subject to accelerated nutrient enrichment from urban sources. Cultural eutrophication due to such enrichment requires the development of efficient management and remediation strategies to protect drinking water sources. This study investigates the effects of using nitrate as part of a management strategy to control nutrient cycling in the Occoquan Reservoir in northern Virginia, USA. A novel aspect of the study is that the reservoir is part of an indirect potable reuse system where the source of nitrate is the product water from an advanced water reclamation facility (WRF).

Field and laboratory studies showed that nitrate at a concentration greater than 1 mg/L N was effective in controlling the release of phosphorus, iron, and manganese from the sediments after the depletion of oxygen from the hypolimnetic waters of the reservoir. However, when the nitrate concentration above the sediment-water interface was less than 1 mg/L N, phosphorus, iron, and manganese release from the sediments was evident. Experiments revealed that the presence of nitrate decreased sediment ammonium release, but did not completely prevent it during anoxic periods. Results also showed that changes in the effective depth (ED) value along the length of the reservoir promoted higher denitrification rates in the upper reaches of the reservoir, thereby decreasing the downstream transport of nitrate. During periods of hypolimnetic anoxia, a nitrate-N input from the WRF of at least 10 mg/L N is needed to maintain an oxidized environment above the sediment-water interface. Therefore, decreasing the nitrate input to the reservoir will likely result in the deterioration of the surface water quality in the reservoir.

Finally, the ED concept was proven to be an effective method to simulate different segments of the reservoir in laboratory-scaled experiments. Similarities between the field and laboratory results suggests that the environment that existed in the waters of the reservoir was closely replicated in the experimental setup, and provides confidence that laboratory results can be extrapolated to natural reservoir conditions.

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Preface

This dissertation describes a series of investigations performed since the fall of 2007 to better understand the effects of nitrates on nutrient cycling in the sediment-water interface of a deep reservoir used as a source for drinking water. This document is a compilation of four manuscripts, included as separate chapters, which will be submitted to peer-reviewed journals related to the environmental sciences. The planned journal submissions include: Chapter 2 to the *Water Resources Research* journal, chapter 3 to *Limnology and Oceanography*, chapter 4 to *Water Research*, and chapter 5 to the *Water Environment Federation* Journal.

The chapters were organized following a logical research sequence where the objectives were to: a) introduce and describe the study site, highlighting the importance of water reuse; b) investigate the effects of using wastewater-derived nitrate as reservoir management strategy; and c) summarize the key findings of this investigation. Chapter 2 describes in detail the effects of using nitrate from a water reclamation plant (WRF) discharge to manage sediment nutrient release. Chapter 3 explains how the morphology of the reservoir affects the longitudinal transport of nitrate. Chapter 4 analyzes thoroughly the effects of nitrate on sediment ammonium release. Chapter 5 summarizes, from a practical point of view, the consequences of decreasing the nitrogen load from the WRF to the reservoir. This last manuscript is intended to reach an audience that works directly in reservoir management and also to the persons who are involved in environmental policy making.

The work described in this document was a collaborative effort of all the committee members. Direct input from all the members was received for every study performed in this research project. The names of the co-authors have been provided accordingly in each chapter.

Chapter 1 - Summary on the effects of nitrate on nutrient cycles in the Occoquan Reservoir

1.1 Introduction

In recent times, many lakes and reservoirs around the world have experienced accelerated productivity (eutrophication) as a direct result of increased nutrient loading. The causes of eutrophication are complex and vary according to the characteristics of the aquatic system. It is well known that nutrient enrichment and decomposition of excess organic matter accelerates the process, resulting in deterioration of surface water quality (Wetzel 2001). Rapid decomposition of organic matter results in high rates of oxygen depletion in the hypolimnia of lakes and reservoirs and is a common symptom of eutrophication. Hypolimnetic anoxia develops in productive lakes and reservoirs that experience thermal stratification during summer periods, and causes increased release of nutrients, organic compounds, and soluble metals from the sediments. This process is known as internal loading, and it may represent a substantial fraction of the total loading (Beutel et al. 2008). In aquatic systems where the external loading of nutrients has been reduced, the internal loading may delay return to a less enriched state. Nutrients released from sediments include species of nitrogen and phosphorus, which have the potential to stimulate phytoplankton productivity and promote algal blooms that are detrimental to aquatic systems. In water supply reservoirs, iron and manganese released from anaerobic deposited sediments may also degrade the aesthetic quality of drinking water and increase drinking water treatment costs (Beutel 2001).

A wide array of management approaches and technologies have been developed for the restoration and remediation of eutrophic systems and for reducing the loads of nutrients. Most lake and reservoir management efforts focus on reducing the external nitrogen and phosphorus loadings which originate in the watershed (Hemond and Lin 2010). The concerns about nitrogen revolve about its role as a nitrogen source for microorganisms, especially in nitrogen limited environments, and because of the toxic effects to aquatic organisms of some nitrogen species (Lewis and Morris 1986, Matthews et al. 2000). Humans have effectively increased the global rate of nitrogen fixation due to the production of nitrogen-based fertilizers for farming activities (Vitousek et al. 1997), and some fraction of this anthropogenic nitrogen influx ultimately reaches streams, lakes, and reservoirs. Excess nitrogen inputs also alter the carbon to nitrogen ratio of

living organisms and influence nitrogen storage and transport across biomes affecting the flow of energy through food webs (Dodds et al. 2004). However, decreasing external nitrogen loads is not always beneficial from a lake management perspective. Nitrogen species such as nitrate can have a role different from the synthesis of amino acids and proteins in aquatic ecosystems. For example, nitrate can serve as an electron acceptor in the absence of molecular oxygen and contribute to the oxidation capacity of the system (Hemond and Lin 2010, Stumm and Morgan 1996). Finally, decreasing external nitrogen loads can result in an increase in the internal loading due to the release of nutrients from the sediments or through nitrogen fixation by certain microorganisms (Beutel et al. 2008).

From the array of available management strategies for the remediation of eutrophic systems, the use of nitrate to maintain an oxidized environment above the sediment-water interface has been used efficiently in the Occoquan Reservoir. Many studies (Andersen 1982, Mortimer 1941, Prestigiacomo et al. 2009, Thirunavukkarasu et al. 2000) have shown that nitrate is capable of maintaining a relative high oxidation reduction potential (ORP) after dissolved oxygen (DO) is depleted from the hypolimnion, thereby preventing the release of reduced substances from the sediments. Nitrate, in the absence of oxygen, is used as an alternate electron acceptor by certain microorganisms to harness the energy released from the oxidation of organic compounds. Consistent with the thermodynamic constraints of microbially-mediated redox processes, nitrate is generally used after molecular oxygen is exhausted (Madigan et al. 2003, Stumm and Morgan 1996). Thus, nitrate delays the establishment of complete anaerobic conditions by poising the system ORP at a level that will prevent the reduction of Fe(III) to Fe(II) and, subsequently, the release of iron bound phosphorus. The absence of nitrates in the system may also result in further decreases to the ratio of inorganic nitrogen to soluble reactive phosphorus (N:P) as a result of decreased inorganic nitrogen species and increased release of phosphorus from the sediments under anoxic conditions. Lowering the N:P ratio may result in elevated populations of cyanobacteria, thereby deteriorating the surface water quality (Baldwin and Williams 2007).

In recent years, there have been opposing views in the literature suggesting that the presence of nitrate will influence the release of ammonium from sediments and those that concluded the opposite. Another topic of debate among many researchers is the source of ammonium and the mechanisms that control its release from sediments under anoxic conditions. It has been

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demonstrated that ammonium accumulation in the water column is mainly a result of release from the sediments. Stief (2001) concluded that ammonium was released from sediments because the concentration increased over the initial value when the ammonium inputs were low, while Baldwin and Williams (2007) observed that the rates of ammonium accumulation were higher than those of nitrate depletion. Although it is known that sediment ammonium release is significant in lake and reservoirs, the mechanisms that control this phenomenon remain uncertain, with researchers supporting different views: (1) that it is mainly a result of mineralization of sediment organic matter (Baldwin and Williams 2007) or (2) that it is due to assimilatory or dissimilatory processes (Arango et al. 2008).

1.2 Study area

The Occoquan Reservoir is a constructed impoundment created in the 1950s to supply drinking water to the rapidly growing northern Virginia suburban population. The Occoquan Watershed is situated on the southwestern periphery of the Virginia suburbs of Washington D.C. (Figure 1-1). The watershed is formed by four headwater basins that drain to the Occoquan Reservoir which serves as an important water supply and recreational resource for 1.2 million people (OWML 2005). The reservoir has a surface area of 6.16 km^2, a volume of 31.4×10^6 m^3, a mean depth of 5.1 m, and a maximum depth of 20 m at full pool elevation (Xu et al. 2007). The tributary watershed drains 1,530 km^2 and is about 54% forest, 11% agricultural, 7% pasture, and 28% urban (Northern Virginia Regional Commission land use information, 2006).

In the early 1960s, rapid development in the watershed, increasing transformation of rural areas to urban areas, and high loads of both point and non-point pollution sources contributed to the eutrophication of the reservoir (Randall and Grizzard 1995). In response to the observed water quality deterioration in the reservoir, the authorities developed a strategic plan, which has been known as the Occoquan Policy (SWCB 1971). This Policy, which was a milestone in water quality management, highlighted the importance and value of reclaimed water as a resource, and established stringent measures necessary to protect public health when reclaimed water was to be discharged in a water supply reservoir. This document mandated the construction of a state-of-the-art water reclamation facility (WRF) that would replace 11 existing outdated wastewater treatment plants. The Occoquan Policy also required the establishment of an independent

monitoring program to evaluate the overall water quality of the reservoir and its tributaries, and to monitor the reduction of nutrient loads from both point and non-point sources (OWML 2005). Since 1972, monitoring of stream flow, water quality, precipitation, and land use has been performed by the Occoquan Watershed Monitoring Laboratory (OWML) and the reservoir-watershed system is among the best characterized in the nation (Holbrook et al. 2006).
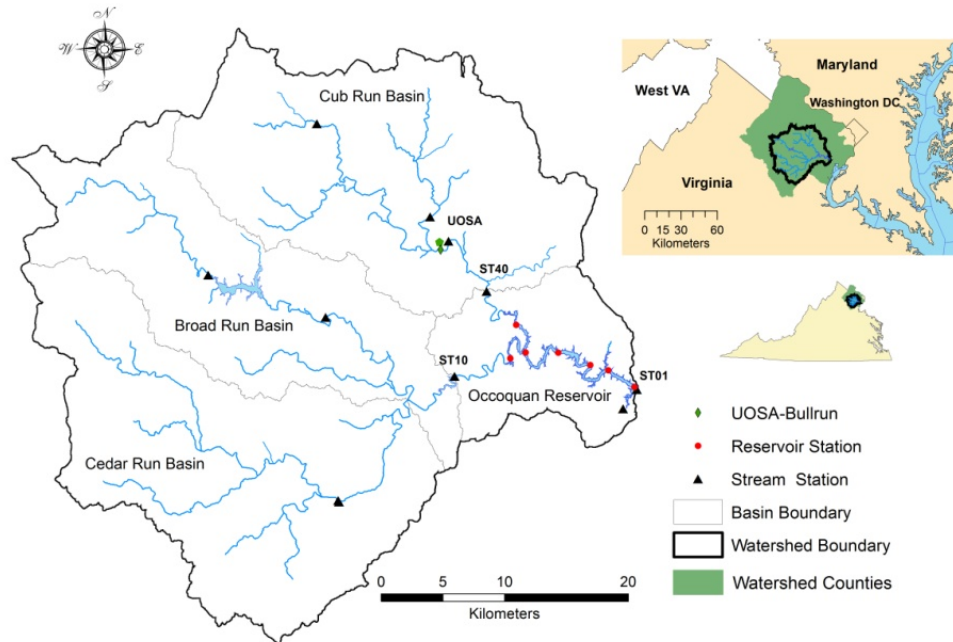
Figure 1-1. Occoquan Watershed.

1.3 Use of nitrate as a management strategy in the Occoquan Reservoir

The Occoquan Reservoir plays a unique role locally, nationally, and worldwide with respect to public water supply and indirect potable reuse of reclaimed water. The Upper Occoquan Service Authority (UOSA) WRF discharges high quality reclaimed water into one of the principal tributaries to the reservoir, and increases the safe drinking water yield by supplementing natural streamflow. In addition, the WRF discharge contains high concentrations of nitrate, which have been shown to play an important role in managing the release of undesirable substances from the deposited sediments of the reservoir at a relatively low cost (OWML 2005). Research performed in previous years by the Occoquan Laboratory determined that there are water quality benefits

associated with discharging nitrate in the reclaimed water instead of removing it in the treatment works (Banchuen 2003, Randall and Grizzard 1995). Although nitrate application has been used as a lake management technique (Andersen 1982, Cooke et al. 2005, Ripl 1976, Senn and Hemond 2002), the use of a WRF-derived source is unique, and represents an innovative approach to water quality management.

The physical and biochemical characteristics of the Occoquan Reservoir favor denitrification in the hypolimnetic waters during anoxia, which is the main process in nitrogen removal. The physical properties are determined by the morphology of the reservoir. It has been previously noted that changes in the morphology of lakes and streams alter the different physical and biochemical processes that occur in them (Wetzel 2001). Thus, the unique shape of the reservoir, together with the seasonal high concentrations of nitrate that enter in streamflows are important in determining nitrogen retention in the impoundment. Because the unique use of wastewater-derived nitrate has been a key component of the successful management and water quality improvement in the Occoquan Reservoir, several questions have been raised about the unintended consequences of implementing wastewater treatment regulations, particularly with respect to nitrogen removal. Currently, point source nutrient control requirements mandate the UOSA WRF to remove total nitrogen (TN) to an annual average of 8 mg/L in the plant discharge at an annual average flow of 54 MGD (OWML 2005). Future management strategies have been proposed that will require the WRF to decrease the total nitrogen load to the reservoir, but the consequences of such actions remain unknown. Therefore, it seems prudent to fully assess the chemistry and biochemistry of the system prior to recommending or initiating any major changes in operating protocols.

1.4 Scope and objectives

This research project was designed to investigate the water quality effects of using nitrate as an alternate external electron acceptor in a deep water supply reservoir. The specific objective was to evaluate the consequences of using nitrate to prevent the release of nutrients and constituents from the sediments. The transport of nitrate along the length of the reservoir and the effects of the morphology of the reservoir on denitrification rates were also investigated. The final goal was to determine the capacity of the reservoir to store and consume nitrate, and to determine an

optimum concentration to use in a management strategy without allowing an excess amount in the reservoir overflow. The study also contributes to a better understanding of nutrient cycles and interactions at the water-sediment-microbe interface. Further knowledge of the biogeochemical processes that occur at the sediment-water interface is crucial in order to propose sustainable and effective management alternatives to address the cultural eutrophication of reservoirs and lakes.

The specific objectives of this research were to:

1. Study the effects of using nitrate as an alternate electron acceptor on the water quality of the Occoquan Reservoir.

2. Determine the optimum concentration of nitrate to minimize nutrient release from sediments in the area closest to the dam without exceeding any established nitrogen limit in the reservoir and its outlet flows.

3. Study the fate of nitrate in the Occoquan Reservoir from the WRF point of discharge to the area closest to the dam (drinking water intake) by observing the impact of changing water volume to sediment area ratio along the length of the reservoir.

4. Measure and estimate the denitrification rate coefficients (k) and mass transfer coefficients for denitrification along the length of the Occoquan Reservoir.

5. Investigate the effects on ammonium release from sediments of using nitrate as an alternate electron acceptor in the Occoquan Reservoir by:

    a. Determining rates of ammonium release from sediments under both aerobic and anaerobic environments.

    b. Determining the effects of the carbon to nitrogen ratio (C:N) on sediment ammonium release under both aerobic and anaerobic conditions.

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Chapter 2 - Investigation into the Effects of External Electron Acceptors from an Advanced Water Reclamation Plant on Sediment-Water Interactions in the Occoquan Reservoir

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2.1 Abstract

The Occoquan Reservoir is an artificial impoundment constructed to serve as a drinking water source for the suburbs of Washington D.C. in northern Virginia, USA. For over 30 years, the reservoir has been part of an indirect potable reuse system where an advanced water reclamation facility (WRF) discharges high quality reclaimed water into a major tributary, thereby increasing the drinking water safe yield by supplementing natural streamflow. In addition, the WRF is operated to either remove nitrogen or produce a nitrified discharge, which has been shown to play a role in managing the release of undesirable substances from the deposited sediments of the reservoir. Observations made *in situ* during periods of deep water anoxia, and in continuous flow microcosms constructed with similar water volume to surficial sediment area ratios as the reservoir, were used to study the effects of various nitrate concentrations on releases of selected constituents from the sediments.

Nitrate concentrations lower than 2 mg/L N entering the test microcosms were insufficient to prevent the onset of anaerobic conditions and the subsequent release of phosphorus, iron, and manganese from the deposited sediments. When initial concentrations of nitrate were increased, anaerobic conditions were delayed, and when inflow concentrations exceeded 5 mg/L as N,

anaerobic conditions were prevented, resulting in low concentrations of phosphorus, iron, and manganese in the water column, despite the absence of molecular oxygen. Results from field observations also suggested that maintaining a minimum concentration of approximately 2 mg/L N in the reservoir may considerably delay the release of phosphorus and organic matter to the water column. No correlation was found between the rate of ammonium release and the concentration of nitrate in the system. In fact, sediment ammonium release rates were similar for every inflow nitrate concentration, suggesting that the sediment ammonium release mechanisms were different from those for other constituents. However, correlations between ammonium release and organic matter, and between organic matter and nitrate at the sediment-water interface were found, suggesting a possible indirect relationship between sediment ammonium release and nitrate concentration in the water column.

Keywords: water reuse, nitrate, ammonium, iron, phosphorus, water volume-sediment area ratio

2.2 Introduction

Many lakes and reservoirs around the world are experiencing accelerated productivity (eutrophication) as a direct result of increased loadings of nutrients. Although the causes of eutrophication are complex and vary for different aquatic systems, it is well known that nutrient enrichment and decomposition of excess organic matter accelerates this process, and may result in deterioration of surface water quality (Wetzel 2001). Hypolimnetic anoxia in thermally stratified lakes and reservoirs occurs in productive systems during summer periods. The resulting hypoxic condition increases the release of nutrients from the sediments, including nitrogen and phosphorus. This nutrient source, often termed the internal loading, may be a substantial fraction of the total loading (Beutel et al. 2008a). An array of management approaches and technologies have been developed and applied for rehabilitation and remediation of degraded hypolimnetic oxygen resources, and for reducing the limiting nutrient loads. Most lake management efforts focus on reducing the external nitrogen and phosphorus loadings to the water bodies either by placing stringent regulations on wastewater treatment plant discharges or by controlling non-point sources. Although reduction of nitrogen is considered to be beneficial from a lake restoration perspective, there are some cases where nitrogen plays a role different

from that of a nutrient. For instance, nitrate which is in the oxidized form may contribute to the oxidation capacity of water (Hemond and Lin 2010).

A distinctive feature of the Occoquan Reservoir is that an advanced WRF discharges high quality reclaimed water to one of the main tributaries of the reservoir approximately 30 km upstream of the drinking water treatment plant raw water intake. This discharge supplements the natural streamflow of the watershed and serves to increase the safe drinking water yield of the system, especially during periods of low natural inflow to the reservoir. In addition, the WRP operations may be configured to alter the concentrations of nitrate discharged to the stream. During periods of thermal stratification in the reservoir, the WRP may be operated to provide high concentrations of nitrate in the reclaimed water. Research performed in previous years determined that there were more benefits than negative effects in the reservoir water quality when nitrate was not completely removed from the WRP discharge (OWML 2005, Randall and Grizzard 1995).

Many studies (Andersen 1982, Foy 1986, Mortimer 1941, Prestigiacomo et al. 2009, Ripl 1976) have shown that the presence of nitrate maintained a relatively high oxidation reduction potential (ORP) after dissolved oxygen (DO) had been depleted from anoxic hypolimnia of thermally stratified lakes. This phenomenon occurs when nitrate serves as an alternate terminal electron acceptor for certain microorganisms in the absence of molecular oxygen, providing an adequate amount of organic matter is present. Thus, nitrate may delay the onset of complete anaerobic conditions by poising the system ORP at a level that will prevent the reduction of Fe(III) to Fe(II) and sulfate (SO_4^{2-}) to sulfide S^{2-}, thereby preventing also the release of iron-bound phosphorus to solution. The causes of phosphorus release from sediments under anoxic conditions are numerous and complex, and have been principally attributed to the microbial reduction of iron (III) oxide complexes containing phosphates, resulting in the release of both ferrous iron and microbially available inorganic phosphate into solution (Beutel et al. 2008b, Golterman 2001). Elevated concentration of phosphate in the water column may contribute to the excessive production of autotrophs, especially algae and cyanobacteria (Correll 1998). Nitrate may have an influence on the cycling of other macronutrients, including ammonium, iron, sulfur, and manganese, and maintaining an adequate ORP level can prevent the release of

toxic substances such as mercury into the water column from the sediments (Effler and Matthews 2008).

In the case of the Occoquan Reservoir, where there is a continuous source of nitrate year-round, the effects on nutrient cycles are being studied in both field and microcosm investigations in this research work. Overall, the goal of the study is to have a better understanding of both the beneficial and negative effects that might occur when using nitrates as a reservoir management alternative during the period of thermal stratification. By dosing different concentrations of nitrate to manipulate the ORP level in lab-scaled reactors, the concentrations required to manage other nutrient concentrations at acceptable values may be determined.

2.3 Study area

The Occoquan Watershed, which is shown in Figure 2-1, is situated in the eastern U.S., on the southwestern periphery of the Virginia suburbs of Washington D.C. The watershed is formed by four headwater basins that drain to the Occoquan Reservoir. The watershed drains 1,530 km^2 and is about 54% forest land, 11% agricultural, pasture 7%, and 28% urban. The hydrologic characteristics of the watershed have been described elsewhere (Xu et al. 2007). In the southern part of the watershed, two of the headwater basins drain to Broad Run and Cedar Run which, together, form Occoquan Creek. In the northern part of the watershed, Cub Run basin drains into Bull Run. Occoquan Creek and Bull Run are the two main tributaries of the Reservoir. At the full pool elevation, the main body of the Reservoir extends from the high dam upstream to the confluence of Bull Run and Occoquan Creek. From there, it extends further upstream to station ST10 on the Occoquan Creek arm and to station ST40 on the Bull Run arm (Figure 2-1). The outflow from the Occoquan Reservoir discharges to an embayment of the tidal Potomac River, which is one of the principal sub-basins of the Chesapeake Bay Watershed. The physical characteristics of the reservoir are summarized in Table 2-1.

The Upper Occoquan Service Authority (UOSA) water reclamation facility (WRF) discharges into the Bull Run arm of the reservoir approximately 10 km upstream from the confluence of Bull Run and Occoquan River, as shown in Figure 2-1. The plant has the capacity for biological nitrogen removal (nitrification/denitrification), or to discharge a completely nitrified product water. During the periods where there is no thermal stratification in the reservoir and most of the

water column is fully oxygenated, UOSA operates to remove nitrogen in order to assure a low nitrogen concentration in the final discharge. Following the establishment of the thermal stratification in early summer, and the subsequent period of hypoxia in the hypolimnion, the UOSA WRF is operated to provide a nitrified discharge that can be used to delay the onset of anaerobic conditions in the reservoir.

2.4 Materials and methods

2.4.1 Monitoring data

This study focused on reservoir water quality in the reach just upstream of the main raw drinking water intake which is denoted as section 1 (Figure 2-2). Water quality data from the Occoquan Watershed Monitoring Laboratory (OWML) database obtained from a field sampling at station RE02 was used to describe the water quality characteristics for section 1. Field sampling in the reservoir is conducted weekly for most of the year by OWML staff. For this study, data from the years 2004, 2006, and 2007 were used to demonstrate the effects of different concentrations of nitrate on the water quality of the reservoir. To represent periods of thermal stratification and hypoxia, the data used were obtained from the period ranging from mid April to early October for each year.

2.4.2 Effective depth concept

The morphological characteristics of the Occoquan Reservoir cause a gradual change in the ratio of the surficial sediment layer in contact with the overlying volume of water along the length of the reservoir. In the Reservoir, when moving downstream from the riverine zone (i.e. from Bull Run or the upper reaches of the reservoir) to the lacustrine zone (downstream in the reservoir and closer to the dam) there is an increase in the water volume overlying a specific sediment area. Previous research had concluded that nutrient flux rates are affected by both the exposed area of the sediment and the volume of water in contact with the exposed sediment (OWML 2005, Yung 1990). Banchuen (2003) observed that denitrification rates increased when the sediment surface area under a fixed volume of water increased. In the present study, water volume to sediment area ratio was used to replicate corresponding segments of the reservoir in laboratory scale models. This was done to minimize the effects on nutrient release and depletion rates caused by

having a variable sediment area underlying a specific water volume in the reservoir. The water volume to sediment area ratio was defined as the effective depth (ED) (Birgand et al. 2007).

2.4.3 Experimental setup

Using the ED value (Z_{ED}) as the key parameter for designing the bench-scale experiments, key descriptive parameters for the full-scale system were used to configure a microcosm simulation of Reservoir Section 1 (Table 2-2). The Z_{ED} was obtained by dividing the segment hypolimnion volume by the associated sediment area. The physical characteristics for section 1 of the reservoir were obtained from a bathymetric survey described in OWML (2006) and the data were analyzed using the ESRI ArcGIS Desktop® 9.3 software. Because the Z_{ED} is a volume:area ratio, the exposed sediment area and the water volume in the microcosms may be manipulated to provide the same Z_{ED} as the full scale reservoir section. The summer base flow was obtained by averaging the total inflow during the summer months, and eliminating high flows events that were produced by storms for the years being considered.

Three continuous flow laboratory-scale reactors were operated in parallel for a period of 90 days in an effort to simulate an entire thermally-stratified summer season in the reservoir. The reactors were Plexiglas cylinders with a maximum capacity of approximately 11 liters and were sealed to the atmosphere to sustain an anoxic environment. Adequate mixing was achieved by using a paddle connected to a variable speed motor and by installing baffles that prevented vortex formation and subsequent sediment resuspension.

Sediment samples used in each reactor were taken from sampling station RE02 in mid-April, 2008, using an Ekman dredge. The recovered sediment samples were placed in glass bottles and stored over ice in insulated coolers until transported to the laboratory. Once at the laboratory, the sediments were stored at 4°C until sample preparation. Two 20 mL beakers were used in this experiment to hold the sediments and to give a total exposed sediment area of approximately 10.5 cm². This area, as may be seen in Table 2-2, was required in order to produce a Z_{ED} of 9.5 m. The water used to fill the reactors was collected from station RE02, which had a low concentration of nitrate + nitrite (OxN). Fully nitrified discharge waters from the UOSA WRF were mixed with the reservoir waters in ratios computed to achieve the desired initial concentrations of OxN in each reactor. Reactors 1, 2 and 3 were adjusted to initial OxN

concentrations of 2, 5, and 8 mg/L as N, respectively, at an initial volume of 10 liters. Adjustable flow peristaltic pumps were used to deliver water to each reactor at a flow rate required to achieve a retention time of 13 days (Table 2-2). The reactors were placed in a temperature controlled room adjusted to 20°C and were covered to prevent algae growth due to penetration of ambient light.

2.4.4 Analytical

A HACH® LDO1-01 probe and a PHC101-01 probe were used to measure DO and pH, respectively, using a HACH® HQ40d dual – input multimeter. ORP was measured using a HACH® ORP Sension Gel – filled electrode probe using a HACH® HQ20 multimeter. Redox potential values were corrected by referencing them to the potential of the standard hydrogen electrode at pH 7 and 25°C. Water samples were taken using a syringe, filtered, and preserved when necessary either by acid addition or by freezing the samples. Oxidized nitrogen (NO_3^- + NO_2^-) (4500-NO_3-F), ammonia nitrogen (4500-NH_3 G), total nitrogen and total phosphorus (4500-P-J), Orthophosphate (4500-P-F), Chemical Oxygen Demand (COD), and total and dissolved organic content (5310C) were analyzed in accordance with Standard Methods (AWWA et al. 2005). Iron (Fe) and Manganese (Mn) samples were preserved with nitric acid and concentrations measured using inductively coupled plasma mass spectrometry (ICP-MS) (AWWA et al. 2005).

2.5 Results and Discussion

2.5.1 Water Reuse

Occoquan creek, as seen in Figure 2-1, drains the larger of the two principal sub-basins of the watershed (880 km^2), and during periods of high rainfall it contributes most of the inflow to the reservoir. Bull Run, which has a much smaller drainage area (470.3 km^2), receives the reclaimed water discharge from the UOSA WRF throughout the year. As a consequence, Bull Run may be expected to exhibit a sustained base flow during periods of low precipitation in the watershed.

Figure 2-3 shows a typical inflow distribution to the reservoir for a time period characterized by extended periods of low precipitation. During the season, most of the inflow to the mainstem of the reservoir originated in the Bull Run arm, which includes the discharge from the UOSA WRF.

From July to September, more than 50% of the water entering the reservoir originated from UOSA, thereby demonstrating the importance of the reclaimed water supplement to the water supply yield, especially during periods of low precipitation. After the month of October, when precipitation increased, the inflow distribution gradually changed, and by January, Occoquan creek became the major contributor of water to the reservoir.

 The summer flow dominance by the UOSA WRF discharge is very important from a water quality perspective. Since beginning operation in the late 1970s, the UOSA WRF has discharged very high quality reclaimed water to the Occoquan Reservoir, and the input of at least one constituent, nitrate, has had the unusual effect of actually improving and protecting water quality in the Occoquan Reservoir (Randall and Grizzard 1995). Figure 2-4 shows the distribution of flow-weighted nitrogen loads to the reservoir for 2006 – 2009 represented by species and source. This figure shows that OxN was the most abundant form of nitrogen entering the reservoir, and essentially all of the OxN was in the form of nitrate (NO_3^-), with very little nitrite (NO_2^-) (OWML 2005). The WRF contributed over half of the OxN entering the reservoir, while the remaining amount originated in the Occoquan Creek and Bull Run. In terms of total nitrogen (TN) entering the reservoir, almost half of it originated from the UOSA WRF. Bull Run, although it drains a smaller area than Occoquan Creek, was the second greatest source of OxN and TN to the reservoir. The loads for Bull Run were higher due to the more urban character of the watershed. The resulting increases in impervious surfaces and managed green space contributed to higher nonpoint source and urban runoff nutrient loads (Dougherty et al. 2006). This was not the case for ammonium, which was found to be slightly higher for the less developed Occoquan Creek sub-watershed. The contribution of ammonium to the reservoir from the UOSA WRF was negligible compared to other sources.

One of the distinguishing features of the Occoquan Reservoir is its capability to 'consume' most of the nitrate that enters the system. Periods of low hypolimnetic oxygen concentrations and high productivity favor the biological denitrification process, the main mechanism proposed to explain nitrate depletion in the reservoir (Randall and Grizzard 1995). Figure 2-5 shows seasonal average time series plots for OxN concentrations in the inflows and outflow (ST01) of the Occoquan Reservoir for the period of record. During the winter season, UOSA produced a low OxN discharge with an average concentration of less than 5 mg/L N. This was done to

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maintain a low TN concentration in the reservoir when denitrification was low. During the summer months, UOSA operationally increased the OxN concentration in the reclaimed water discharge to compensate for the rapid loss of OxN and to assure a minimum residual concentration of nitrate in the reservoir. Although the OxN concentration occasionally increased to values greater than 10 mg/L N at ST40, the concentrations measured at the dam (ST01) remained low, and never exceeded 2 mg/L N, during the period illustrated.

2.5.2 Reservoir water quality data

The Occoquan Reservoir, like most deep reservoirs in temperate climates, undergoes an annual thermal stratification. During the period of thermal isolation of the hypolimnion from the atmosphere, and in the absence of other available inorganic electron acceptors, respiratory loss of oxygen in the hypolimnion is rapidly followed by the establishment of anaerobic conditions. Such conditions have been long known to promote the release of undesirable substances from deposited sediments in lakes and reservoirs (Mortimer 1941). The addition of nitrate to oxygen-depleted waters to produce an oxidized environment over deposited sediments has been previously proposed by several investigators as a lake and reservoir restoration technique (Andersen 1982, Ripl 1976). The management strategy based on the use of nitrate as a terminal electron acceptor in the hypolimnetic waters of the Occoquan Reservoir is unique because of the derivation from reclaimed wastewater. To illustrate the effects of nitrate in the bottom waters of the Occoquan Reservoir, subsets of data from the deep water station upstream of the Occoquan High Dam (RE02) were extracted. The data were selected from the same time period previously described when the reservoir was thermally stratified and anoxic conditions had begun to develop.

The time series shown for 2004 in Figure 2-6a depicts a year when OxN was present in the hypolimnion of the reservoir for most of the summer, even during the periods of DO depletion. The average OxN concentration from May – September was 1.1 mg/L N. This concentration of OxN proved to be sufficient to maintain a relatively oxidized environment which, in turn, reduced phosphorus release from the deposited sediments. The average concentrations for OP and TSP for the period were 0.01 and 0.02 mg/L P, respectively, which (in both cases) was almost one order of magnitude lower than for 2006 and 2007. This observation was in agreement with previous authors who have suggested that 1.0 mg/L N of nitrate was sufficient to

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prevent phosphorus release from sediments (Andersen 1982), and with others that found that NO_3^- concentrations above 0.5 mg/L N promoted phosphorus sorption in sediments (Søndergaard et al. 2000). The phenomenon occurs because, in the absence of molecular oxygen, nitrate is used as an alternate electron acceptor by certain bacteria to harness the energy released in the oxidation of reduced carbon to CO_2. Concomitantly, the NO_3^- is reduced to N_2, following the sequence of microbially mediated redox processes based on thermodynamics constraints (Arango et al. 2007, Madigan et al. 2003). When this happens, it poises the ORP at a sufficiently high level to retard the reduction of Fe(III), and prevents the release of iron bound phosphorus from the sediments (Moore and Reddy 1994, Stumm and Morgan 1996). It should also be noted that the process removes the reduced nitrogen from the system in the gaseous form, thereby simultaneously achieving an algal nutrient control objective.

During naturally occurring periods of anoxia, substantial release of stored phosphorus from the bottom sediments occurred. Figure 2-6b shows that after both DO and OxN were depleted from the water column in 2006, phosphorus began to appear. The peak concentration of TSP was approximately 0.9 mg/L. Phosphorus concentrations measured as orthophosphate (OP) and total soluble phosphorus (TSP) were approximately equal and were released at similar rates, suggesting that most of the TSP measured was OP. For TSP, a similar case was observed in the following year, with the exception that there was a difference in the relative concentrations of OP and TSP in the water column after the month of July. Figure 2-6c shows that in 2007, immediately after DO and nitrate were depleted from the water column above the water-sediment interface, both OP and TSP were released from sediments at similar rates. Approximately two months after phosphorus began to appear in the hypolimnetic water column, the concentration of OP began to decline until it stabilized at a value of approximately 0.1 mg/L P, which remained constant for the remainder of the anoxic period, with the exception of some peaks that appeared during the month of October.

During 2006, most of the phosphorus measured in the water column was in the form of OP. This form of phosphorus, as suggested by many authors, is believed to be largely iron-bound, and released to the water column when iron is reduced to Fe(II) due to low ORP conditions in the water-sediment interface (Moore and Reddy 1994, Wauer et al. 2005, Weston et al. 2005). However, during 2007, the concentration of OP differed from TSP through most of the summer.

For 2007, the period of truly anaerobic conditions was longer than the previous year because nitrates were completely depleted from the deep waters two months earlier than in 2006. At the beginning of the anaerobic period for 2007, and until the month of August, the mechanisms of sediment phosphorus release were similar to those for 2006, but as the anaerobic period extended, the mechanisms of phosphorus release appeared to change. It is thought that during extended periods of anaerobic conditions at the sediment-water interface, bacterial populations may shift to alternate metabolic pathways, including anaerobic fermentation. When fermentation occurs, some of the organic matter present will remain as fatty acids and similar organic compounds. Therefore, bacteria need to ferment a larger part of the organic matter in order to get the same amount of energy which results in phosphorus release (Golterman 2001). Phosphorus released as a result of fermentation processes taking place within the sediments is principally in the form of organic-P. Ahlgren (2011) also concluded that phosphorus release under anaerobic conditions is also a result of mineralization of polyphosphates or iron associated organic compounds. The release of phosphorus observed during extended periods of anoxia, which is shown as an increase in the TSP concentration (Figure 2-6c), may be related to the incremental change in organic matter (OM), measured as TOC (Figure 2-7), suggesting that most of the phosphorus released was in the form of organic-P. The rapid decrease in OP observed in the anoxic period of 2007 may be the results of phosphorus uptake by microorganisms or algae present in the water column above the water-sediment interface. Although the relationship between the increase in TSP and OM can explain the gap that exists between the OP and the TSP, more experimental evidence is needed to support this speculation.

Figure 2-7 shows a time series for DO, OxN, ammonium, and organic matter measured as TOC for the previously discussed years. When DO concentrations began to decline, increases in NH_4^+ concentrations were observed in the water column, with the likely source being the sediments. Initially, when OxN was still present, ammonium concentrations rose to about 1 mg/L as N, but after depletion of OxN, the ammonium concentration in the water column increased rapidly, ultimately reaching a peak value of over 4 mg/L as N for the years 2006 and 2007. In the summer of 2004, when nitrate was always present in the bottom waters of the reservoir, the ammonium concentration was less than in the other two years. These observations suggest that the presence of nitrate affected the ammonium concentration. The observed data also suggest

that the presence of OxN did not completely prevent the release of ammonium from the sediments, but did serve to keep the concentrations low in the water column.

Figure 2-7 also shows that for all years illustrated, during periods of anoxia, there was an increase in the amount of organic matter in the water column. It appears, at least from the available data, that the source was release from the sediments. The average TOC concentrations for the aerobic period (January – May) anteceding the anoxic period for 2007, 2006 and 2004 were 4.4, 3.6, and 3.4 mg/L, respectively. Inspection of the figure will also show that for the years where both DO and OxN were depleted, the concentration of OM increased up to 3 times its original value. For the year 2004, where nitrate was continuously present in the bottom waters of the reservoir, the TOC increase was less and the average concentration was lower than for the other two years. During the years of nitrate depletion, a strong correlation was observed between the TOC and ammonium concentrations measured in the waters above the sediment-water interface ($R^2 = 0.67$, n = 30 and $R^2 = 0.86$, n = 25 for 2007 and 2006, respectively). For 2004, when nitrate was not depleted, no significant correlation was found ($R^2 = 0.10$, n = 23). This correlation suggests that the mechanisms governing sediment release of ammonium and organic matter may be interrelated during periods of anoxia.

It is possible that the increase in TOC could be due to a reduction in organic matter consumption by microorganisms as a result of the reducing environment present during extended periods of anoxia. When molecular oxygen is not present and alternate electron acceptors are used, microbial growth rates and cell yields are lower (Madigan et al. 2003, Stumm and Morgan 1996) and may directly impact organic carbon depletion rates by causing the excess OM produced in the sediments to be released into the water column. Alternatively, the increase in TOC may be the result of organic byproducts released from fermentation processes during extended anaerobic periods within the sediments and released to the water column as was also reflected by the increment in TSP. Further investigation is needed to better determine the processes involved in sediment OM release.

2.5.3 Microcosm studies

Laboratory experiments were divided into two phases. The first phase was designed to measure nitrate depletion rates, and to observe and quantify the effects of both oxygen and nitrate

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depletion at the sediment-water interface using sediments from section 1 of the Occoquan Reservoir. Three reactors with a Z_{ED} of 9.5 m and an initial concentration of 2, 5, and 8 mg/L OxN were operated in a continuously mixed batch mode until all OxN was depleted. The second phase of the experiment began at day 45, when anaerobic conditions had been established in all reactors. Once this condition was achieved, a continuous flow containing a concentration of OxN equal to the initial value was pumped through each reactor. The flow was adjusted to achieve a retention time of 13 days, which is an approximation of the full-scale residence time in the hypolimnetic waters of section 1 of the reservoir during the summer stratification period. This phase was designed to observe the effects of introducing nitrate back into the system and to observe the OxN removal efficiency in reactors with different feed water concentrations. The objective was to determine the highest concentration of nitrate that each system could deplete without having an excess amount of nitrate in the discharge. With knowledge of the depletion rates, it should be possible to predict the concentration of nitrate that could be introduced into section 1 without producing an excess amount of nitrogen in the outflow of the reservoir. The initial DO concentration for all of the three reactors was equal at the start of the experiment and declined from approximately 9.8 mg/L to less than 0.1 mg/L after day 11, and fluctuated around this value for the rest of the study. The average DO concentration for the reactors having 2, 5 and 8 mg/L of OxN was 0.10, 0.19, and 0.17 mg/L, respectively. A comparison of means revealed that there was no statistically significant difference between the values (p value = 0.55). This suggests that the DO concentrations did not influence the outcomes.

Figure 2-8 shows a time series for all the parameters measured in each reactor for the duration of the experiment. From Figure 2-8a, it may be seen how the OxN concentration for each reactor decreased over time during the first part of the experiment. OxN in the reactors having initial concentrations of 2 and 5 mg/L was depleted after day 15 and day 30, respectively. However, OxN was never completely depleted during the 45 day period from the reactor having the 8 mg/L initial concentration. During the second part of the experiment, OxN was observed to gradually increase as it was introduced back to each reactor until approximately steady-state conditions, with respect to nitrate, were reached towards the end of the experiment. The average OxN concentrations in the water column for reactors 1, 2 and 3 during the second part of the experiment were 0.16, 0.75, and 1.92 mg/L N, respectively, and the values were found to be statistically different from each other ($P < 0.05$). These results suggest that the laboratory-scaled

representation of section 1 of the reservoir was able to eliminate most of the OxN in the water column when the input concentration was lower than 5 mg/L N with a retention time of 13 days for the selected Z_{ED}. However, when the initial OxN concentration was increased to 8 mg/L N, the removal efficiency was reduced from values as high as 90% to about 75% of the influent values. This result suggests that when section 1 of the reservoir is under thermal stratification and anoxic, it may deplete an input nitrate concentration of up to 5 mg/L N. Table 2-3 show OxN depletion rates for the first phase of the experiment. It may be seen that the rates were different for each reactor. As expected, and as some authors suggest, the rates of denitrification were found to increase as the input concentration of nitrate was increased (Arango et al. 2008, Arango et al. 2007). Although the rate for denitrification increased for reactor three, it was not high enough to deplete the entire influent nitrate load.

The initial OP concentration for the three reactors was approximately 0.02 mg/L and rapidly decreased to very low values by the fourth day of the experiment. In the first part of the experiment, when nitrate depletion was taking place, OP concentrations were low in each reactor, and remained so until OxN was totally depleted from the first and second reactor (Figure 2-8b). OP concentrations began to increase in reactor 1 a few days after all OxN had been depleted and peaked at a maximum value of 0.07 mg/L at day 45. The same pattern was observed in reactor 2 where OP increased to 0.025 mg/L a few days after all OxN was consumed. After OxN was introduced back to reactor 1, the OP concentration decreased until it reached a value of approximately 0.04 mg/L. A similar situation was observed for reactor two. When OxN was introduced back to the system the release of OP ceased and the concentration declined to an average value of 0.025 mg/L. The OP concentration for the reactor fed with the highest feedwater OxN concentration (reactor 3) was observed to be very low and essentially constant for the duration of the experiment. This occurred because the OxN concentration in reactor 3 never decreased below 1.0 mg/L N, and was sufficient to poise the oxidation-reduction potential at a value sufficiently high to prevent the reduction of Fe(III) and prevent the subsequent release of iron bound phosphorus to the water column.

The average OP concentrations from day 50 - 90 for reactors 1, 2 and 3 were 0.041, 0.025, 0.008 mg/L P, respectively. A statistical analysis on the OP means revealed that there was a significant difference between these values ($P < 0.05$, $n = 14$). It was evident from the results that

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maintaining different values of OxN resulted in different concentrations of OP in the water column, with higher OxN concentrations producing lower OP concentrations. It is possible that the higher concentration of OxN helped diffuse nitrate deeper into the sediment, thereby increasing the oxidized layer thickness in the sediments and decreasing phosphorus release. Foy (1986) observed that in sediment core incubations, the onset of phosphorus release became progressively delayed as nitrate input increased. Figure 2-8c shows that TSP followed a trend similar to that observed for OP. During the first part of the experiment, TSP increased in reactors 1 and 2 as soon as nitrate was depleted, but did not increase for the reactor that had the highest initial amount of OxN. The average TSP concentrations from day 50 - 90 for reactors 1, 2, and 3 were 0.055, 0.032, and 0.012 mg/L, respectively, and there was a statistically significant difference between the values ($P < 0.05$). The similarity in the trends and the concentrations between OP and TSP for each reactor suggests that most of the total soluble phosphorus measured was in the form of OP. These results were similar to the field observations during the year 2006 where most of the TSP released from the sediment was composed of OP. This similarity also suggests that the duration of the anaerobic period in the reactors was not long enough to establish an environment that would have allowed the development of an observable difference between the concentrations of OP and TSP as the one observed in the reservoir during the summer of 2007.

Total soluble iron and manganese were also measured during the microcosm experiments, and the results are shown in Figures 2-8d and e. Iron appeared in the water column first in reactor 1 and later in reactor 2, and in both cases iron was released from the sediments immediately after OxN was depleted from the system. The depletion of nitrate caused the ORP to decrease to a point where Mn(II) and Fe(II) releases began, and the concentrations of the two metals increased to maxima just prior to the reintroduction of OxN during the continuous flow phase. Iron and manganese releases of this type have been explained as resulting from microbial and chemical reduction of metal oxides due to the reduced environment (Beutel et al. 2008b, Effler and Matthews 2008). When OxN was introduced back to the reactors, Fe concentrations began to decline in both reactors, but at different rates. The higher feedwater concentration of OxN in reactor 2 resulted in a more rapid increase in the water column ORP, which reduced the concentration of sediment iron more rapidly than in reactor 1. For the duration of the

experiment, the OxN concentration in reactor 3 always remained higher than 1 mg/L N, which proved sufficient to maintain a system ORP that prevented the release of iron (Figure 2-8d).

Phosphorus accumulation in the water column was a result of the reduction of phosphate-binding Fe oxides which promoted the diffusion of Fe(II) and phosphate from sediments. To illustrate this effect, a regression analysis was conducted between the paired OP and soluble Fe data for the reactor having the lowest concentration of OxN (reactor 1) from day 5 to day 75. The results show that there was a positive correlation between iron and OP for this period of time ($R^2 = 0.63$, $n = 11$). However, by the end of the experiment, OP concentrations were still detected in reactor 1, although most of the iron was eliminated before reaching day 90. This result suggested that by the end of the experimental run, there were additional mechanisms involved in phosphorus release than those related to iron reduction.

Figure 2-8e shows that the concentration of manganese began to increase when denitrification was taking place in all reactors. This is consistent with the findings of some authors who have suggested that Mn(IV) is reduced at higher ORP values than Fe(III) (Beutel et al. 2008b). Therefore, some manganese might be released in the presence of nitrate because manganese reduction occurs at a similar ORP value as nitrate reduction (Foy 1986, Stumm and Morgan 1996). Concentrations of Mn continued to increase and reached peak values of approximately 0.5 mg/L for reactor 1 and 2 after OxN was completely depleted. However, the maximum manganese concentration observed for the reactor having the highest concentration of OxN was lower than in the other two reactors. Manganese release was also observed to stop after OxN was reintroduced to the reactors during the continuous flow phase of the experiment, and decrease in all reactors toward the end of the experiment.

Sediment ammonium release was also observed in a similar manner for all three reactors, as shown in Figure 2-8f. After day 20, ammonium began to appear in the water column but decreased rapidly after approximately day 30. It is possible that the decrease in ammonium concentration was caused by assimilation of NH_4^+ or possibly by another mechanism such as anaerobic ammonium oxidation. Some studies have shown that ammonium is frequently used as the first choice for nitrogen for bacterial growth (Arango et al. 2008, Kemp and Dodds 2002). After day 35, prior to the start of the second phase of the experiment, and also during the second

phase when OxN was reintroduced to each reactor, ammonium release continued and the water column concentrations increased. The ammonium release rates were similar for all three reactors (Table 2-3) and although NH_4^+ concentrations were observed to be lowest in reactor 3 (which had OxN present for the entire experiment), there was no strong evidence suggesting that nitrate had a direct effect on ammonium release. Nitrate did not appear to delay the release of ammonium as it did with phosphorus, iron and manganese, and different concentrations of OxN in the water column did not appear to affect the amount or rate at which ammonium was released. Similar results were observed in studies by others who have concluded that nitrate does not influence sediment ammonium release (Beutel et al. 2008a, Martinova 1993). The mechanisms that govern ammonium release from sediment are complex and are not fully understood, and the lack of a mechanistic understanding continues to promote uncertainty regarding sources.   The literature remains divided with views that ammonium release is mainly governed by mineralization of organic matter found in sediments (Baldwin and Williams 2007) or that its accumulation is due to assimilatory or dissimilatory processes (Arango et al. 2008).

Experimental results showed a different trend for ammonium and organic matter release than for the field observations made during the year 2006 and 2007 (Figure 2-7b and c). Microcosm study results showed that there was an inverse relationship between the ammonium concentration and the measured COD. Figure 2-8g shows that a peak in COD concentration was achieved around day 30 in all reactors, and coincided with the decrease in ammonium concentration observed after day 25. When OxN was introduced back in each reactor during the second part of the experiment, COD concentrations declined in all reactors as OM was used for denitrification. The decrease in COD was accompanied by an increase in the ammonium concentration that continued until the end of the experiment. After day 20, there was a relatively high concentration of ammonium in the water column when the COD concentration was low. If this is always the case, then it is still possible that there is an indirect effect on ammonium release created by the presence of nitrate and OM. However, as was explained earlier, in the reservoir during the summer of 2006 and 2007 there was a positive correlation between ammonium and OM measured as TOC in the water column. The difference in these two trends cannot be explained with the existing data, but it may be attributed to differences between the environments that prevailed in the reactors and in the reservoir.

The previously described results may also be compared and related to changes in ORP (Figure 2-8h) caused by the dynamics of nitrate behavior in the microcosm experiments. ORP was clearly affected by the amount of nitrate present in each reactor after DO was depleted. ORP decreased at a higher rate and to a lower value in the reactor that had the lowest concentration of OxN. In reactor 3, however, a minimum concentration of 1 mg/L N was found to poise the ORP at a value no less than 300 mV, which is the point where manganese release may be expected from reduction of Mn(IV) to Mn(II) (Stumm and Morgan 1996). After day 45, the reintroduction of OxN in the feedwater gradually increased the ORP to a relatively oxidized environment and reduced the release of phosphorus, iron and manganese from the sediments.

2.6 Conclusions

Flows from the UOSA WRF have served as a significant supplement to the safe drinking water supply yield of the Occoquan Reservoir, and there has been a clear recognition of the beneficial effects of nitrate discharge on water quality in the Occoquan Reservoir. When low DO conditions prevail in the reservoir hypolimnion, authorities managing the reservoir can take advantage of the benefits from the use of nitrate as an alternate electron acceptor at a relatively low cost. Results from both field and microcosm studies suggest that lowering the oxidized nitrogen concentrations from the UOSA WRF discharge may result in unwanted increases in the phosphorus, iron, and manganese released to the water column, thereby causing water treatment problems during the summer months. It was also observed that sediment ammonium release was not directly affected by the presence of OxN at the sediment-water interface. It appears that ammonium release was determined by poorly understood mechanisms that varied according to the different environments that exist in the reservoir. In addition to providing a mechanism to maintain oxidizing conditions in the reservoir, the nitrate itself was removed during the process, mostly via denitrification. Experimental results showed that section 1 of the reservoir, under the conditions studied, can deplete an inflow concentration up to 5 mg/L of OxN. Finally, the use of nitrate may prove to be a good management option for lakes and reservoirs that are subject to extended periods of hypoxia.

2.7 Acknowledgements

2.8 References

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Table 2-1. Summary of Occoquan Reservoir characteristics

Parameter	Value
Volume at maximum pool elevation	31.4×10^6 m^3
Surface Area	6.23 km^2
Mean depth	5.1 m
Maximum depth	20 m
Maximum pool elevation above sea level	37.2 m
Hydraulic residence time[a]	19.6 days
Safe yield including WRF discharge	2.5×10^5 m^3/day

Note: adapted from Xu et al. (2007)

[a] HRT based on a yearly average flow of 1.6×10^6 m^3/day which includes UOSA WRF daily discharge

Table 2-2. Parameters simulated in microcosm studies for section 1 of the Reservoir

Parameter	Occoquan Reservoir Section 1	Reactor with fixed volume
Surface Sediment Area	5.75×10^5 m^2	10.5 cm^2
Hypolimnion Volume	5.47×10^6 m^3	**10 L**
Effective Depth	9.5 m	9.5 m
Hydraulic Retention Time	13 day	13 day
Base Flow	4.9 m^3/seg	0.77 L/day

Table 2-3. Denitrification rates for the first part of the experiment and sediment ammonium release rates in mg/m^2·d

Initial OxN	OxN	NH$_4^+$
R1 = 2 mg/L	0.82	0.10
R2 = 5 mg/L	1.35	0.12
R3 = 8 mg/L	1.47	0.09

Figure 2-1. Occoquan Watershed and reservoir
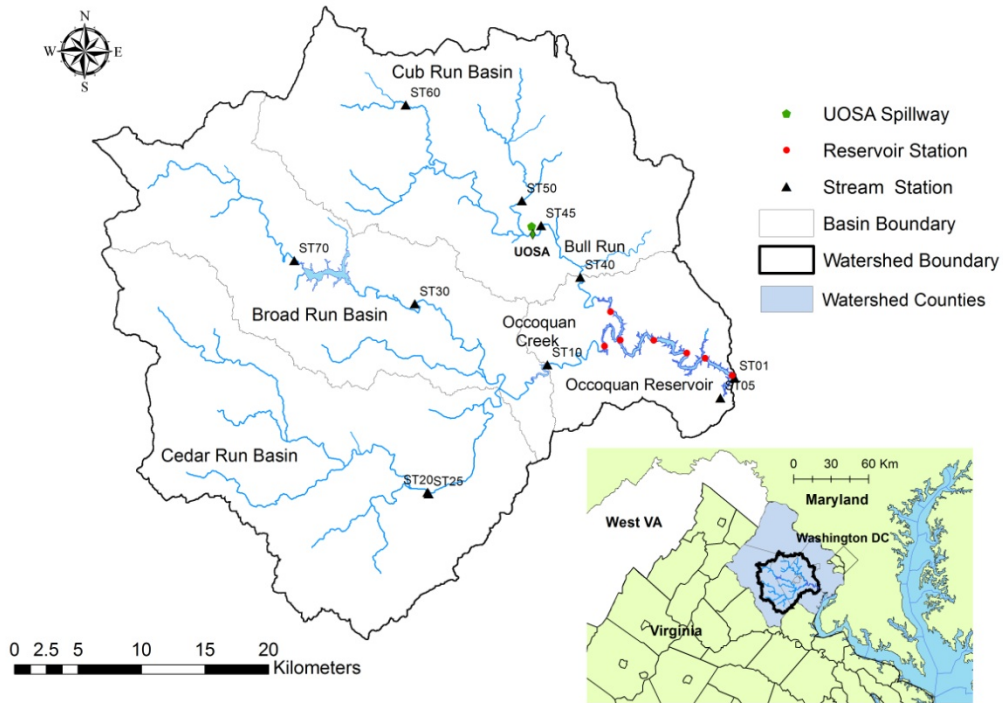
Figure 2-2. Occoquan Reservoir and sampling stations
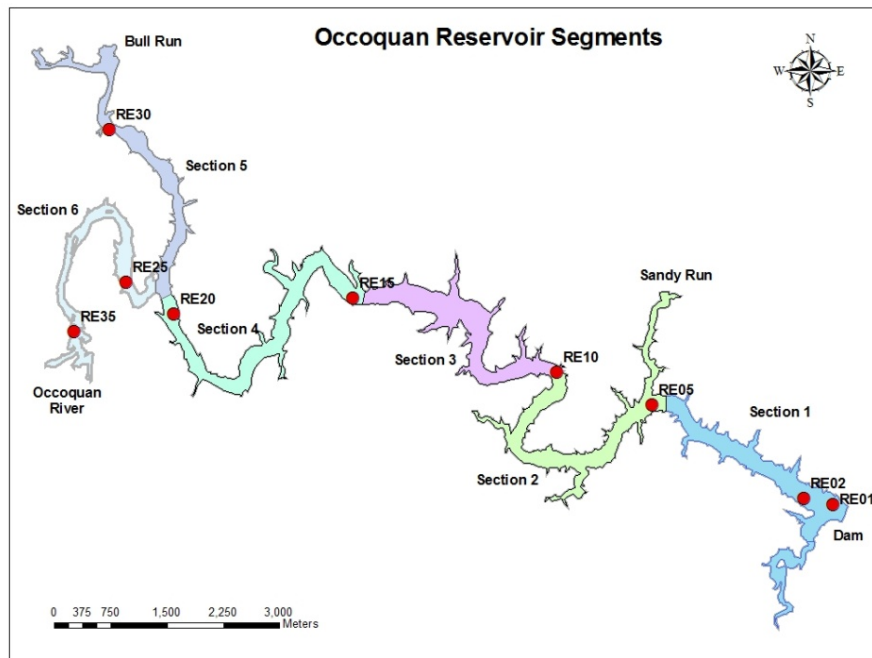
Figure 2-3. Monthly inflow distribution to the Occoquan Reservoir from May 2007 to April 2008.
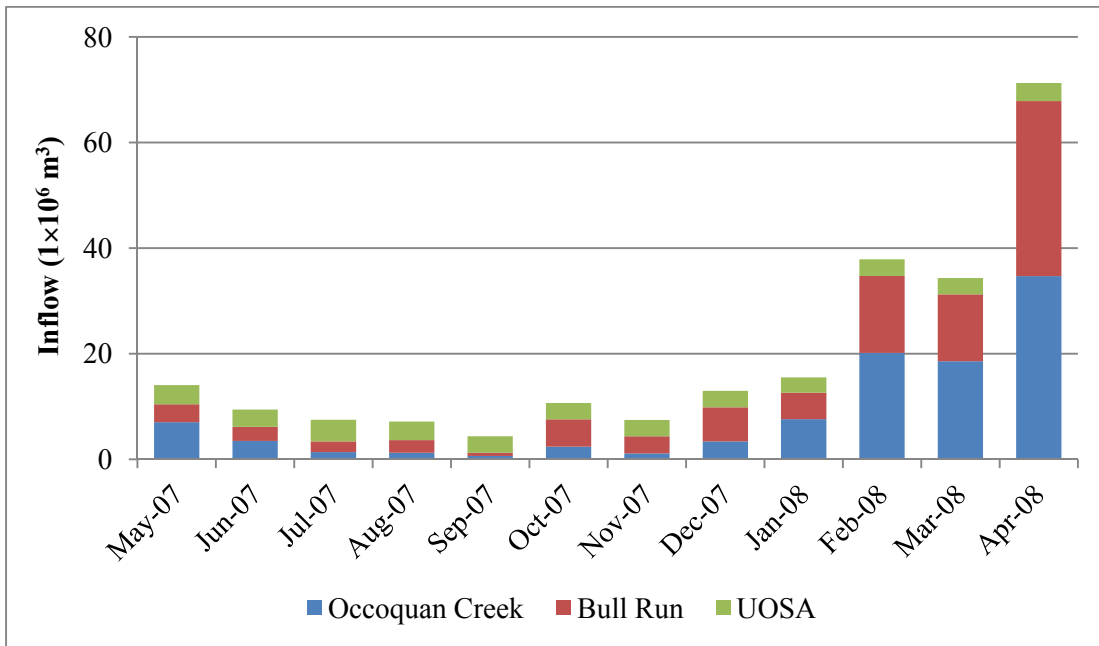
Figure 2-4. Flow-weighted nitrogen loads for 2006 -2009 by species and source. NH_4^+ concentration in 1×10^{-1} mg/L-N.
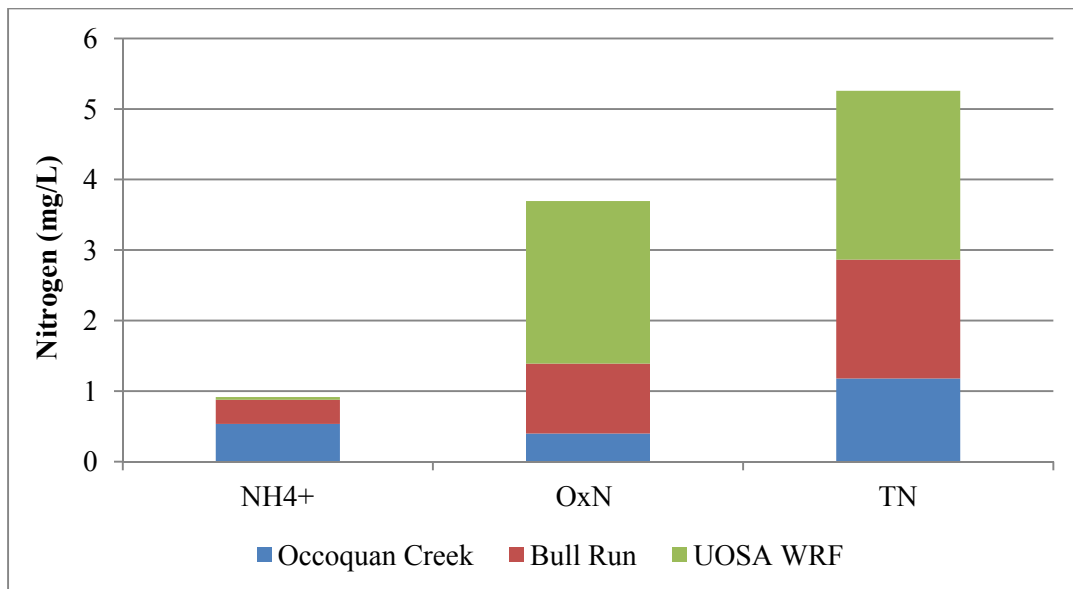
Figure 2-5. Monthly average OxN concentration in flows entering and leaving the Occoquan Reservoir.
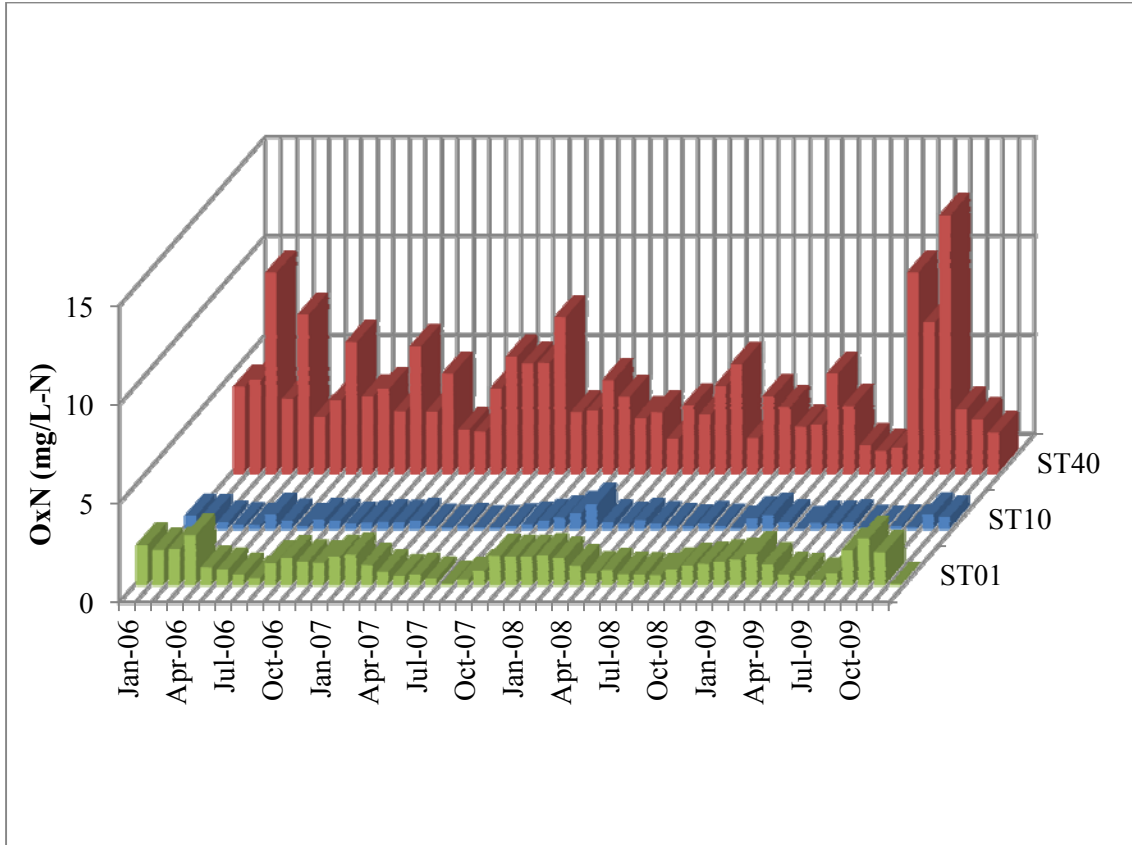
Figure 2-6. Time series for DO, OxN, OP, and TSP in hypolimentic waters at the Occoquan Dam (RE02) for (a) 2004, (b) 2006, and (c) 2007.
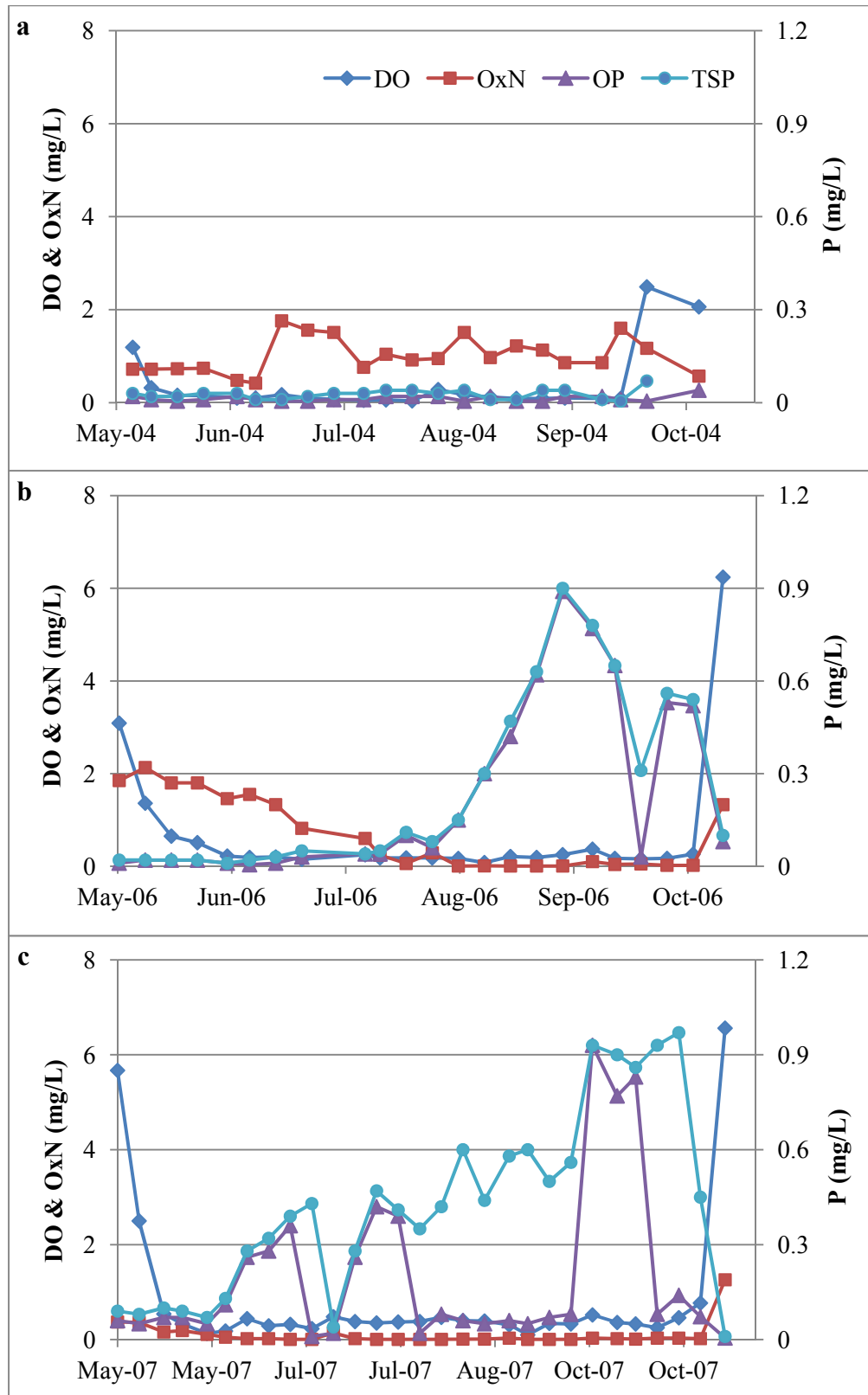
Figure 2-7. Time series for DO, OxN, NH_4^+, and TOC in hypolimnetic waters at the Occoquan Dam for (a) 2004, (b) 2006, and (c) 2007.
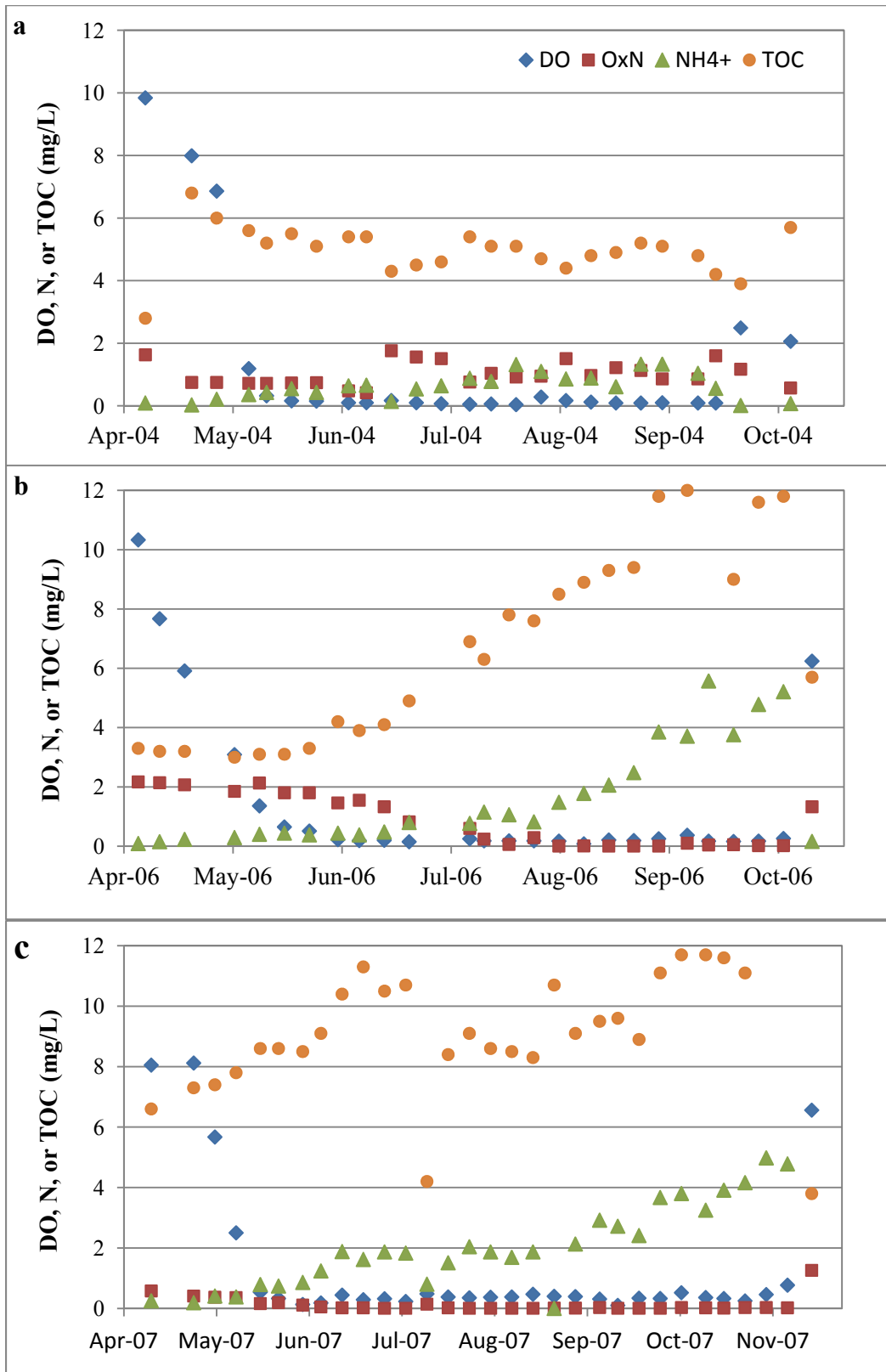
Figure 2-8. Time series for OxN, NH$_4^+$, phosphorus, Fe, Mn, OM and ORP for microcosm study.
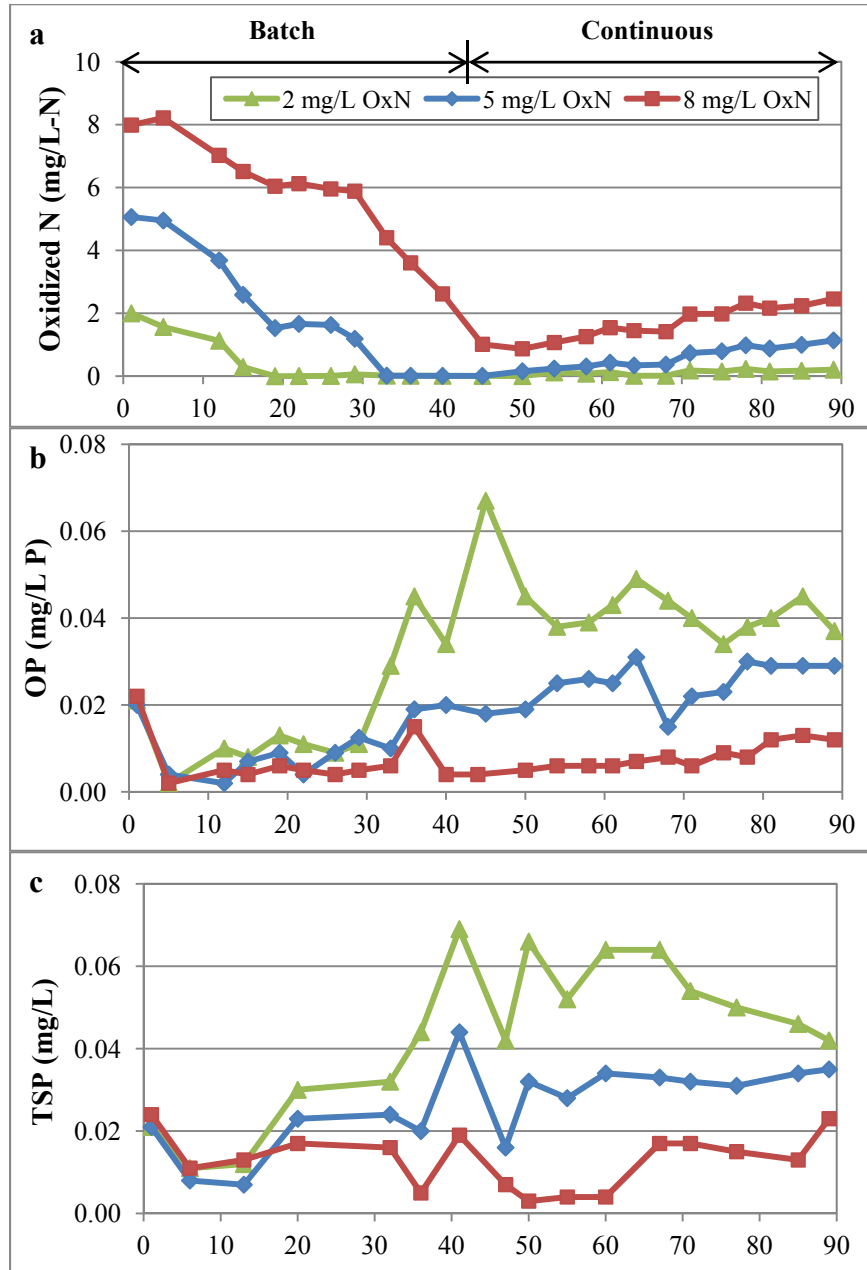
Figure 2-8 continued…
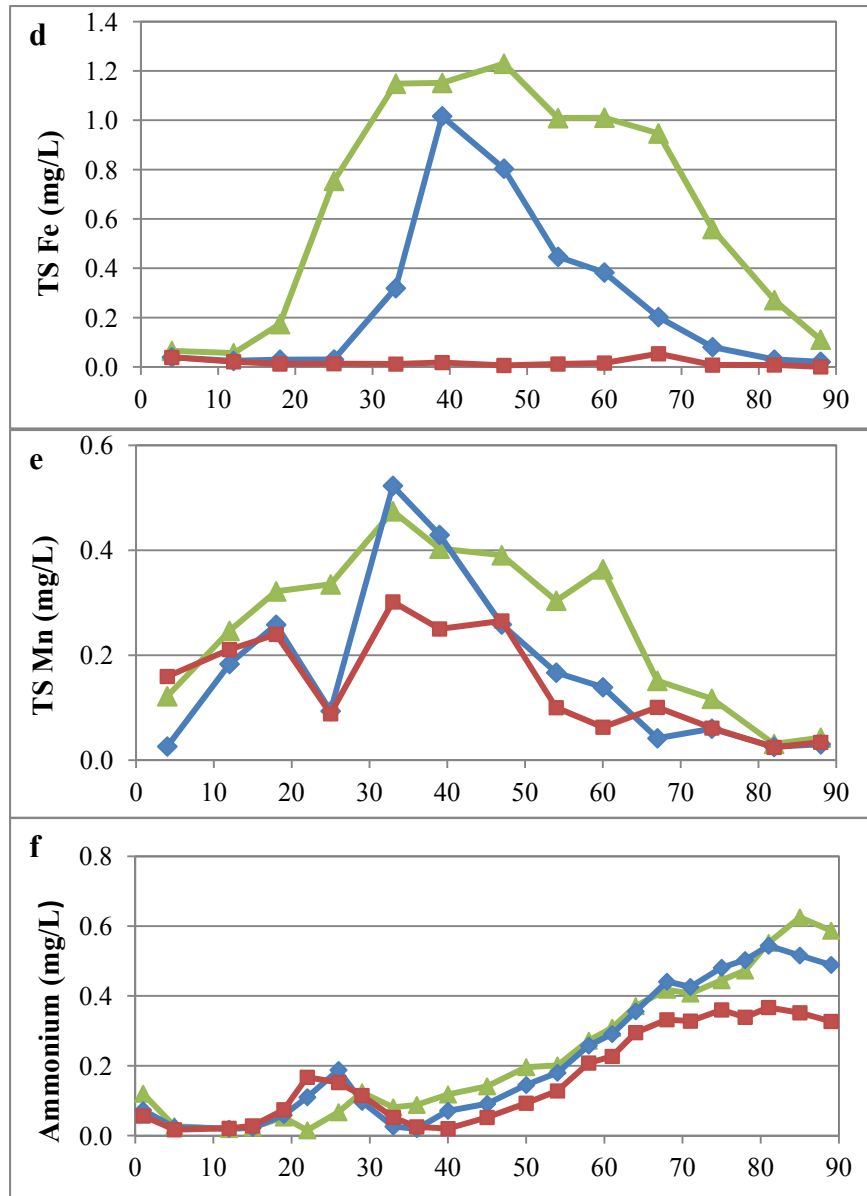
Figure 2-8 continued…
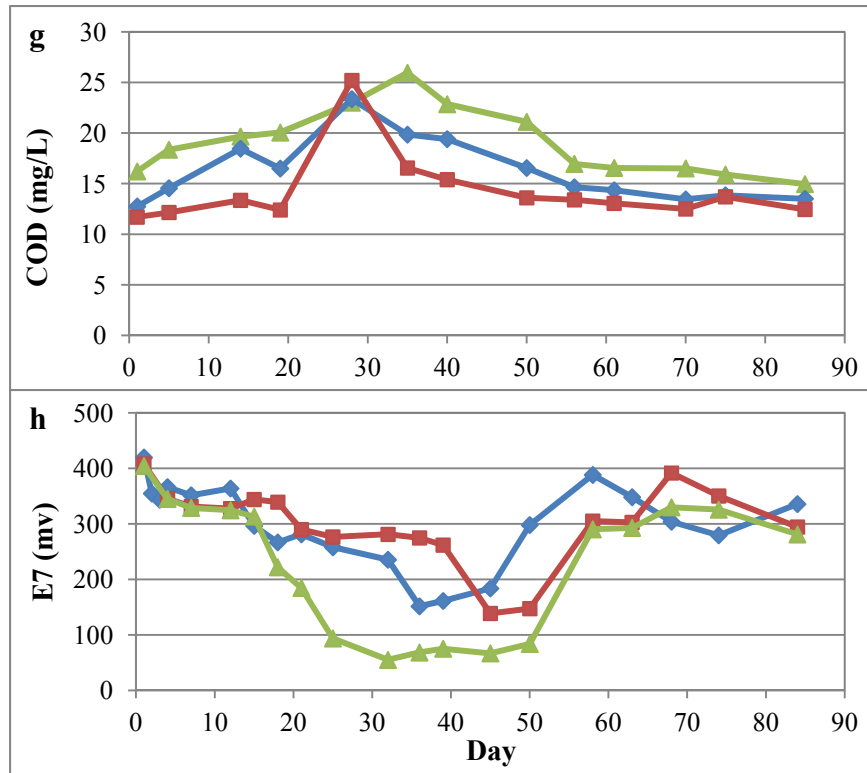
Chapter 3 - The effect of water volume to sediment area ratio on nitrogen removal rates in the hypolimnetic waters of the Occoquan Reservoir

Francisco Cubas, John T. Novak, Adil N. Godrej, R. David Holbrook, and Thomas J. Grizzard

3.1 Abstract

The Occoquan Reservoir is an artificial impoundment constructed to serve as a water supply that is part of an indirect potable reuse system for the suburbs of Washington D.C in northern Virginia. The reservoir receives a highly nitrified discharge from an advanced water reclamation facility (WRF) that is used as a management strategy during periods of hypolimnetic anoxia to prevent the release of undesirable substances from the sediments. The elongated narrow shape of the impoundment causes a longitudinal change in the ratio of water volume to sediment area, which has operationally defined as the effective depth (ED) of the system. This gradual change in the effective depth value (Z_{ED}) resulted in variable denitrification rates along the length of the reservoir. Both the change in the Z_{ED} and density gradients in the inlet of the reservoir, typical of the summer months, resulted in flow patterns that enhanced the transport of nitrate to the bottom waters of the reservoir.

Field observations made during periods of deep water anoxia, and microcosm studies designed to replicate different segments of the reservoir, showed that measured denitrification rate coefficients varied inversely with Z_{ED}. Results suggested that the higher denitrification rate coefficients observed in the upper reaches of the reservoir, as a consequence of the low Z_{ED}, resulted in reduced transport of nitrate downstream in the reservoir. Mass transfer coefficients (MTC) were calculated to determine if differences existed between denitrification rates across experiments and within the reservoir. Results showed that MTCs did not vary considerably among laboratory experiments and field observations, and ranged from 0.1 – 1.4 m/d. These results suggest that biotic removal of nitrogen was almost constant in all experiments and that the denitrification rate coefficient was mainly affected by changes in the Z_{ED}. Finally, the ED concept can be used to replicate stream and lakes in laboratory-scaled environments by downscaling morphological factors such as water volume, sediment area, and flows by keeping Z_{ED} constant. In this manner, laboratory experimental results can be more accurately extrapolated to represent natural aquatic systems.

Keywords: nitrogen, reservoir, morphology, water volume to sediment area ratio, effective depth, denitrification, denitrification rate coefficient, mass transfer coefficient

3.2 Introduction

The networks of streams, lakes, and reservoirs that receive a substantial load of nutrients from terrestrial ecosystems have the potential to act as nutrient sinks, thereby decreasing their transport to coastal systems. Among these nutrients, nitrogen is of great concern because it may promote increased phytoplankton growth, thereby enhancing the eutrophication process in aquatic systems (Beutel et al. 2008c, Hemond and Lin 2010, James et al. 2008). After nitrogen enters the river network, it is transported downstream where it is subject to retention through biotic and abiotic processes (Royer et al. 2004). Mass balances studies done in streams and reservoirs have shown that aquatic environments are capable of retaining a large portion of the nitrogen inputs (David et al. 2006). As nitrogen moves downstream, it can cycle between organic nitrogen retained in biomass or suspended particles and dissolved inorganic species in the water column such as ammonium, nitrate or nitrite. Of the processes that affect nitrogen retention in aquatic systems, assimilatory uptake by plants, algae or other microorganisms remove nitrogen only for a short period of time while denitrification results in a permanent loss from aquatic systems (Mulholland et al. 2008, Royer et al. 2004).

Streams and rivers are important sites for nitrogen removal because of their hydrologic and geomorphologic characteristics as well as their interconnectivity with terrestrial ecosystems. Streams have a relatively large streambed underneath a volume of water where high rates of biological activity that favor denitrification take place (Mulholland et al. 2008). The geomorphology of streams influences characteristics such as depth, flows, and hydraulic retention time (HRT) that will impact the transport and removal of nitrogen. Aquatic systems such as lakes and reservoirs also have the capacity to remove nitrogen as it is transported through the landscape. Deep, productive lakes, which typically experience seasonal periods of hypolimnetic anoxia and high concentrations of organic matter, create a suitable environment for nitrogen removal via denitrification (Piña-Ochoa and Álvarez-Cobelas 2006). Longer HRT, slower water velocities, and enhanced nutrient settling in deep reservoirs favor the denitrification process (Wetzel 2001). Although reservoirs occupy only about 6% of the global lentic area,

Harrison et al. (2009) estimated that of the total amount of nitrogen removed in lentic systems, approximately 33% was removed in reservoirs.

In the case of the Occoquan Reservoir, where the system receives a high input of nitrate during the summer months, most of the nitrogen is removed before leaving the reservoir. The Occoquan Reservoir, which is an artificial impoundment built to serve as a drinking water supply, is part of an indirect potable reuse system where an advanced WRF discharges high quality reclaimed water into one of the main tributaries of the reservoir, thereby increasing the drinking water safe yield. The reservoir undergoes an annual thermal stratification period during the summer months resulting in seasonal hypolimnetic anoxia. The public service authorities charged with managing the reservoir use a highly nitrified discharge from the WRF to keep a relatively oxidized environment in the bottom waters. Nitrate is capable of preventing the onset of truly anaerobic conditions by serving as an inorganic electron acceptor after DO depletion in the hypolimnion. By delaying the establishment of reducing conditions, the release of undesirable substances from the sediments is reduced (Andersen 1982, Prestigiacomo et al. 2009, Ripl 1976).

Denitrification, defined as the microbial oxidation of organic matter in which either nitrate or nitrite as the terminal electron acceptor is reduced to N_2 (Arango et al. 2007, Birgand et al. 2007, Seitzinger et al. 2006, Wetzel 2001), is the proposed mechanism for nitrogen removal in the Occoquan Reservoir (Cubas et al. 2012b, Randall and Grizzard 1995). Denitrification is known to be affected by physical, chemical, and biological factors such as water temperature, nitrate and DO concentrations, pH, available organic matter, flow, water residence time, hydraulic load, mixing regimes, and water depth or proportion of water volume to sediment area (Birgand et al. 2007, Kelly et al. 1987, Seitzinger et al. 2006, Tomaszek and Czerwieniec 2003). Because all the factors that control denitrification vary within a system and across different systems, the denitrification rates may also vary locally and between systems.

There are many different ways to report nitrogen removal from streams and lakes and many approaches are used in the literature. When denitrification is modeled as a first order reaction, a denitrification rate coefficient (k) may be obtained from a mass balance. The advantage of using the rate coefficient is that it gives a good approximation of the effectiveness of nitrogen removal

(Birgand et al. 2007). However, the disadvantage is that it cannot be used to directly compare nitrogen removal among different systems because k varies with the stream and lake physical and hydrological characteristics such as the channel size and water depth (Alexander et al. 2000). In the Occoquan Reservoir, the elongated narrow shape of the impoundment causes a change in the ratio of water volume overlying a specific sediment area as the waters move downstream. Longitudinal changes in the morphology of streams and lakes are known to cause changes in the physical, chemical, and biological parameters of the system, thereby altering the different processes that occur in them (Wetzel 2001). Thus, the morphology of the reservoir might be expected to cause changes in the denitrification rates along the longitudinal axis of the impoundment.

The objective of this study is to observe how the k value varied longitudinally as a function of the hypolimnetic water volume to sediment area ratio. The ability to include a spatially-variable denitrification rate coefficient is expected to improve model simulations in streams, lakes and reservoirs. Finally, a method to replicate different sections of a reservoir in laboratory-scaled microcosm studies using the water volume to sediment area ratio is proposed. By using this procedure, laboratory experimental results can be more accurately extrapolated to represent natural stream and reservoir conditions.

3.3 Study Area

The Occoquan Watershed is situated on the southwestern periphery of the Virginia suburbs of Washington D.C. The watershed is formed by four headwater basins that drain into the two main tributaries of the Occoquan Reservoir, which serves as a water supply source and recreational resource for over 1.2 million people (OWML 2005). The watershed is 1,530 km^2 in size and is about 54% forest land, 11% agricultural, pasture 7%, and 28% urban (Northern Virginia Regional Commission land use information, 2006). The hydrologic characteristics of the watershed have been described elsewhere (Xu et al. 2007). To the south, Occoquan Creek drains the two largest sub-basins (Cedar Run and Broad Run) of the watershed (880 km^2). In the northern part of the watershed, Cub Run is tributary to Bull Run, which drains a much smaller area (470 km^2), but also receives a year round, and relatively constant, flow from the UOSA WRF. As a consequence, during periods of low precipitation, Bull Run and the WRF discharge

contribute most of the base flow of the reservoir. The watershed and its principal tributaries are shown in Figure 3-1.

At full pool, the main body of the Occoquan Reservoir extends upstream from the dam to the confluence of Occoquan Creek and Bull Run. From that confluence, it extends approximately 3.5 km upstream into each of the tributaries. The UOSA WRF discharges a high quality reclaimed water into Bull Run approximately 10 km upstream from the confluence as seen in Figure 3-1. The WRF has the capacity for biological nitrogen removal (nitrification/denitrification) or may be operated to discharge a completely nitrified product water. Following the establishment of the thermal stratification in the early summer, the nitrified product water from UOSA is used as a reservoir management alternative to delay the onset of anaerobic conditions in the deep waters. During the summer, input concentrations of nitrate to the reservoir can reach values higher than 10 mg/L N (OWML 2005). During the colder months of the year, when most of the water column of the reservoir is fully oxygenated, the WRF is operated in nitrification/denitrification mode to remove most of the nitrogen in the discharge to comply with the existing regulations.

3.4 Materials and methods

3.4.1 Effective depth concept

The Occoquan Reservoir is a long narrow reservoir composed of a riverine upstream section that gradually transitions to a lentic water body as it moves downstream. When moving from the riverine to lacustrine zones in this type of reservoir, there is a gradual change in the ratio of the active sediment that is in contact with the volume of water that flows over a specific area. This longitudinal change of water volume and sediment area is known to affect various processes that take place in this type of reservoir, including denitrification (Wetzel 2001). Previous research conducted at the Occoquan Watershed Monitoring Laboratory (OWML) had concluded that nutrient uptake flux rates and nutrient release rates from the sediments were affected by changes in the water volume to sediment area ratio (Banchuen 2003, Yung 1990). The ED concept was used in this study to investigate the effects of variation in water volume to sediment area ratio on denitrification rates along the length of the reservoir.

The Z_{ED} is the ratio of the hypolimnion water volume to the surficial sediment area underlying that water volume and it is expressed in units of length. The Z_{ED} may also be defined as the ratio of the water body cross sectional area to the wetted perimeter an. In this study, the Z_{ED} was used instead of the depth value to study the nitrogen removal process in the reservoir as it was explained by Birgand et al. (2007) in their review. The Z_{ED} was also used in this study to simulate different segments of the Occoquan Reservoir in laboratory scale microcosm studies. By maintaining constant values of Z_{ED} and HRT for various reservoir segments, it was possible to scale down morphological characteristics such as water volume, sediment area and flows in laboratory experiments. Banchuen (2003) and Cubas et al. (2012b) used this relationship to model different segments of the Occoquan Reservoir in laboratory experiments.

3.4.2 Field Monitoring Data

To study the effect of Z_{ED} on denitrification, the reservoir was divided into segments of known physical characteristics and the rates for nitrogen removal were calculated in each segment. The reservoir was divided into five segments using the existing sampling stations as boundaries for each segment as shown in Figure 3-2. The morphology of the reservoir and its segments were obtained from a recent bathymetric survey that was performed with a GPS for spatial reference, and an acoustic sounder for depth measurements (OWML 2006). The survey data were imported and analyzed using the ESRI ArcGIS Desktop® 9.3. The resulting morphology features obtained for each segment are summarized in Table 3-1.

The time period for the study corresponded to the months of April to September for the years 2006 – 2010, when the reservoir was thermally stratified. This time period was chosen in order to measure the denitrification rates during periods of anoxia when the nitrate inputs to the reservoir from the UOSA WRF were high. The hypolimnion volume was calculated by defining the depth of the thermocline as determined from temperature and density profiles of the reservoir. The thermocline depth was the average distance from the surface to the point of highest density gradient calculated for the time period described earlier. The sediment area was taken as the total area in contact with the hypolimnion water. The HRT for each segment was calculated from the relationship of V/Q, where Q was the summer average flow for the time frame of the study, with discharges from large storms eliminated.

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Nitrogen removal rates were calculated from oxidized nitrogen (OxN) data collected from water samples above the sediment-water interface for the time period in consideration. Weekly samples were taken by OWML staff. Previous nitrogen studies performed at OWML have demonstrated that, in comparison to nitrate, nitrite (NO_2^-) concentrations in the Occoquan Reservoir are very low. For this reason, the OxN concentrations measured in the reservoir may be taken to consist mostly of nitrate (OWML 2005). DO profiles were used to determine the time at which oxygen was depleted from the water column, thereby creating a suitable environment for denitrification. Profiles of temperature, DO, and OxN concentrations were constructed from in situ measurements in the reservoir by deploying a probe and taking readings at 60 cm increments for the first 3 meters and at 1.5 meters thereafter. DO and temperature were measured using an YSI 600 XL Sonde®. Nitrate was measured with a Satlantic SUN® optical nitrate probe.

3.4.3 Denitrification rate coefficient

The denitrification rate coefficients for this study were computed in two ways: (1) directly in the bottom waters of the reservoir by performing a mass balance on the nitrate entering and leaving each segment, and (2) in microcosm studies simulating different segments of the reservoir. The long and narrow shape of the reservoir allows it to be modeled as a plug-flow system, which was approximated as the sum of five completely stirred tank reactors (CSTRs) in series. The denitrification rate coefficient (k) for the different segments of the reservoir and for experimental reactors operated in a continuous flow mode were calculated by solving k from the following mass balance equation:

$$\frac{dC}{dt}V = QC_{in} - QC_{out} - kVC_{out} \qquad \text{Eq. 3-1}$$

where C is the nitrate concentration, V is the hypolimnetic volume of each segment and Q is the flow through each segment. The following assumptions where made: (1) the hypolimnion was well mixed within each segment, (2) that Q and V were maintained constant in each segment at the moment of the mass balance, (3) that the k value was a first order reaction rate, and (4) that surface water evaporation did not change the water balances. Values of k were also obtained by

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modeling each segment as an individual plug flow system to compare and verify that the values obtained were consistent from both methods. The laboratory k values obtained from batch reactors were obtained by measuring the denitrification rate and solving for k form the following equation:

$$C = C_0 \cdot e^{-kt}$$
<div align="right">Eq. 3-2</div>

where C_o is the initial nitrate concentration and C is the nitrate concentration at time t.

The areal denitrification rate (U), expressed in mg/m$^2 \cdot$ d, was also calculated in this study. The values of U were calculated as the slope of the least squares best-fit line of mass with time (Beutel et al. 2008b) multiplied by the Z_{ED}. The value of U represents the total flux of nutrients from the water column to the stream bottom expressed on the basis of the sediment area under normal nutrient concentrations (Stream Solute Workshop 1990). Changes in OxN concentrations due to transformation into algal biomass or removal through sedimentation were not measured and were assumed to be small compared to the other terms of the mass balance as has been done in other studies (David et al. 2006).

Because it is assumed that k is a first order reaction rate, it can be expressed as a function of U, which changes linearly with concentration (Wollheim et al. 2006). This first order assumption states that U is linearly related to the nitrate concentration by the mass transfer coefficient value (v_f) by the following relationship:

$$U = v_f \cdot C$$
<div align="right">Eq. 3-3</div>

where C is the background nitrate concentration (mg/m^3).

The MTC generally refers to the vertical velocity (m/d) at which a soluble constituent moves from the water column through the sediment-water interface. It may be associated with denitrification or with both denitrification and nitrogen burial into sediments (Alexander et al. 2009, Harrison et al. 2009, Stream Solute Workshop 1990). The value of v_f may be related to k by the following equation:

$$\upsilon_f = \boldsymbol{k} \cdot \boldsymbol{h} \qquad\qquad\qquad \text{Eq. 3-4}$$

where h is the entire water depth (m) in the experimental site.

3.4.4 Experimental setup

Laboratory experiments with different Z_{ED} values were used to measure denitrification rates under different initial conditions. Different segments of the reservoir were downscaled to microcosm experiments using equivalent Z_{ED} values. Denitrification was measured when DO values were low (close to zero) to assure there was no negative effect on denitrification created by DO intrusion. Laboratory-scaled reactors were operated for time periods ranging from 45 – 60 days, and were used to simulate the thermally stratified season of different segments of the reservoir. The reactors were Plexiglas cylinders with a maximum capacity of approximately 11 liters, and were sealed to the atmosphere to sustain an anoxic environment. Glass beakers of different sizes were filled with sediments from the reservoir and placed in each reactor so that the sum of the exposed surface areas would achieve different Z_{ED} values with a fixed water volume. In most experiments, the reactors were operated in batch mode, although several experiments were conducted in a continuous flow mode. Sediment samples used in each reactor were taken from the corresponding sampling stations in the reservoir. Sediment samples were collected using an Ekman dredge, placed in glass bottles, and stored over ice in insulated coolers until transported to the laboratory. Once at the laboratory, the sediments were stored in the dark at 4°C until sample preparation. The water used to fill the reactors was collected from the reservoir, and adjusted to the desired initial OxN concentration by adding nitrified discharge water from the UOSA WRF. After setup, the reactors were sealed from the atmosphere and covered to prevent light penetration so as to avoid algae growth.

3.4.5 Analytical

Laboratory DO was measured by introducing a probe through a small diameter reactor sampling port which extended below the water surface. A HACH® LDO1-01 probe and a HACH® HQ40d dual-input multi parameter were used to measure DO. Water samples from each reactor were taken using a syringe, filtered (0.45 μm), and preserved when necessary either by acid addition

or by freezing the samples. Oxidized nitrogen ($NO_3^- + NO_2^-$) (4500-NO_3-F) and total dissolved organic content (5310C) were analyzed using Standard Methods (AWWA et al. 2005) in both field and laboratory samples.

3.5 Results

The Occoquan reservoir was an ideal system to observe the removal of nitrogen, mostly in the form of nitrate, in the downstream direction from the WRF point of discharge to the high dam. During periods of thermal stratification in the Occoquan Reservoir, the free-flowing waters of Bull Run arm were generally at a lower temperature than the surface waters of the impoundment. Figure 3-3 shows a three year time series that illustrates how the Bull Run waters that entered the reservoir measured at ST40 during the summer months were generally colder than the surface waters of the reservoir inlet (RE30). The figure also shows that the temperature measured on the bottom waters of the inlet was similar to the temperature of the water entering the reservoir (ST40) during the summer months. This condition was common during the period of thermal stratification in the reservoir, although it was occasionally disrupted by high flows from large rainfall events and resulted in short-term mixing in the vertical dimension. During the colder months of the year, typically from late September to early April, the water temperatures measured at ST40 and at the surface and bottom of station RE30 were similar.

The outcome of the temperature difference is illustrated in Figure 3-4. Summer densities in the free-flowing waters of Bull Run (abscissa) were higher than the surface water density of the reservoir for common dates (squares). The same stream waters were almost at the same density as the near-bottom waters of the reservoir for the same dates. As a result of these differences in water density, the Bull Run flow for the summer months plunged directly towards the bottom waters as it entered the main body of the reservoir. Figure 3-5 shows OxN profiles from different points along the longitudinal axis of the reservoir on September 1st, 2010. Station numbers and distance upstream of the high dam are shown below each profile. The stations labeled as RE12, RE18, and RE28 are not part of the regular sampling network, but instead are located at midpoints between those stations. The figure illustrates a typical longitudinal trend for OxN concentrations during the late summer season when the WRF discharges the greatest amount of nitrate to the reservoir. The difference in OxN concentrations between the surface and

the bottom waters at each station confirmed that nitrate was preferentially delivered to the bottom waters of the reservoir. Nitrate-rich waters began to plunge at station RE30, and the profile was maintained across the midpoint station RE28, and towards the confluence of Bull Run and the Occoquan Creek at station RE20. At RE20, the OxN concentrations decreased considerably because of dilution with low-nitrate waters entering the reservoir from Occoquan Creek. The Occoquan Creek (RE35) average summer OxN concentration for 2010 was 0.23 mg/L-N.

Another important feature to observe from the plot is the decrease in deep water OxN concentrations with decreasing distance to the high dam. The OxN concentration at the sediment-water interface was near 0 mg/L-N at stations RE02, RE05, and RE10 and was also relatively low at stations RE12 and RE15. At stations RE02 and RE05, most of the OxN that reached the hypolimnion had been consumed. These results suggested that most of the nitrate that entered the reservoir was consumed in the upper reaches of the reservoir. Figure 3-5 also shows that the OxN concentration close to the surface (epilimnion) was approximately 1 mg/L-N at station RE20, and was maintained at a similar value for most of the distance to the high dam.

The k values for the different segments of the reservoir and for experimental reactors operated in a continuous flow mode were calculated using equation 3-1 and for batch reactors using equation 3-2. Both the field and experimental denitrification constant were plotted against their corresponding Z_{ED} as shown in Figure 3-6. Figure 3-6a shows how the k values measured in the laboratory microcosm studies changed as a function of Z_{ED}. The values of k decreased linearly when the sediment area under a fixed water volume for each reactor decreased. These results were as expected because denitrification occurs mainly in the sediments and by decreasing the sediment area under a fixed volume, the denitrification site decreased. The same trend was observed in Figure 3-6b for the k values computed directly from the Occoquan Reservoir data, where it may be seen that the k values also decreased as the effective depth increased. This suggested that nitrate in the inflow was removed mostly in the upstream reaches of the reservoir where the water volume to sediment area ratio was lower. Also, when nitrate moved further downstream in the reservoir, it was removed at a slower rate due to the decrease in Z_{ED}.

Figure 3-6b shows a high value for k at the corresponding Z_{ED} value of 3. It is possible that this point was affected more by other factors that influenced denitrification rather than being solely the effect of the change in Z_{ED}. Also, it is important to observe that the slope of the trend line for both scenarios was very similar although the R^2 value for Figure 3-6b was low. If the high value for the Z_{ED} of 3 is treated as an outlier and is removed from the analysis, then the R^2 values increased to 0.50, but the slope decreased to -0.01. The decrease in slope for this case can be attributed to the lack of data for the lower values of Z_{ED} in the reservoir. The lower Z_{ED} values in the reservoir corresponded to segments located in the upper reaches, where the waters are in the transition from riverine to lacustrine. It was more difficult to compute the in situ denitrification rates at these locations because the process was affected by factors such as low HRTs and sporadic intrusions of DO to the bottom waters.

The v_f was calculated for both field and laboratory data to examine differences among computed and measured denitrification rate values, and to identify possible factors that may have influenced the process, excluding the effects caused by the change in Z_{ED}. Field and laboratory results were compared within this study. The field and laboratory v_f were calculated by substituting h with Z_{ED} in equation 3-4 (Birgand et al. 2007), and the results are shown in Table 3-2. DOC and OxN concentrations were measured in both field and laboratory experiments to determine if the amount of nitrate or organic matter present had any evident effect on the denitrification rates. The MTCs were expected to vary little if the environmental conditions were kept similar for all cases. The results summarized in Table 3-2 show that the v_f did not vary considerably among treatments and scenarios, and ranged from $0.1 - 1.4$ (m/d) in this study. Although the purpose of this study was not to determine the principal causes that resulted in MTC decrease or increase, it can be seen from Table 3-2 that some of the high v_f values corresponded to high values of organic matter measured as DOC or to high OxN inflow concentrations.

Plots of v_f against Z_{ED}, DOC, and OxN were constructed from all the field and laboratory experiment data points available to determine if any trends were evident. Figure 3-7a shows that the MTC did not vary considerably between different points in the reservoir as a function of Z_{ED}. This suggested that the MTC was generally consistent along the length of the reservoir and within laboratory-scaled models representing different segments of the reservoir. The small

difference observed in the values of v_f may have been due to specific changes in the amount of organic matter and/or nitrate available for denitrification or other parameters such as DO intrusion or differences in HRT. Figures 3-7b and c show that there was no trend between the MTC and the DOC and OxN concentration. Although, some high values of v_f were seen to be coincident with high concentrations of organic matter or OxN, it was not possible to conclude from the data that a significant trend existed.

3.6 Discussion

The Occoquan Reservoir received a seasonally variable inflow of a nitrified product water from a WRF as part of a management strategy to prevent or retard the development of anaerobic environments in the bottom waters during the summer months. Lentic water bodies, such as lakes and reservoirs, have the potential to act as important sinks for nitrogen because many factors that favor nitrogen burial or permanent loss due to denitrification are encountered in such systems (Harrison et al. 2009, Wetzel 2001). In the case of the Occoquan Reservoir, periods of low oxygen and high concentrations of nitrate and organic matter promoted and enhanced the biological denitrification process which is the main mechanism proposed to explain the nitrate depletion in the reservoir (Cubas et al. 2012a, Randall and Grizzard 1995). Another factor that contributed to the removal of nitrate from the waters of the reservoir was the geomorphology of the system. The shape of the reservoir caused a change in the ED as well as a change in water velocity along the longitudinal dimension of the reservoir. The morphology of the reservoir also contributed to the plug flow nature of the water flow, which promoted strong advective fluxes that influenced mixing patterns at the sediment-water interface and contributed to the formation of density currents, typical of this kind of reservoir (Marcé et al. 2008).

The formation of density currents in the Occoquan Reservoir is also a consequence of temperature gradients typical of the summer months (OWML 2005). The difference in temperatures between the inflow and the surface waters of the reservoir created a gradient where the waters entering the reservoir were at densities similar to those of the bottom waters at the inlet (Figure 3-4). Therefore, the denser water of the inflow from the tributaries plunged until it encountered waters of similar densities in the bottom of the reservoir. The intrusion depth is generally controlled by the density difference between the river and the reservoir prior to the

point of plunging, by the extent of the mixing processes (turbulence), and by the geometry of the inflow zone (Effler et al. 2009, Rueda et al. 2007).

In the case of the Occoquan Reservoir, the plunging water phenomenon had important implications for water quality and nitrogen removal. The streamflow from Bull Run, particularly during the summer months, contained high concentrations of nitrate due to the UOSA WRF discharge. Because of the plunging phenomenon, nutrients were preferentially delivered to the bottom waters of the upper reaches of the reservoir. This nutrient routing caused preferential delivery of organic matter and nitrate to the deeper parts of the reservoir, which were already anoxic, thereby creating a suitable environment for denitrification. It is important to consider that, although streamflow plunging into the reservoir was a common scenario, a consistent fraction of flow carrying nutrients was expected to reach the epilimnion of the reservoir. A thorough analysis on nitrate profiles and a mass balance on nitrate performed during the summer months of 2006 and 2007 (data not shown) revealed that approximately 15-20 % of the nitrate that entered the reservoir was not carried with the waters plunging to the bottom waters of the reservoir, but was instead delivered into the epilimnetic waters. This distribution of the flow between the epilimnetic and hypolimnetic layers is believed to be the result of ambient mixing processes that occurred at the inlet of the reservoir (Effler et al. 2009).

The delivery of nitrate into the bottom waters proved to be beneficial to water quality in the Occoquan Reservoir because, as nitrate moved downstream in the hypolimnion, it maintained an oxidized environment that prevented the release of undesirable substance from the sediments (Cubas et al. 2012a, Randall and Grizzard 1995). The beneficial effects were observed to be greater in the upstream regions of the reservoir, and diminished gradually as the flow moved downstream to areas closer to the dam (Banchuen 2003). The diminishing effect in the downstream direction was attributed in this study to (1) limits on the mass of nitrate delivered from the WRF, and (2) the enhanced rates of denitrification in the upper reaches of the reservoir.

The vertical profiles of OxN along the length of the reservoir shown in Figure 3-5 demonstrated that nitrate in the bottom waters was mainly consumed between stations RE10 and RE20. At station RE20 (located immediately downstream of the confluence of Occoquan Creek and Bull Run), the concentration of OxN was considerably reduced to approximately 5.5 mg/L N due to

the combined effect of denitrification and dilution from Occoquan Creek. Downstream from station RE20, hypolimnetic OxN continued to decrease all the way to station RE10. Finally, at station RE05, OxN was completely eliminated from the bottom waters, and at station RE02 it was completely eliminated from the hypolimnion. Thus, it can be concluded that most of the nitrate that entered the hypolimnion during periods of thermal stratification in the reservoir was consumed in the upper reaches of the reservoir for the date shown.

These results are consistent with previous studies that illustrated the capacity of the reservoir to decrease nitrate loads entering the system during periods of thermal stratification. Although inflow OxN concentration to the reservoir may reach values higher than 10 mg/L N, concentrations above 2 mg/L N in the raw water intake have seldom been observed (Cubas et al. 2012a, OWML 2005). Figure 3-5 also provides confirmation that a fraction of the delivered OxN load reached the surface waters of the reservoir. At station RE20, the concentration in the surface waters was approximately 1.5 mg/L N and slightly decreased downstream until it reached a value of 1 mg/L N at station RE02. The small change in OxN concentration at the surface waters of the reservoir suggest that there was no significant net transport of nitrate from the epilimnion to the hypolimnion, and further, that assimilation of nitrate in the water column was low, assuming that nitrogen loss in the water column is mainly caused by assimilation processes rather than by denitrification (Arango et al. 2008).

It has been hypothesized in this study that denitrification rates in the upper reaches of the reservoir were sufficiently high to prevent nitrate from reaching the area closest to the dam. As explained earlier, the morphology of the reservoir caused a longitudinal change in Z_{ED}, and it was expected that the denitrification rates would vary as one moves downstream. Seitzinger et al. (2006) suggested that as the morphology and hydrological characteristics varied throughout a river and lake network, the denitrification rates also changed. Other researchers have found that stream size and order played an important role in nitrogen transport by changing the uptake rates due to lower mean depth and changes in stream volume to sediment surface area ratios (Alexander et al. 2007, James et al. 2008, Wollheim et al. 2001, Wollheim et al. 2006).

It was observed in this study that values of k computed from reservoir data and measured in laboratory experiments increased when Z_{ED} decreased (Figure 3-6). Small differences observed

among values corresponding to a same Z_{ED} were probably caused by small differences in the initial OxN concentration, or by small changes in the average DOC for each experiment (Table 3-2 - laboratory data). In the reservoir, the k values for each Z_{ED} were computed from observed data from different years. It was possible that the biochemical factors that controlled the denitrification process changed during each year resulting in slight differences in the denitrification rates. Figure 3-8 shows that both sets of data followed similar trends for the values of k measured or computed for corresponding values of Z_{ED}. This suggests that the change in water volume to sediment area ratio had the same effect on the k values for the laboratory controlled environment and the reservoir.

The changes in denitrification rates as one moved along the length of the reservoir are related to the surface area of sediment in contact with a specific amount of overlying water volume. The relationship between this volume of water and the sediment area was defined in our study as the Z_{ED}. This depth, as explained by Alexander et al. (2000), can be considered as a measure of the hypolimnetic water volume available for processing by unit area of benthic sediment. This depth will have an effect on the settling and the direct supply of nitrogen for denitrification in the sediment-water interface. Therefore, the water column fraction that can potentially reach the adsorption and diffusion sites is inversely proportional to the column depth or height (Birgand et al. 2007). In other words, nitrogen settling and removal efficiency by denitrification should decrease as the effective depth increases, unless the exchange mechanism in the benthic sediment somehow increases proportionally to the depth through other processes.

This finding demonstrates a consistency with the available literature where nitrogen loss estimates in streams and reservoirs of different characteristics were expressed by the denitrification rate coefficients and examined as a function of water depth. Some researchers have observed similar trends in field observations and in model simulations where they related morphology factors such as water depth and residence time to k values or percentage of nitrate retention. In some studies, the same trend was observed when the mean depth of streams and reservoirs normalized by the retention time was related to the denitrification rate coefficient (David et al. 2006, Howarth et al. 1996, Seitzinger et al. 2006). In these studies, the k values for streams, some of agricultural drainage with high nitrate concentrations, decreased as the mean depth/residence time increased. In other cases, researchers have related k values to mean depth

for streams obtained from both modeling studies and observed data from a wide variety of streams (Alexander et al. 2009, Alexander et al. 2000, Böhlke et al. 2009). In these studies, they also found the same trend where k decreased as the mean depth increased. In some cases, the k values corresponding to a specific value of mean depth or depth/HRT were different from those found in our study.

The change in concentration per unit time was affected by the change in Z_{ED}, and it was reflected by having variable values of k throughout the length of the reservoir. In this study, Z_{ED} was used instead of the mean depth value (h) to relate the morphological factors to the variable values of k. This was done because most of the denitrification that was measured in the reservoir occurred in the hypolimnion where the conditions for the denitrification process were favorable and because the net transport of OxN from the epilimnion to the hypolimnion was nearly zero as was noted earlier. The use of Z_{ED} instead of the mean depth has also been justified by other researchers (Turlan et al. 2007). Birgand et al. (2007) demonstrated that the $K_c = v_f / D_e$ assuming that the nitrate removal rate per projected stream bed area (U) was proportional to the background concentration, as shown in equation 3-3, where K_c is the decay coefficient rate in units of time^{-1} and D_e was the effective depth in meters. Therefore, equation 3-4 can be modified by replacing h by Z_{ED} to relate the k for denitrification with the MTC as seen in equation 3-5.

$$\upsilon_f = \boldsymbol{k} \cdot \boldsymbol{Z_{ED}} \qquad\qquad \text{Eq. 3-5}$$

When denitrification is modeled as a first order reaction, the k value is commonly used. The advantage of this decay coefficient is that it gives a good approximation of the effectiveness of nitrogen removal (Birgand et al. 2007). However, the disadvantage is that it cannot be used to compare nitrogen removal among different systems because it varies with the stream and lake physical and hydrological characteristics, as has been shown in this study. Because the k values vary widely along the geometry of a stream or reservoir, it is often difficult to choose a single decay coefficient to represent nitrogen depletion in such systems, as explained by Seitzinger et al. (2006).

An alternative way to report removal rates is by expressing the mass of nitrogen removed per unit of time normalized by the area of the sediments. This expression is referred to as the areal

nitrogen removal rate which expresses the gross uptake that includes the biotic and abiotic uptake of nitrogen from the water column. In other words, a specific area of sediment is capable of supporting removal of a certain amount of nitrogen from the water column regardless of chemical and physical parameters (Arango et al. 2008, Birgand et al. 2007, Stream Solute Workshop 1990). Values of U may be used to compare nitrogen removal rates among different streams and lakes. Another way to express nitrogen removal is to calculate the MTC from equation 3-3. The MTC is the vertical velocity at which nitrate mass is transported from the water column to the sediments where it becomes available for denitrification (Alexander et al. 2009, Royer et al. 2004). The v_f value may also be used to compare nitrogen uptake rates among streams and lakes of different characteristics.

In this study, the MTCs calculated from the field data did not exhibit much variability. In fact, the values were in the same order of magnitude with the exception of two values that corresponded to the upper reaches of the reservoir. It is possible that the higher values were affected by higher concentrations of OxN which are typical during the summer months, or by higher amounts of labile organic matter entering the reservoir, thereby increasing the denitrification rate. The values of v_f corresponding to the laboratory data were also similar to each other, with a few exceptions. The small differences between the experimental v_f values might also be the result of higher concentrations of OM and OxN within the experiments. The results obtained were as expected because the MTC values should not differ greatly under similar environment conditions. It may also be seen that both field and laboratory MTC values were similar. This was likely because the laboratory experiments were performed under similar conditions as the reservoir.

Figure 3-7a seems to support this observation, because it was not possible to find any significant correlation or trend for v_f when plotted against the Z_{ED}. The MTC was generally consistent along the different Z_{ED} measured in the reservoir and in laboratory-scaled reactors. These results were as expected and in agreement with the findings of other authors which have concluded that v_f should remain constant under changes in water depth (Stream Solute Workshop 1990). The small difference observed in the values of v_f may be due to specific changes in the amount of organic matter and/or nitrate available for denitrification, or other factors that were not considered in this study such as DO intrusion, differences in HRT, microbial diversity, etc.

Denitrification is affected by physical factors such as HRT, flow, water depth, mixing rates and diffusion, as well as by chemical and biological factors including temperature, pH, light, and concentrations of DO, NO_3^-, and organic matter availability (Arango et al. 2007, Beutel et al. 2008a, Birgand et al. 2007, Mulholland et al. 2008, Seitzinger et al. 2006, Tomaszek and Czerwieniec 2003). The value of k includes all the factors that affect denitrification (physical and biochemical), while the MTC is a compilation of all the biochemical factors that affected denitrification. In other words, the MTC is a measure of the biotic difference in nitrogen removal independent of the physical and hydrological parameters such as flow, water depth, and retention time (Alexander et al. 2009, Wollheim et al. 2006). In our study it was hypothesized that in most cases the Z_{ED} encompassed the physical and hydrological factors that affected the denitrification process. This assumption was made because changes in Z_{ED} along the length of the reservoir resulted in changes in HRT, water depth, water velocity and flow patterns. If this is the case in the Reservoir, then it is possible to relate the physical and biochemical factors to the overall denitrification coefficient using equation 3-5. Thus, the variables v_f and Z_{ED} from equation 3-5 identify the biochemical and physical factors respectively affecting denitrification while the k value is a compilation of all the parameters affecting the denitrification process.

The v_f may be calculated from equation 3-5 when k and the Z_{ED} are known. Z_{ED} may be determined from bathymetry of the water body and k may be obtained from mass balances on nitrogen. Thus, v_f can be used to compare rates for denitrification across different aquatic systems because the effects of the physical properties of a stream or lakes are normalized when solving for the MTC using equation 3-5. In our study, it was not possible to identify any correlation between v_f and DOC or OXN (Figure 3-7b and c) although a trend was expected. In the case of DOC, a trend was not clearly observed because the range of measured DOC was quite small, so it was not possible to draw a definitive conclusion from the data. For OxN, it was possible that the effect of nitrate on v_f was not sufficiently large as to observe any noticeable difference in the MTC. However, determining the principal causes of MTC increase or decrease was not the purpose of this study. Further studies are needed to assess the impact of biochemical factors on the MTC in the Occoquan Reservoir.

Finally, because hydrologic and morphologic factors influence many stream, lake, and reservoir processes, results and conclusions obtained from laboratory studies and computer modeling must

be carefully evaluated before being extrapolated to natural systems (Davidson and Seitzinger 2006, Stream Solute Workshop 1990). Conditions such as water volume to sediment ratio, flows, background solute concentrations, DO concentrations, etc., should be well documented when scaling processes into experimental environments for analysis and when extrapolated back to natural stream and lake conditions. In this study, it was demonstrated that the concept of ED may be used to model and downscale segments of the reservoir into microcosm studies. Results obtained from the laboratory experiments where similar to results obtained directly from field observations in the reservoir when all the remaining conditions where similar. It was also demonstrated that the effect produced in nitrogen uptake by the change in water volume to sediment area ratio can be replicated in microcosm studies by using the Z_{ED}. By considering the Z_{ED} in laboratory experiments better v_f values that can accurately explain the process of denitrification in general may be obtained from laboratory experiments. Difficulties in scaling up laboratory and field data that may lead to poor quantitative understanding of in situ denitrification rates and controlling factors can be reduced by utilizing the ED concept.

3.7 Conclusions

Results demonstrated that changes in Z_{ED} had a significant impact on the denitrification rates computed in the reservoir and measured in microcosm experiments. In the upper reaches of the Occoquan Reservoir, the combined effect of plunging inflows carrying high concentrations of nitrate and organic matter, along with the low Z_{ED}, resulted in high denitrification rates. On the other hand, lower denitrification rates were measured when the Z_{ED} increased in the downstream direction. Similar results were observed in laboratory experiments where k values also decreased when the water Z_{ED} increased. Both field data and experimental results followed a similar trend, thereby highlighting the importance of physical factors, represented by Z_{ED}, on denitrification rates in reservoirs. Values of v_f, which is used to compare denitrification rates among different systems, were calculated for both field and laboratory data. The MTC did not vary significantly among field and laboratory results, suggesting that most of the variability in the denitrification rates was introduced by changes in Z_{ED} along the reservoir. Although denitrification is affected by many factors, such as nitrate and organic matter concentration, it was not possible from the data available to identify any existing trend between v_f and either organic matter or nitrate concentration. Finally, the ED concept was shown to be an effective method to simulate

different segments of the reservoir in laboratory-scaled microcosm. Similarities between the field and laboratory results suggested that the environment that existed in the waters of the reservoir was closely replicated in the experimental work, and provided confidence that laboratory results can be extrapolated to natural reservoir conditions.

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Table 3-1. Summary of the morphology features for each segment of the reservoir used in this study

Segment	Sediment Area (m^2)	Hypolimnion Vol. (m^3)	Effective Depth (m)	HRT (day)
1	575,261	5,466,336	9.5	13.0
2	643,791	3,722,211	5.8	8.8
3	679,166	2,653,811	3.9	6.3
4	619,688	1,868,709	3.0	4.4
5	249,168	350,684	1.4	0.8

[a] HRT based on a summer seasonal average flow of 0.43×10^6 m^3/day which includes UOSA WRF daily discharge

Table 3-2. Mass transfer coefficients, OxN and DOC concentrations for field (top) and lab data (bottom).

Field Data					
Segment	Year	Z_{ED} (m)	MTC (υ_f) (m/d)	Average Inflow OxN Conc. (mg/L)	Average DOC (mg/L)
1	2007	9.5	0.69	0.26	7.53
1	2008	9.5	0.67	0.69	6.38
1	2009	9.5	0.63	0.52	5.70
1	2010	9.5	0.87	0.35	5.21
1	2011	9.5	0.62	0.27	6.55
2	2007	5.8	0.43	0.56	6.44
2	2008	5.8	0.54	0.77	6.13
2	2009	5.8	0.41	0.71	6.63
2	2010	5.8	0.63	0.34	5.00
2	2011	5.8	0.58	0.20	6.73
3	2007	3.9	0.28	0.69	5.50
3	2008	3.9	0.58	0.97	6.01
3	2009	3.9	0.48	0.73	6.20
3	2010	3.9	0.50	0.64	5.60
3	2011	3.9	0.67	0.64	6.53
4	2007	3.0	0.55	0.99	4.51
4	2009	3.0	1.43	1.11	5.84
4	2010	3.0	0.73	0.97	5.44
4	2011	3.0	1.42	1.07	5.56

Laboratory Data				
Z_{ED} (m)	MTC (υ_f) (m/d)	Aerial Denitrification Rate (mg/m2*d)	Initial OxN Conc. (mg/L)	Avg DOC (mg/L)
0.34	0.09	90	5.0	NM
1.08	0.23	40	1.2	4.32
1.08	0.22	175	5.9	3.82
1.13	0.25	234	5.0	NM
2.26	0.58	298	2.3	5.21
2.26	0.61	394	2.2	7.47
2.94	0.92	85	0.6	9.88
2.94	0.66	578	4.9	7.16
3.86	0.60	75	0.5	5.40
3.86	0.50	457	5.2	4.46
4.75	0.60	73	0.4	5.99
4.75	0.57	695	5.0	4.68
4.93	0.81	459	2.5	5.28
4.93	0.84	392	2.6	5.38
5.15	0.59	336	2.6	4.86
7.97	0.78	80	0.4	6.10
7.97	0.78	548	5.2	4.61
7.97	0.58	590	3.0	5.12
7.97	0.80	683	5.0	NM
7.97	0.83	1,227	5.0	5.17
7.97	0.48	397	8.0	3.98

NM = not measured

Figure 3-1. Occoquan Watershed and reservoir
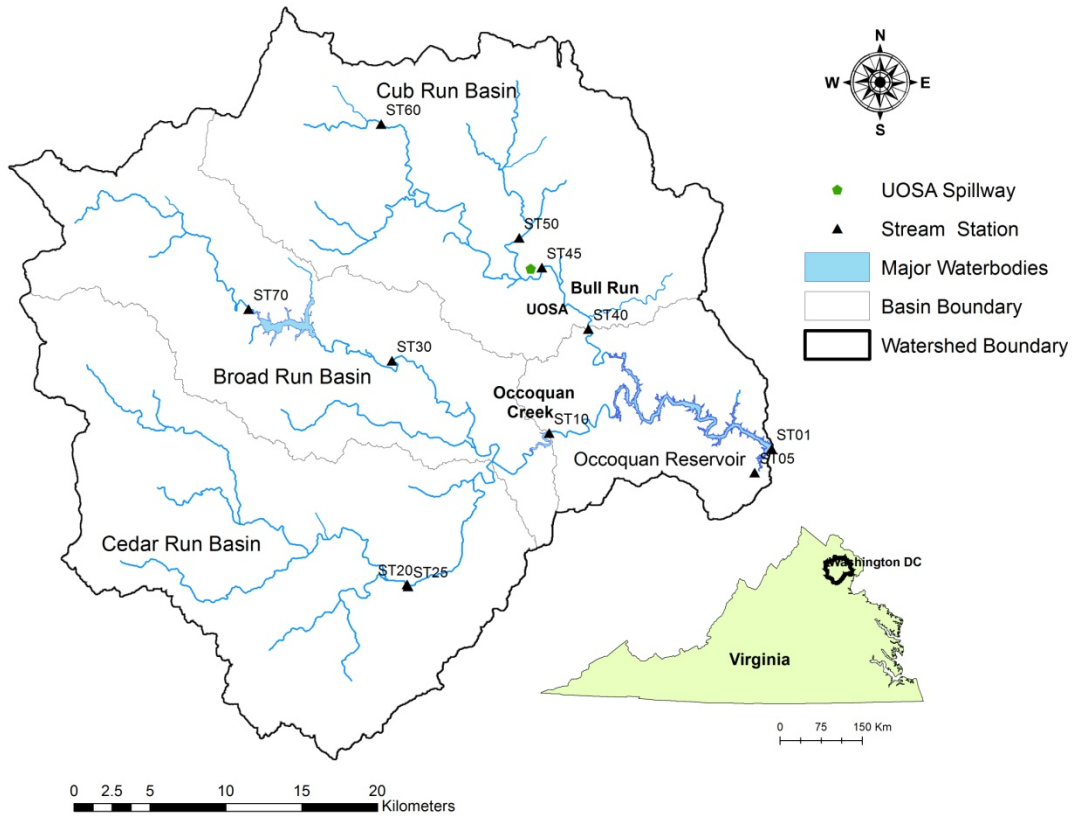
Figure 3-2. Occoquan Reservoir segments and sampling stations (top). Sketch depicting the change in ED along the length of the Occoquan Reservoir (bottom).
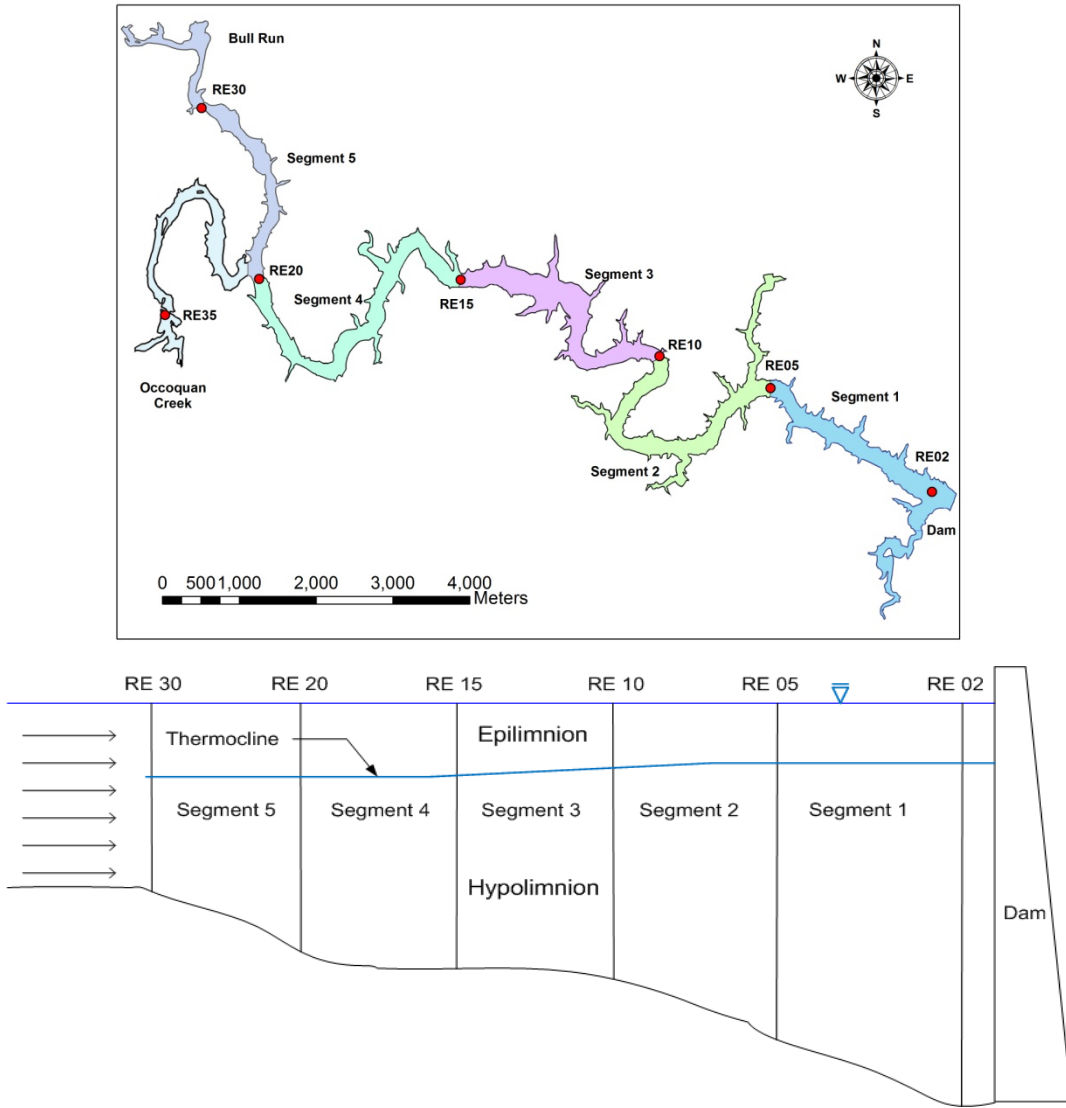
Figure 3-3. Time series for temperature measured in the Bull Run arm (ST40) and at the surface and bottom of the reservoir inlet (RE30).
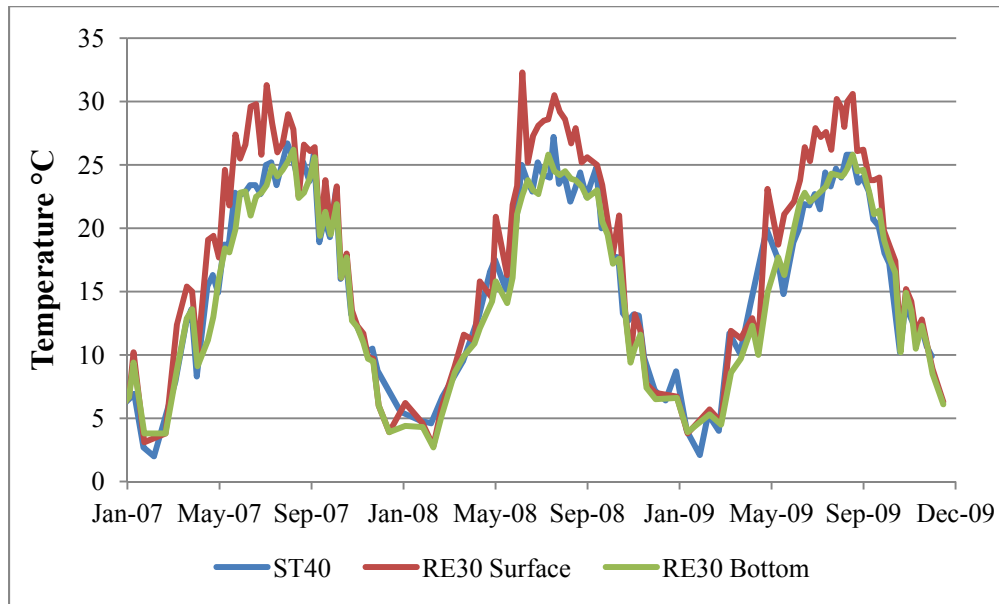
Figure 3-4. Comparison of observed summer surface and bottom densities at RE30 to stream flow densities at ST40.
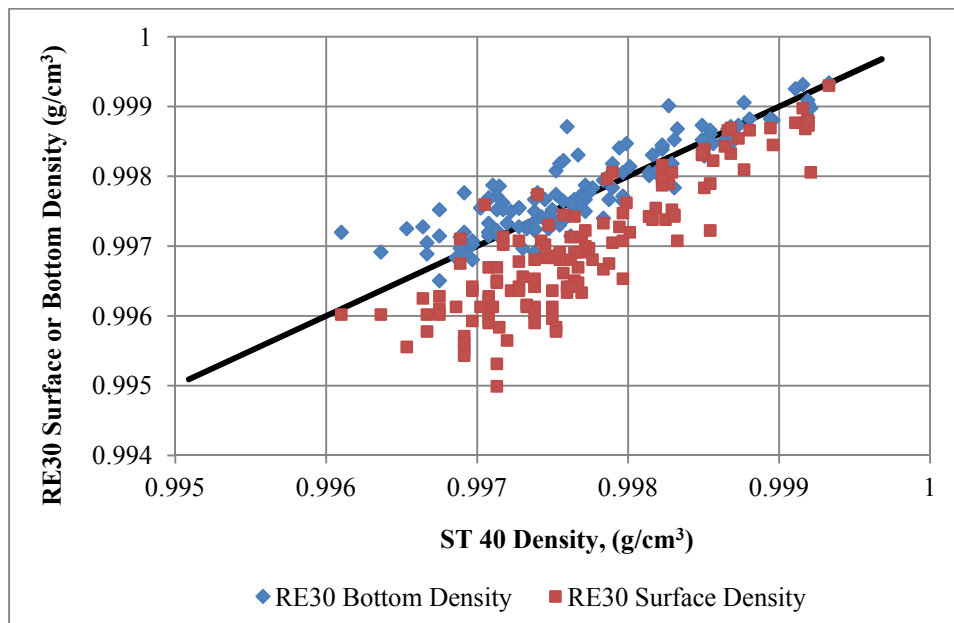
Figure 3-5. OxN profiles taken along the length of the Occoquan Reservoir on Sept 1st, 2010.
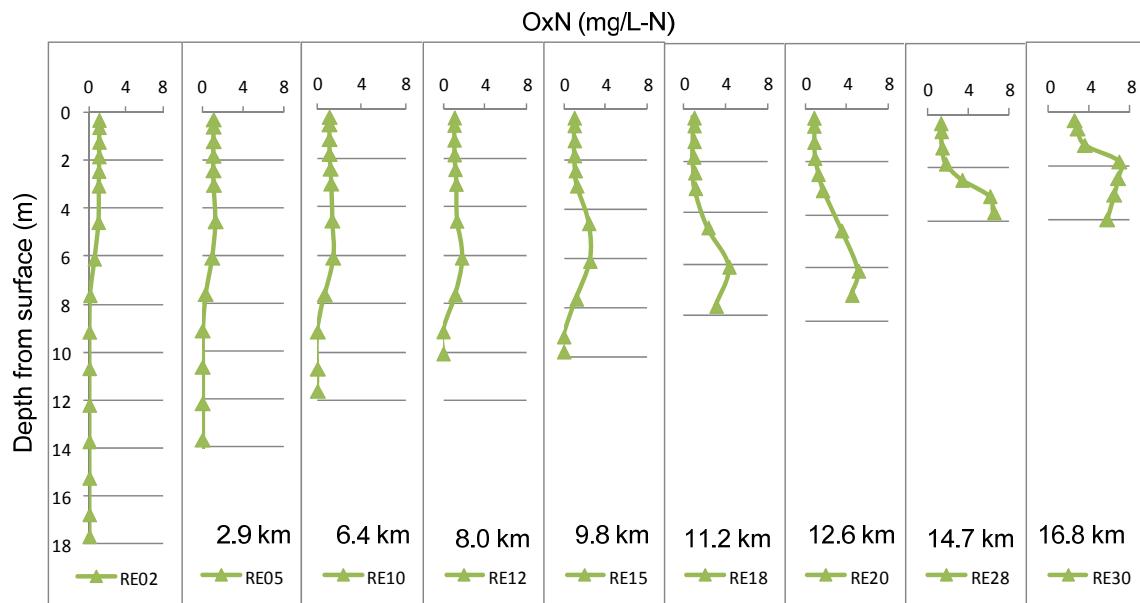
Figure 3-6. Summary of denitrification rates coefficient (*k*) measured in (a) laboratory experiments and (b) in the reservoir.
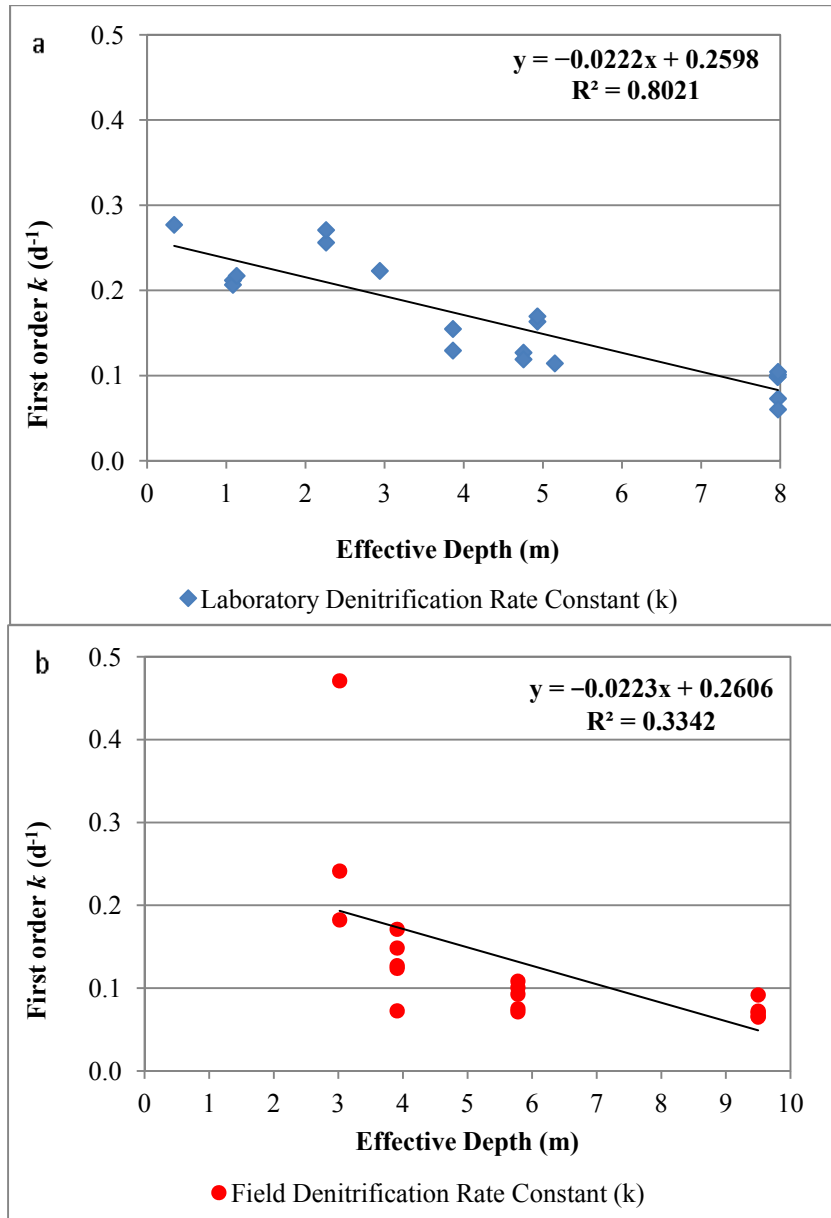
Figure 3-7. Relationship between (a) MTC (v_f) and Z_{ED}, (b) DOC, and (c) OxN concentration.
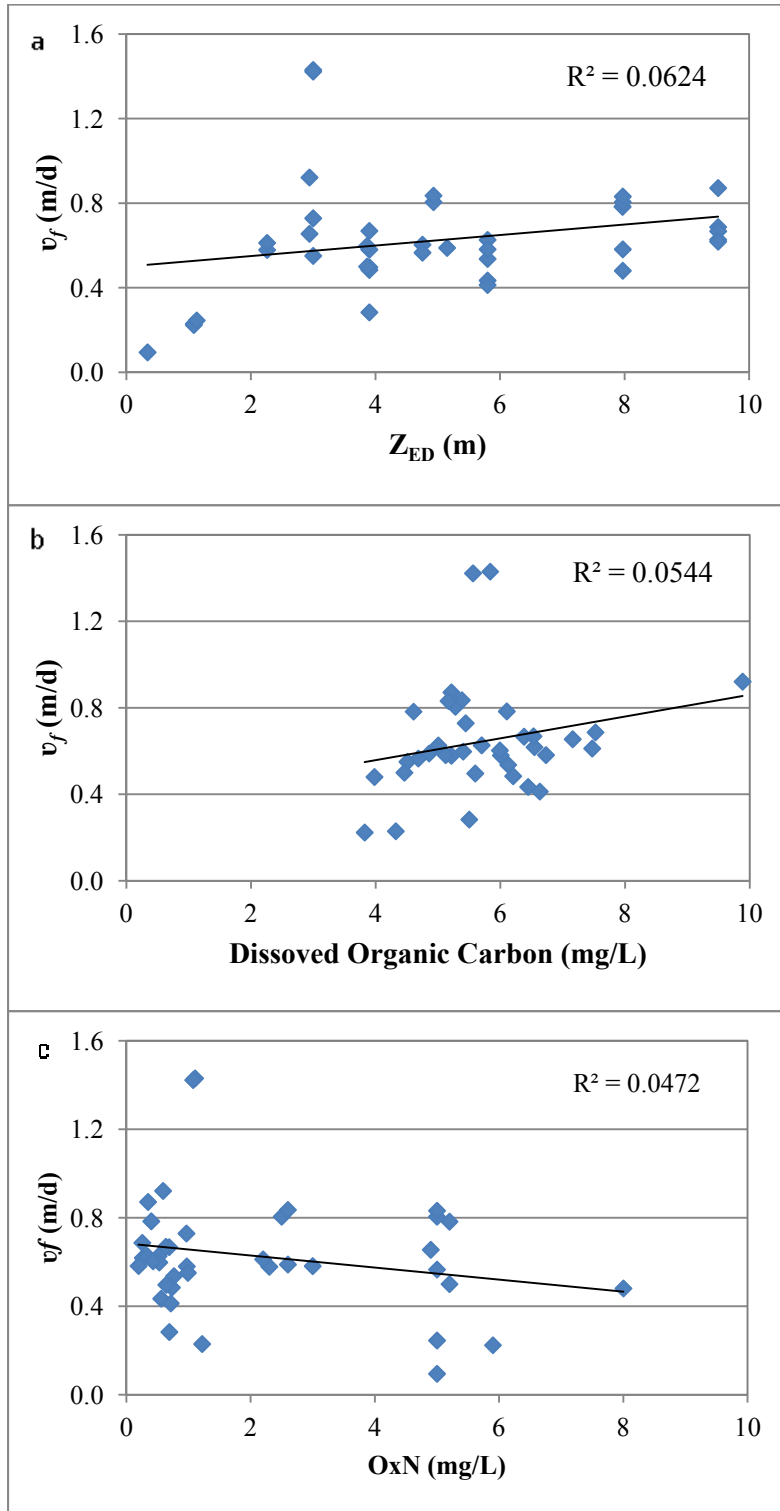
Figure 3-8. Combined denitrification rate coefficient (k) for both laboratory and field data.

$y = -0.0198x + 0.2402$
$R^2 = 0.6971$

First order k (d^{-1})

Effective Depth (m)

♦ Laboratory Data   ● Field Data
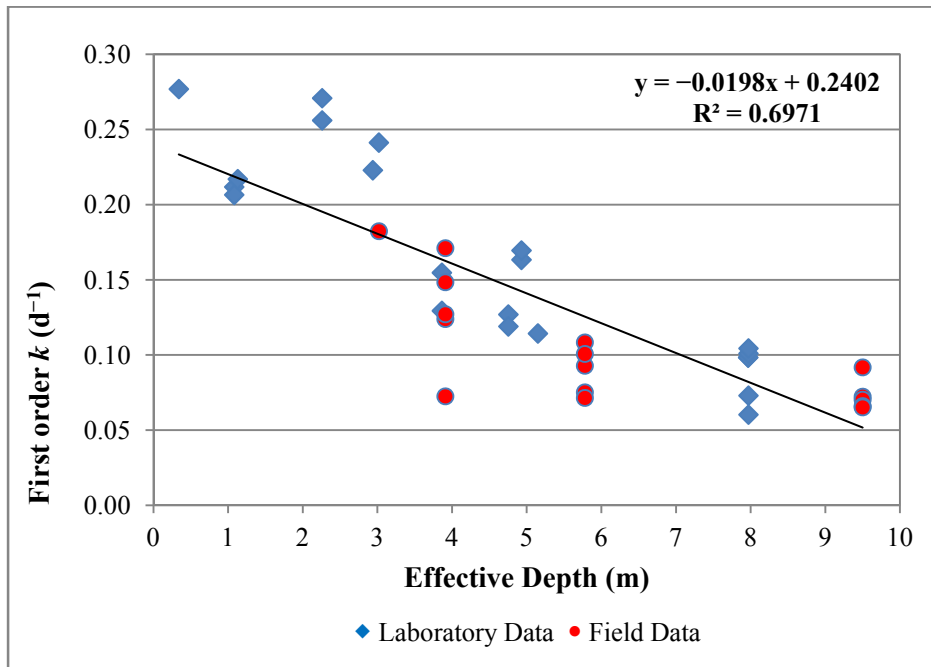
Chapter 4 - The effect of nitrate on ammonium release from the sediments of the Occoquan Reservoir

Francisco Cubas, John T. Novak, Duane F. Berry, Adil N. Godrej, and Thomas J. Grizzard

4.1 Abstract

The Occoquan Reservoir is part of an indirect potable reuse system where an advanced water reclamation facility (WRF) discharges high quality water into a major tributary, thereby increasing the drinking water safe yield of the impoundment. The WRF is capable of producing a high quality nitrified discharge that has been used in the reservoir as a management strategy to prevent the release of undesirable substances from the deposited sediments during periods of hypolimnetic anoxia. Water quality data from field observations showed that ammonium concentrations in the hypolimnion reached values as high as 5 mg/L N by the end of the summer after the depletion of both oxygen and nitrate. The presence of nitrate above the sediment-water interface during periods of anoxia caused decreased sediment ammonium release, but did not completely prevent it. Sediment ammonium release was accompanied by an increase of organic matter in the water column after nitrate was depleted above the sediment-water interface.

Results from laboratory experiments revealed that sediment ammonium release occurred in both aerobic and anaerobic environments at a similar rate. No correlation was found between sediment ammonium release and the concentration of nitrate in the water column, suggesting that ammonium release was mainly the result of the mineralization of nitrogen-rich organic matter. Results showed that sediment ammonium release was inversely related to the carbon to nitrogen ratio (C:N) above the sediment-water interface whether the environment was aerobic or anaerobic. Simultaneous release of ammonium and organic matter from the sediments was not observed during the microcosm experiments, although it was in the reservoir. This suggests that sediment ammonium release was controlled by different mechanisms which may not have been replicated in the microcosm study. Finally, the C:N ratio proved to be a useful indicator to determine the sediment ammonium release potential in aquatic systems.

Keywords: water reuse, ammonium, nitrate, organic matter release, carbon to nitrogen ratio, sediments

4.2 Introduction

Deep, productive lakes and reservoirs in temperate climates experience hypolimnetic anoxia during the warmer months of the year following the development of thermal stratification. Negative water quality impacts related to hypolimnetic anoxia are mainly caused by the release of substances from the sediments such as phosphorus, organic matter and reduced species of nitrogen, iron, manganese, and sulfur (Beutel 2006). Nitrogen release from deposited sediments occurs predominantly as ammonium (NH_4^+), and is one of the first species to be released when following the establishment of anaerobic conditions. Ammonium generally accumulates in the water column shortly after the onset of anaerobic conditions because nitrification is inhibited due to low dissolved oxygen (DO) concentrations (Burger et al. 2007, Wetzel 2001).

Ammonium is the preferred source of nitrogen for growth and cell synthesis for a wide range of microorganisms (Arango et al. 2008, Matthews et al. 2000). However, under anaerobic conditions, ammonium assimilation by microorganisms is typically low when compared to that in aerobic environments (Beutel et al. 2008b). Sediment ammonium release is of great concern in aquatic systems because ammonium provides a source of nitrogen for phytoplankton growth and it also increases the oxygen demand in aquatic systems. Furthermore, ammonia may be toxic to aquatic organisms at low concentrations. The toxicity of ammonia is controlled by the water chemistry which governs the equilibrium between ammonium (NH_4^+) and the un-ionized species ammonia (NH_3). Factors such as temperature, pH, and ionic strength (to a lower degree), which are typically variable in eutrophic systems, will control the toxicity of ammonia in water bodies (Matthews et al. 2000, Stumm and Morgan 1996).

Inputs of ammonium to surface waters may be from external sources such as runoff from fertilized lands within the watershed and from wastewater discharges, as well as from natural internal sources including nitrogen fixation by certain species of cyanobacteria or the mineralization of organic matter containing nitrogen (Frazier et al. 1996). In lakes and reservoirs, nitrogen transformations are mainly controlled by benthic processes that are mediated by microorganisms. Within these processes, ammonification, which is the mineralization of organic nitrogen to ammonium, is suggested to be responsible for the production of ammonium within the sediments (Nizzoli et al. 2010). Ammonium production and release from the

sediments is related to the physical and chemical characteristics of the system such as pH, ORP levels, and cation exchange capacity (CEC) as well as the characteristics of the sediment organic matter (Wang et al. 2008).

From the characteristics of the organic matter, it has been suggested that the C:N ratio is one of the most important factors controlling the release of sediment ammonium (Blackburn and Henriksen 1983, Goldman et al. 1987, Wang and Yin 2009). Ammonium release occurs when the nitrogen source is an organic compound and when the substrate C:N ratio is lower than the C:N ratio found in the bacterial biomass. This may occur when the readily available organic matter is rapidly depleted and nitrogen rich organic compounds such as amino acids are then used for energy and as a carbon source, resulting in lower C:N ratios and concurrent ammonium release (Goldman and Dennett 1991, Goldman and Dennett 2000). The catabolism of amino acids requires the removal of the amino group, which upon removal from the carbon skeleton is transformed to NH_4^+. When ammonium is used as the nitrogen source, it may be rapidly utilized by microorganisms and recycled back into microbial cells, thereby effectively reducing the amount of ammonium release (Goldman and Dennett 2000).

Ammonium produced within the sediments may be sorbed to the sediment surface depending on physical properties such as the CEC and the organic matter content. The CEC is affected by the type of sediment and by the concentration of cations in the water above the sediment-water interface. When the exchange capacity is high and the sediment organic matter content is low, ammonium exchange to the pore water can be low (Blackburn and Henriksen 1983), although some studies suggest that ammonium can also be sorbed to organic matter (Rosenfeld 1979). It has also been proposed that the sorptive capacity of the sediments decreases when the oxidized microzone within the sediments is lost (Wetzel 2001). The literature remains divided regarding the ORP level in the sediments that will influence sediment ammonium release. Some researchers have suggested that an oxidized environment will decrease the amount of ammonium released from the sediments and others believe that ammonium release is completely independent of the ORP (Beutel et al. 2008a, Martinova 1993, Nowlin et al. 2005).

In the Occoquan Reservoir, nitrate from an advanced water reclamation facility (WRF) has been used to poise the ORP to a level that prevents the release of phosphorus, iron, and manganese

from the sediments. There are some cases where the use of nitrate has been proven to be efficient in reducing the amount of ammonium release from the sediments in the reservoir and others where the results are still uncertain (OWML 2005). The purpose of this study was to examine the effects of nitrate on sediment ammonium release and to determine whether nitrate, when used as a management alternative, can be as effective in controlling ammonium release as it is in controlling phosphorus release.

4.3 Study Area

The Occoquan Watershed is situated in the northern suburbs of the Commonwealth of Virginia, southwest of Washington D.C., United States. The watershed is 1,530 km^2 in size and approximately 54% is forest and 28% is urban, while the rest is mostly used for agricultural or pasture purposes. The hydrological characteristics and the physical attributes of the watershed are described elsewhere (Xu et al. 2007). The southern part of the watershed is formed by the two largest sub-basins which are drained by Cedar Run and Broad Run, and which eventually merge to form Occoquan Creek. The northern part of the watershed (Cub Rain Basin) drains into Bull Run. Together, Occoquan Creek and Bull Run form the main tributaries of the Occoquan Reservoir (Figure 4-1). The physical characteristics of the Occoquan Reservoir are described elsewhere (Cubas et al. 2012a).

The Upper Occoquan Service Authority (UOSA) WRF discharges a high quality reclaimed water into Bull Run approximately 10 km upstream from the confluence with Occoquan Creek (Figure 4-1). As a consequence, during extended periods of low precipitation, Bull Run contributes most of the baseflow of the reservoir. The WRF has the capacity for biological nitrogen removal, but may also be operated to discharge a highly nitrified product water. In the Occoquan Reservoir, after the establishment of the thermal stratification in the early summer, loss of oxygen in the hypolimnion due to high microbial activity is rapidly followed by the establishment of anaerobic conditions. To delay the establishment of completely anaerobic conditions in the hypolimnion of the reservoir, the UOSA WRF is operated to provide a high concentration of nitrate in the summer months. During the summer, the input nitrate concentration to the reservoir may reach values greater than 10 mg/L N (OWML 2005). The reservoir has the capacity to consume most of the nitrate that reaches the hypolimnion while preventing the release of undesirable substances

from the sediments. A small percentage of the total nitrate input seasonally reaches the further downstream sections of the reservoir, but seldom a nitrate concentration greater than 1 mg/L N is measured at the discharge of the reservoir (Cubas et al. 2012a, Cubas et al. 2012b).

4.4 Material and methods

4.4.1 Field observations and monitoring data

This study focused on the effect of nitrate on sediment ammonium release in the sections of the reservoir located upstream of the principal raw drinking water intake. Water quality data from the Occoquan Watershed Monitoring Laboratory (OWML) database obtained from field sampling at stations RE02, RE05, and RE10 were used to assess the effect of nitrate on sediment ammonium release. The data corresponded to water samples collected at approximately 30 cm above the sediment water interface. Sediment samples used to determine the C:N ratio were taken from station RE02. Station RE02 is located approximately 300 m from the dam, while stations RE05 and RE10 are located 2.9 and 6.4 km upstream the dam respectively (Figure 4-2). Field sampling in the reservoir was conducted weekly by OWML staff. The data used to explain the relationship between nitrate and sediment ammonium release were subsets from the overall data corresponding to the summer periods for the years 2004 - 2010. To represent periods of thermal stratification and hypoxia in the reservoir, the data used were obtained from the periods ranging from early April to late October for each year. The ammonium input to the reservoir from the two principal tributaries was measured at stations ST10 and ST40 (Figure 4-1).

4.4.2 Microcosm studies

Laboratory-scale reactors were operated for a period of approximately 40 days in an effort to simulate the conditions that existed in the reservoir during the summer months. The reactors were Plexiglas cylinders and were sealed from the atmosphere to sustain an anoxic environment or were open to the atmosphere and aerated to maintain an aerobic environment. Oxygen was provided using a pump that supplied air through diffuser stones located near the bottom of each reactor to maintain a saturated DO concentration. Adequate mixing in each reactor was achieved by using a paddle connected to a variable speed motor and by installing baffles that prevented sediment resuspension. The reactors were operated in batch mode and the water sampled for

analysis was replaced with makeup water from the reservoir which had a low concentration of ammonium.

Sediment samples used in each reactor were taken from sampling stations RE02 and RE05 in April, 2010, 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. Fully nitrified waters from the UOSA WRF discharge were mixed with the reservoir waters to achieve the desired initial OxN concentration for each reactor. The total water volume for all reactors was 10 liters.

The first set of experiments consisted of four independent batch reactors (R1-R4) that were operated under anoxic conditions to quantify ammonium release from the sediments when nitrate was present in the water column. In the second set of experiments, 5 reactors (R5-R9) were operated to observe the effects of varying the C:N ratio on sediment ammonium release. The reactors were operated for approximately 40 days under different environmental conditions as described in Table 4-1. Nitrapyrin (2-chloro-6-(Trichloromethyl) pyridine) was used as a nitrification inhibitor in reactors 6 and 7 at a dose of 0.32 g per 300 mL of water. The C:N ratio was adjusted in each reactor by either adding sucrose to increase the carbon content or by adding water that had a high concentration of nitrate at computed ratios to achieve the desired C:N ratio values. The C:N ratio in reactor 5 was not altered throughout the experiment. The reactors were adjusted to the initial OxN concentration showed in Table 4-1. When a high concentration of OxN was required throughout the duration of the experiment, water extracted for analysis was replaced with water having high OxN concentration. On the other hand, when a low concentration of nitrate was needed, the reactors were fed with makeup water containing a low OxN concentration.

4.4.3 Analytical Methods
A HACH® LDO1-01 probe, a PHC101-01 probe, and a HACH® ORP Sension Gel-filled electrode probe were used to measure DO, pH, and ORP respectively, using a HACH® HQ40d

dual-input multimeter. Redox potential values were corrected by referencing them to the potential of the standard hydrogen electrode at pH 7 and 25°C. Water samples were taken using a syringe, filtered, and preserved when necessary either by acid addition or by freezing the samples. Oxidized nitrogen ($NO_3^- + NO_2^-$) (4500-NO_3-F), ammonia nitrogen (4500-NH_3 G), Orthophosphate (4500-P-F), and total and dissolved organic content (5310C) were analyzed in accordance with Standard Methods (AWWA et al. 2005). Total carbon and nitrogen from the sediments was measured using a Thermo Finnigan Italia S.p.A NC soil analyzer Flash EA 1112™.

4.5 Results and Discussion

Analysis of data collected during the last 34 years has demonstrated that the use of nitrate as a management alternative has helped reduce the release of undesirable substances from the deposited sediments under conditions of anoxia, thereby improving the water quality of the Occoquan Reservoir. The management strategy and the benefits provided to the reservoir are described elsewhere (Cubas et al. 2012a, OWML 2005, Randall and Grizzard 1995).

4.5.1 Field observations

During periods of hypolimnetic anoxia in the reservoir, ammonium began to accumulate in the water column as it was released from the sediments. The ammonium concentration in the input to the reservoir was low compared to the concentrations that were measured in the hypolimnion during periods of extended anoxia. Figure 4-3 shows monthly mean ammonium concentrations entering the reservoir through the two main tributaries from the year 2006 – 2009. Ammonium concentrations in Occoquan Creek were measured at Station ST10, while concentrations in Bull Run (including the UOSA WRF discharge) were measured at station ST40. From the figure, it may be seen that the mean ammonium concentration never exceeded 0.2 mg/L N for the period of record, except for the month of July 2007 where the concentration at ST10 reached a value of 0.28 mg/L N. It may also be seen from the plot that the ammonium concentration varied seasonally each year. The highest NH_4^+ concentrations were measured in both tributary streams during the summer months while the lowest concentrations were measured during the winter months. This same trend was observed in the main body of the reservoir and has been reported as well in other water bodies (York et al. 2010). Possible explanations for the observed pattern

are discussed later in this manuscript. Figure 4-4 shows that the highest ammonium concentration measured in the bottom waters of the Reservoir was more than an order of magnitude greater than the concentrations measured in the tributaries, suggesting that most of the ammonium measured in the reservoir originated from the sediments and was not imported directly from the watershed.

In the Occoquan Reservoir, periods of hypolimnetic anoxia developed shortly after the depletion of both DO and OxN from the water column. Shortly after DO and OxN were depleted, ammonium accumulated in the water column and the concentrations measured at different stations of the reservoir reached values as high as 5 mg/L N. Figure 4-4 shows an example of ammonium accumulation in the water column above the sediment-water interface at three different sampling stations during the years 2007 and 2010. During the month of April, before the DO and OxN were depleted from the water column, the ammonium concentration was low at the three sampling stations shown. After the development of the thermal stratification by mid May, sediment ammonium release became evident as ammonium accumulated in the water column. During the years 2007 and 2010, the concentration of both DO and OxN in the hypolimnion of stations RE02, RE05, and RE10 was very low (close to zero) starting in mid-May and remained constant throughout most of the summer. During the summer, ammonium began to accumulate in all three sampling stations at a similar rate, and the concentration at each station increased until it reached a maximum value by early fall before the overturn. The mean sediment ammonium release rate for the stations shown in Figure 4-4 was 508.7 ± 362.8 mg/d·m^2 and it ranged from $115 - 911$ mg/d·m^2 after correcting for inflows and outflows for each section.

At station RE02, the hypolimnetic ammonium concentrations in 2007 and 2010 increased until early November where peak values in excess of 4 mg/L N were reached. At stations RE05 and RE10, the ammonium concentration decreased by mid September after DO and OxN appeared in the water column and remained low through the rest of the year. Station RE02 is located at the deepest section of the reservoir ($\sim$ 20 m) near the high dam, and it generally takes longer for DO to reach the bottom waters after the disruption of the thermal stratification. Therefore, ammonium typically accumulates for a longer period of time at station RE02.

Ammonium, as it was released from the sediments, accumulated in the hypolimnion because the oxidation of NH_4^+ to nitrate by microbial nitrification was inhibited due to the low concentrations of DO that prevailed during the periods of anoxia (Beutel et al. 2008a, Wetzel 2001). Ammonium accumulation was also the result of lower assimilation rates that are commonly observed in anaerobic environments. It is known that microbial metabolism is reduced due to the lower energy yields obtained when alternate electron acceptors are used and results in lower growth and cell synthesis (Beutel et al. 2008b, Nizzoli et al. 2010, Stumm and Morgan 1996). After the fall turnover, when the bottom water DO was replenished, ammonium concentrations decreased due to rapid oxidation to nitrate.

During periods of hypolimnetic anoxia in the reservoir, the sediments released other substances besides ammonium, including phosphorus, iron, manganese, and organic matter. Of these substances, there is a particular interest in organic matter because of a possible relationship that may exist with sediment ammonium release. It was observed in the reservoir that during anaerobic periods, organic matter was released from the sediments after both DO and OxN were depleted above the sediment-water interface. Figure 4-5 shows that during the summer of 2010 for station RE02 and during the summer of 2007 and 2010 for station RE05, organic matter measured as TOC increased during the summer months. The average TOC concentrations from the beginning of the year until just before the development of the anoxic environment for RE02 in 2010 and for RE05 during 2007 and 2010 was 4.1, 5.5, and 4.6 mg/L, respectively. During the anaerobic period, the concentration of TOC for stations RE02 in 2010 and RE05 in 2007 increased to values greater than 10 mg/L while in station RE05 for 2010 the TOC concentration peaked at a value greater than 9 mg/L. The increase in TOC observed during the summer months was not accompanied by a TOC increase in the waters entering the reservoir. This suggests that the observed increase in the TOC concentration for all cases was due to the release of organic matter from the sediments.

The mechanisms that control sediment organic matter release in the Occoquan Reservoir are not fully understood. Decomposition of organic matter when the sediments are rich in organic content results in the release of particulate and dissolved organic matter in surface waters (Geurts et al. 2010). It is possible that the increase in the concentration of TOC could be the result of organic byproducts released from fermentation processes that are common in the sediments

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during extended anaerobic periods (Golterman 2001). A fraction of the released organic matter from these fermentation processes may likely be of high molecular weight compounds which are difficult for microorganisms to degrade. If this is the case, then the combined effect of having high molecular weight organic matter release and low consumption rates, typical of anaerobic environments, would result in organic matter accumulation in the water column.

The data shown in Figure 4-5 revealed that ammonium and organic matter released from the sediments followed similar trends. For the three years illustrated, it may be seen that ammonium and organic matter concentrations were relatively low before oxygen was depleted. In the case of ammonium, the concentration was close to 0 mg/L, while the TOC concentration was generally less than half the peak values reached later in the summer. After DO and OxN depletion, ammonium and TOC concentrations began to increase at almost constant (and similar) rates. Also, during this period, both ammonium and TOC concentrations fluctuated in a similar pattern. For example, when NH_4^+ decreased, TOC also decreased, and when NH_4^+ increased again in the water column, TOC also increased. This pattern may be clearly seen in Figures 4-5a and 4-5c. Finally, when DO was introduced back into the system, both ammonium and TOC decreased at a similar rate. A strong correlation was observed between the TOC and ammonium concentrations during the months following the nitrate depletion measured in the water above the sediment-water interface for stations RE02 and RE05 in 2010 ($R^2 = 0.85$, n = 25 for RE02 and $R^2 = 0.84$, n = 24 for RE05). A lower correlation was observed at station RE05 during the same months for the year 2007 ($R^2 = 0.51$, n = 21).

Figure 4-6 shows the relationship between ammonium and TOC concentrations pooled from the datasets previously shown in Figure 4-5. The plot shows that there was a good correlation between the TOC and NH_4^+ concentrations ($R^2 = 0.67$, n = 70), which prompts speculation that similar mechanisms affected both ammonium and organic matter release from the sediments during periods of anoxia. It is possible that sediment ammonium release was controlled by processes related to organic matter consumption and production (van Luijn et al. 1999, Wang et al. 2008). The correlation shows that both organic matter and ammonium accumulated in the water column at related rates during the anaerobic period of the summer months. This pattern was observed not only during the years shown in Figure 4-5, but as a general trend during the

summer months of most years. Further investigation is needed to better understand the processes involved in sediment organic matter release and the relationship with ammonium release.

Figure 4-7 shows a set of data extracted from the reservoir water quality dataset, and demonstrates how sediment ammonium release was reduced when OxN was present in the water column above the sediment-water interface. In Figure 4-7a, it can be seen that immediately after DO depletion, the OxN concentration was approximately 2.0 mg/L and began to decrease until it reached very low values in mid-July. During this period, sediment ammonium release was delayed and concentrations remained low compared to those that were observed when a completely anaerobic environment prevailed. After OxN was depleted from the water column, NH_4^+ began to accumulate until it reached a maximum concentration of ~ 6 mg/L N by the end of the summer. Figure 4-7b shows a case when OxN was not entirely depleted above the sediment-water interface during most of the summer. The average OxN concentration for the period shown in the plot after DO depletion was 0.85 mg/L N, and appeared to be sufficient to reduce sediment ammonium release. As long as a minimum OxN concentration of 0.5 mg/L N was present in the water column, the ammonium concentration at station RE10 never exceeded a value of 0.8 mg/L N. Finally, Figure 4-7c shows that when both DO and OxN were very low above the sediment-water interface, ammonium concentrations increased until OxN was reintroduced back into the system. Figure 4-7c shows that when the OxN concentration increased to values greater than 1 mg/L N, ammonium concentrations leveled off at approximately 1.0 mg/L N and remained constant until the end of the summer. The highest ammonium concentration measured for the three cases previously detailed was lower than the concentrations observed during the anoxic periods shown in Figure 4-4. These results suggest that OxN had an impact on the rate and the amount of ammonium release from the sediments in the reservoir. Although maintaining a relatively oxidized environment did not completely prevent sediment ammonium release, it was observed that OxN significantly reduced the ammonium concentration in the water column after DO was depleted.

Sediment ammonium release is mainly attributed to high rates of mineralization of nitrogen-rich organic matter where excess NH_4^+ is produced and released into the water column (Frazier et al. 1996, Satoh et al. 2002). If the release of ammonium from the reservoir sediments was mainly affected by the microbial decomposition of organic matter containing nitrogen, then ammonium

release should have occurred year round, independent of the ORP level of the system. However, the results show that nitrate and the ORP level affected the sediment ammonium release in the reservoir. Some of the ammonium produced by the mineralization of organic matter may be sorbed to the sediments, depending on the type of sediment (i.e., clays or sands) and their CEC (Blackburn and Henriksen 1983, Morin and Morse 1999, Verdouw et al. 1985). It was also possible that the ORP affected sediment ammonium release by changing the CEC of the sediments. Some authors have suggested that the sorptive capacity of the deposited sediments is greatly reduced when there is a loss of the oxidized environment at the sediment-water interface under anaerobic conditions (Wetzel 2001). After nitrate depletion in the water column, the oxidized environment at the sediment-water interface was lost. As a consequence, it was possible that exchangeable ammonium was desorbed from the sediment and resulted in ammonium accumulation in the water column. If this was the case, then sediment ammonium release during anaerobic periods would have been due to the combined effect of mineralization of nitrogen-rich organic matter and the decrease of the sediment CEC due to the establishment of anaerobic conditions.

A statistical analysis was conducted to determine if there was a significant difference between the mean summer ammonium concentrations in the hypolimnion when the OxN concentration was either high or low at stations RE02 and RE05 of the reservoir. Table 4-2 shows the mean concentration of OxN and ammonium during the summer months when DO was completely absent from the water column above the sediment-water interface. As can be seen from the table, the mean OxN concentration at station RE02 for the years 2004 and 2005 was approximately 1 mg/L N, while during the summer of 2009 and 2010 the concentration was almost zero.

The statistical analysis revealed that all the means for the ammonium concentration for station RE02 were not equal (p-value < 0.05). A multiple comparison test further showed that the mean ammonium concentrations at RE02 for the years 2004 and 2005 were equal but different from the means corresponding to the years 2009 and 2010. The mean ammonium concentrations for 2009 and 2010 were equal. A similar analysis done for the data corresponding to station RE05 revealed that all the means for ammonium concentration were not equal (p-value < 0.05). It can be seen from Table 4-2 that the OxN concentrations for 2007 and 2010 were very low compared

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to those from 2008 and 2009. A multiple comparison test showed that the mean ammonium concentrations for 2007 and 2010 and the mean concentrations for 2008 and 2009 were equal. However, the mean ammonium concentration for the years 2007 and 2010 was different from those for 2008 and 2009. Figures 4-8a and b illustrate the differences between the medians for the ammonium concentrations and the dispersion of the data for each year in stations RE02 and RE05.

These results show that there was a difference in sediment ammonium release and ammonium accumulation in the water column under anoxic conditions when the OxN concentration above the sediment-water interface was above 1 mg/L N. During the years when OxN was not completely depleted from the water column, the ammonium concentration was lower than when OxN was present above the sediment-water interface. Although the presence of OxN in the water column did not completely prevent the release of ammonium from the sediments, it was evident from the results that the presence of nitrate was associated with a decrease in the ammonium release when DO was not present. Although this observation clearly shows that nitrate in the Occoquan Reservoir had an impact on the amount of sediment ammonium release, it does not explain the mechanisms.

4.5.2 Microcosm experiments

Laboratory experiments were designed to determine if nitrate had a direct effect on sediment ammonium release during anoxic conditions and to elucidate the possible causes that controlled the phenomenon. The first two reactors from the first set of experiments had an initial OxN concentration of approximately 5 mg/L N. A time series for OxN and ammonium concentrations is shown in Figure 4-9a. From the figure it may be seen that OxN was depleted at approximately day 15 in both reactors as a result of denitrification. Also, sediment ammonium release began before OxN was completely depleted. In reactor 1 (R1), ammonium began to accumulate in the water column around day 5 and increased to a concentration value of ~ 1 mg/L N when the OxN concentration was still at 1 mg/L in the water column. The same trend was observed in R2, where ammonium began to accumulate in the water column on the second day of the experiment and the concentration constantly increased until the end of the experiment. By the time OxN was completely depleted from R2, the concentration of ammonium in the water column was already 3.1 mg/L N. Sediment ammonium release continued at a similar rate after OxN was depleted in

both reactors until it reached a maximum concentration of 1.7 and 4.0 mg/L N for R1 and R2, respectively.

In the next experiment, two reactors were operated in a similar manner with the exception that the water extracted for sampling was replaced with water containing a high OxN concentration (~ 10 mg/L N). This was done to maintain a high concentration of OxN in both reactors for the duration of the experiment. The results obtained from this part of the experiment are shown in Figure 4-9b. The OxN concentration was maintained above 4 mg/L N and 1.5 mg/L N in R3 and R4, respectively. Although both reactors always had a high concentration of OxN in the water column, sediment ammonium release was not prevented, as may be seen in Figure 4-9b. For R3, the ammonium concentration observed at the end of the experiment was high despite the high concentration of OxN in that reactor. In this reactor, the ammonium concentration peaked at a value of 0.9 mg/L N when the OxN concentration was 4.1 mg/L N. In R4, sediment ammonium release was evident although the OxN concentration remained above 1.5 mg/L N. The results also revealed that ammonium was released from the sediments at a similar rate regardless of the magnitude of the OxN concentration in the water column during the first 30 days of the experiment.

These results indicate that sediment ammonium release in the reactors was not affected by the different concentrations of nitrate in the water column when DO was absent from the system or by changes in the ORP level. This finding is in agreement with other researchers who have proposed that nitrate does not affect sediment ammonium release and that the mechanisms controlling this phenomenon are independent of the ORP levels (Beutel et al. 2008a, Martinova 1993, Weston et al. 2005). As explained earlier, if sediment ammonium release was the result of the mineralization of nitrogen in the organic matter, then ammonium release should occur despite the ORP level or the amount of nitrate in the water column, which was the case of the microcosm studies. As in the reservoir, ammonium accumulation in the water column was a result of inhibited nitrification due to the absence of DO in the water column and the lower microbial assimilation rates.

It was possible that there were other factors, such as the C:N ratio, that affected sediment ammonium release. Ammonium release due to mineralization depends on the amount of

nitrogen contained in the organic matter and the type of organic matter used as a source of energy and/or as a source for carbon (Goldman and Dennett 2000). The organic matter available to microorganisms may range from recalcitrant to readily available and the corresponding C:N ratio is expected to have an impact in the production of ammonium. Most of the recalcitrant organic matter in the sediments comes from humic substances that typically have low amounts of nitrogen (high C:N ratio) (Goldman et al. 1987). Readily available organic matter, on the other hand, may have a lower C:N ratio and may be comprised of smaller size molecules compared to humic substances. Unfortunately, because of the wide diversity of carbon and nitrogen substrates available in natural waters, the nature of organic matter supporting growth and the exact resulting C:N ratio are poorly known (Goldman and Dennett 1991, Weston et al. 2010).

To determine if the C:N ratio influenced sediment ammonium release in the reservoir, a series of experiments using sediment obtained from the reservoir was conducted. Five reactors, operated in parallel under different conditions, were used to measure sediment ammonium release during both aerobic and anoxic conditions, and to determine if it was dependent on the C:N ratio of the water above the sediment-water interface. The characteristics of the reactors are summarized in Table 4-3. Three reactors (R5-R7) were operated under aerobic conditions, while the remaining two (R8-R9) were kept anoxic throughout the duration of the experiment. The results were plotted and are shown in Figure 4-10.

R5 was designed as a control and was operated under aerobic conditions to observe if ammonium accumulated in the water column under normal conditions without altering any of the initial variables. This was done to replicate the aerobic environment that exists in the reservoir when there is no thermal stratification and when DO is distributed throughout the water column. The initial OxN concentration for this reactor was ~ 2 mg/L N and slowly decreased to 1.2 mg/L N by the end of the experiment, as was expected. The decrease in OxN was due to the replacement of the water volume used for sampling with low OxN containing water. Results showed that ammonium did not accumulate in the water column throughout the duration of the experiment.

R6 and R7 were aerobic and were operated under similar conditions as R5 with the exception that the two reactors were treated with a nitrification inhibitor to prevent the oxidation of

ammonium to nitrate. Both reactors had an initial OxN concentration of ~ 1.6 mg/L N, but R6 had a higher C:N ratio than R7, as shown in Table 4-3. The mean OxN concentration was lower in R6 than in R7 because the OxN concentration for R6 decreased to a lower value than R7 at the end of the experiment. It was possible that in R6, microorganisms assimilated more nitrogen due to the high organic matter concentration in this reactor. The high C:N ratio was maintained by adding sucrose to the makeup water used to replace the sampling water volumes. This readily available organic matter was available to the microorganisms within the sediments and also increased the C:N ratio because the nitrogen concentration was kept constant. Results showed that when nitrification was inhibited and the C:N ratio was low (R7), ammonium was released from the sediments. This result also shows that sediment ammonium release occurs when the environment is aerobic. Although a high sediment ammonium release rate was not expected, it was not uncommon to observe ammonium release when there was a high concentration of DO and OxN in R7. This phenomenon has been observed elsewhere (Beutel et al. 2008b).

Figure 4-10 shows that ammonium did not accumulate in R6 as it did in R7 although both reactors were aerobic and dosed with a nitrification inhibitor. However, reactor R6 was operated at a higher C:N ratio. By providing readily available organic matter to increase the C:N ratio, the system was prevented from being carbon limited so microorganisms would not scavenge for carbon as they did in R7. It can be seen from the plot that in R6, for the duration of the experiment, the ammonium concentration never exceeded 0.2 mg/L N despite the fact that a nitrification inhibitor was used in this reactor. The high C:N ratio in R6 prevented sediment ammonium release. It was expected that by providing readily available organic matter, microorganisms would use it preferentially as an energy source rather than other nitrogen containing organic matter such as amino acids, resulting in low ammonium production (Goldman and Dennett 1991). It was possible that by providing the system with high amounts of organic matter, not only was ammonium release prevented, but ammonium assimilation was enhanced. It is known that some microorganisms utilize ammonium as their preferred nitrogen source (Arango et al. 2008, Tupas and Koike 1991). Therefore, high concentrations of organic matter could have enhanced the assimilation of the ammonium that was released from the sediments. If this was the case in R6, then ammonium assimilation rates are higher than the ammonium production rates.

For a high assimilation rate to occur in the reactors, the increase in concentration of carbon and nitrogen should be accompanied by an increase in phosphorus concentration. The reactors used in this experiment were built with sediments and water from the reservoir so they were expected to be phosphorus limited. The reactors were not spiked with phosphorus during the experiment, but a small release of orthophosphate from the sediments was measured in R7. Phosphorus release was not expected in R6 and R7 because both reactors had a well oxidized environment, but phosphorus release from the sediments may be governed by mechanisms different from the classical iron-bound phosphorus explanation as explained by Golterman (2001) and Cubas et al. (2012a). As mentioned earlier, R6 and R7 were operated under similar conditions so the same amount of phosphorus release, if any, should have occurred. Results plotted in Figure 4-11 showed that orthophosphate (OP) accumulated only in R7 while the OP concentration decreased in R6. It was possible that the small amount of OP that was released from the sediment in R6 was rapidly assimilated by microorganisms along with ammonium when the concentration of organic matter was high. This suggests that the low ammonium concentration in R6 may was due to the high C:N ratio and the assimilation of ammonium that was released from the sediments.

A similar scenario regarding sediment ammonium release and the C:N ratio was observed in the anoxic environments that existed in R8 and R9. Figure 4-10 shows that sediment ammonium release was low in R8 and high in R9. R8 had an anoxic environment with a high C:N ratio that resulted from the addition of organic matter in the form of sucrose while maintaining the OxN concentration low. R9, on the other hand, had a low C:N ratio that resulted from the high concentration of OxN that was maintained during the experiment. Sediment ammonium release was observed only in R9, which was the reactor that had the lowest C:N ratio, while no significant sediment ammonium release was observed in the reactor that had a high C:N ratio (R8). These results were similar to those observed in the aerobic environment. Ammonium began to accumulate after day 4 at a very similar rate in both R7 and R9 and the concentrations peaked at the end of the experiment at a value greater than 0.9 mg/L N in both reactors. On the other hand, ammonium remained low in the reactors that had a high C:N ratio (R6 and R8). It is important to note that in R8, OP accumulated after day 10 because there was no DO or OxN to poise the ORP at a level that would have prevented the release of phosphorus from the sediments. The fact that OP accumulated in this reactor and was not rapidly assimilated

suggested that ammonium assimilation was also low. Thus, it is possible that the low ammonium concentration observed in R8 was the result of decreased sediment ammonium release due to the high C:N ratio and not the result of high assimilation rates in this reactor.

Nitrification inhibition in the aerated reactors allowed ammonium to accumulate in the water column, which demonstrated that ammonium production occurred regardless of the oxidation state, and that it was released from the sediment at a similar rate as under anaerobic conditions. The ammonium concentrations observed in R7 and R9 suggested that if ammonium was not rapidly oxidized to nitrate in the presence of oxygen then it would accumulate at a similar rate to that under anoxic conditions. The high ammonium production rate under aerobic conditions may be the result of the high microorganism activity due to the high energy yields resulting from the mineralization of organic matter when using oxygen as an electron acceptor. The results also showed that sediment ammonium release took place whether OxN was present or not in the water column under both aerobic and anoxic conditions. Ammonium accumulated in both R7 and R9 despite the high concentration of OxN observed in these two reactors.

The overall results show that the ratio of C:N played an important role in controlling sediment ammonium production and release in both aerobic and anaerobic environments. The low C:N ratio also contributed to the high ammonium production in the sediments. Many researchers had previously observed that when the C:N ratio of a system is low, microorganisms tend to produce an excess of ammonium as they scavenge for carbon to be utilized as a source of energy or cell synthesis (Blackburn and Henriksen 1983, Solaiman et al. 2009). As explained by some authors, this happens when microorganisms use carbon from nitrogen-rich organic matter, such as proteins, as an energy source and obtain the required nitrogen from sources other than ammonium (Goldman and Dennett 1991, Goldman and Dennett 2000, Jorgensen et al. 1994). If microorganisms use ammonium as a source for nitrogen, then ammonium accumulation should be lower than if they obtain nitrogen directly from organic matter containing nitrogen (Goldman et al. 1987). Another possible pathway for ammonium production under low C:N ratio happens when there is a lack of available organic matter and microorganisms obtain the necessary carbon from cell lysis. When cell lysis happens, ammonium is released and it may accumulate in high quantities (Frazier et al. 1996, Goldman et al. 1987). A misinterpretation of the mechanisms influencing sediment ammonium release can arise from the fact that ammonium accumulation is

seldom observed in lakes and reservoirs when they are completely aerobic. This may wrongly suggest that sediment ammonium release does not occur when the system is aerobic or when it is artificially aerated or oxygenated. The C:N ratio for the sediments of the reservoir measured at station RE02 during the spring 2009 averaged a value of 8.1. This ratio, according to the results reported here, and as expressed by other researchers, will not be sufficiently high to prevent ammonium release from the sediments (Goldman and Dennett 1991, Jorgensen et al. 1994). At the ratio observed (and lower), the data suggest that there will be a constant release of ammonium from the sediment and subsequent accumulation in the water column when there is not enough DO to oxidize it to nitrate.

4.6 Conclusions

Sediment ammonium release occurred in both the reservoir and in laboratory experiments as a result of mineralization of nitrogen rich organic matter. In the reservoir, ammonium accumulation in the water column above the sediment-water interface was lower prior to OxN depletion and increased as OxN was consumed within the sediments. Although poising the ORP at high levels by dosing high concentrations of nitrate reduced sediment ammonium release, it was not possible to completely prevent ammonium accumulation in the water column. It appeared that, in the reservoir, sediment ammonium release was a combination of the mineralization of nitrogen-rich organic matter and the release of exchangeable ammonium due to the decrease in ORP in the sediments. Sediment ammonium release was proven to occur in both aerobic and anaerobic environments. This observation supports the importance of considering sediment ammonium release rates when calculating oxygen demands in a lake or reservoir, even if ammonium is not observed in the water column under aerobic conditions. It was demonstrated in the microcosm study that the C:N ratio played a very important role in the production of ammonium in the sediments. When there was a high C:N ratio in the system, ammonium release from the sediments was low under both aerobic and anaerobic conditions. When the C:N ratio was low, then sediment ammonium release was high. Although it may be difficult to control ammonium release by manipulating the carbon or nitrogen content of the system, it may be a useful tool to determine the sediment ammonium release potential and rate. Finally, in the reservoir sediment ammonium release was concomitant with organic matter release, suggesting that a similar mechanism may be controlling both processes.

4.7 References

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Table 4-1. Initial conditions for reactors 5 – 9 used in the second part of the microcosm studies.

Reactor	Environment	Initial OxN (mg/L N)	Nitrification Inhibitor	C:N ratio
R5	Aerobic	2.0	NO	Standard
R6	Aerobic	< 2.0	YES	High
R7	Aerobic	< 2.0	YES	Low
R8	Anoxic	2.0	NO	High
R9	Anoxic	5.0	NO	Low

Table 4-2. Mean OxN and ammonium concentrations above the sediment-water interface at stations RE02 and RE05 during anoxic periods of the years selected.

Station	Year	OxN (mg/L N)	NH_4^+ (mg/L N)
RE02	2004	1.04	0.78
	2005	1.08	0.79
	2009	0.25	2.19
	2010	0.04	2.31
RE05	2007	0.13	2.16
	2008	0.63	0.63
	2009	1.48	0.79
	2010	0.10	1.70

Table 4-3. Characteristics for the reactors used in the second part of the experiment.

Reactor	Mean DO (mg/L)	Initial OxN (mg/L N)	Mean OxN (mg/L)	C:N ratio
R5	8.95 ± 0.25	2.05	1.49 ± 0.26	2.1 ± 0.3
R6	8.77 ± 0.79	1.62	0.62 ± 0.59	10.6 ± 9.2
R7	8.90 ± 0.69	1.65	0.99 ± 0.38	2.2 ± 0.2
R8	0.06 ± 0.02	2.16	0.02 ± 0.01*	10.1 ± 3.9
R9	0.13 ± 0.17	5.52	4.58 ± 0.42	0.8 ± 0.1

* Mean OxN concentration from day 10 – 50 after the initial OxN concentration was depleted

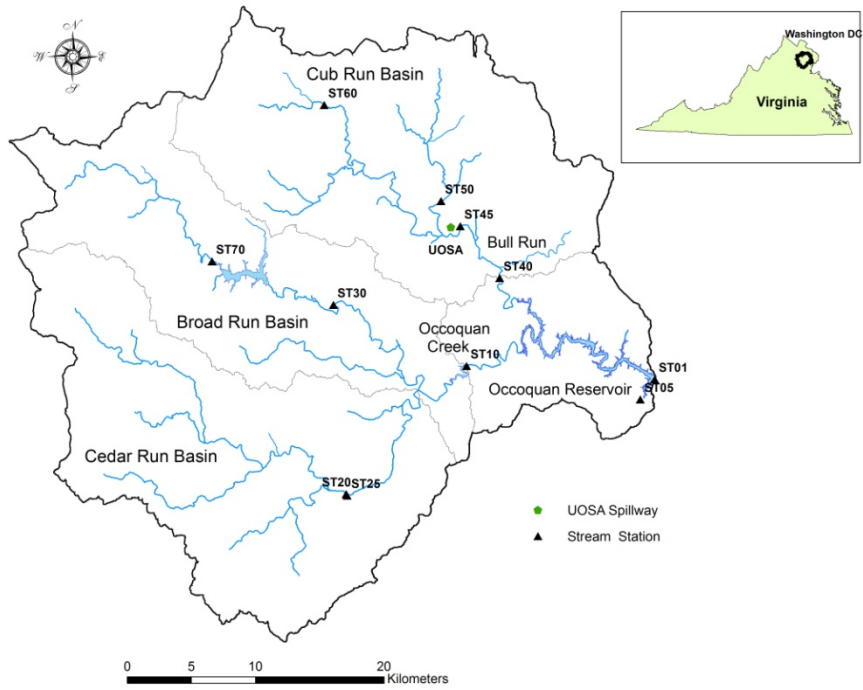**Figure 4-1.** The Occoquan Watershed and Reservoir.

Figure 4-2. Map of the Occoquan Reservoir showing sampling stations. Stations RE02, RE05, and RE10 were used to characterize the water quality of sections 1 and 2 of the reservoir shown in light blue.
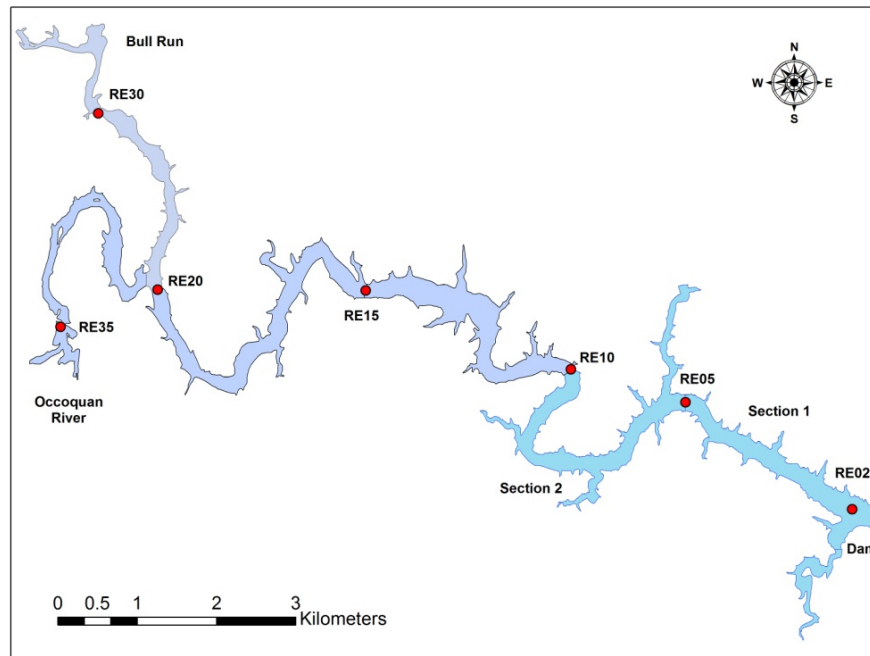
Figure 4-3. Monthly mean NH_4^+ concentrations measured in the two main tributaries of the Occoquan Reservoir from 2006 – 2009.
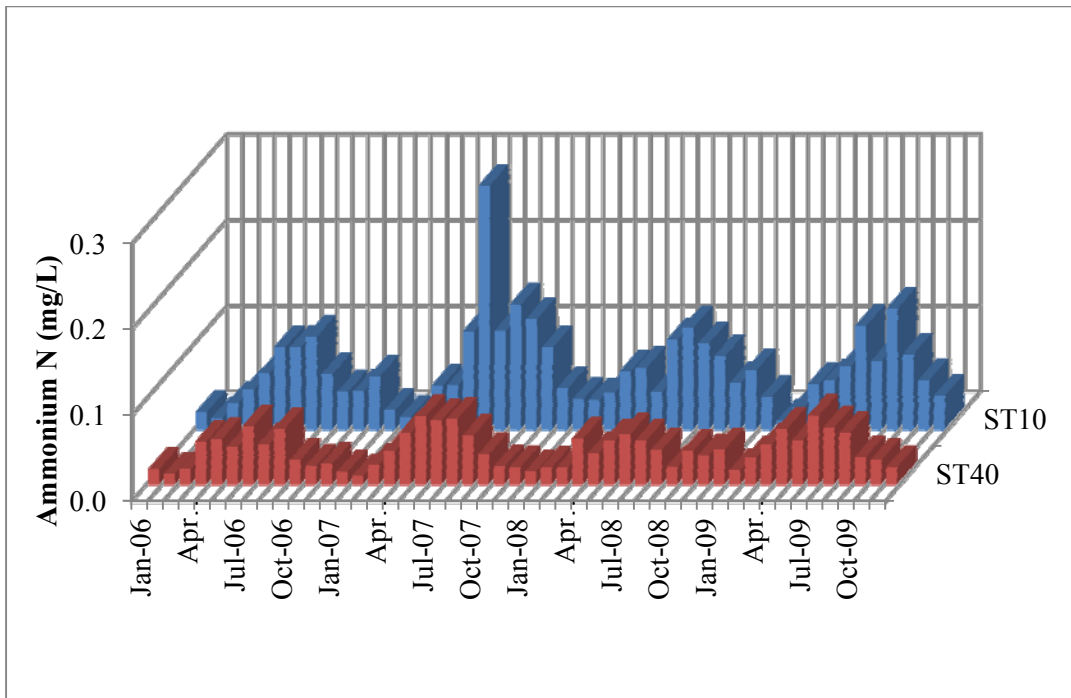
Figure 4-4. Time series for NH_4^+ concentration above the sediment-water interface for stations RE02, RE05 and RE10 of the Occoquan Reservoir.

Figure 4-5. Time series for DO, OxN, NH₄⁺ and TOC measured above the sediment-water interface of stations (a) RE02 2010, (b) RE05 2007, and (c) RE05 2010.
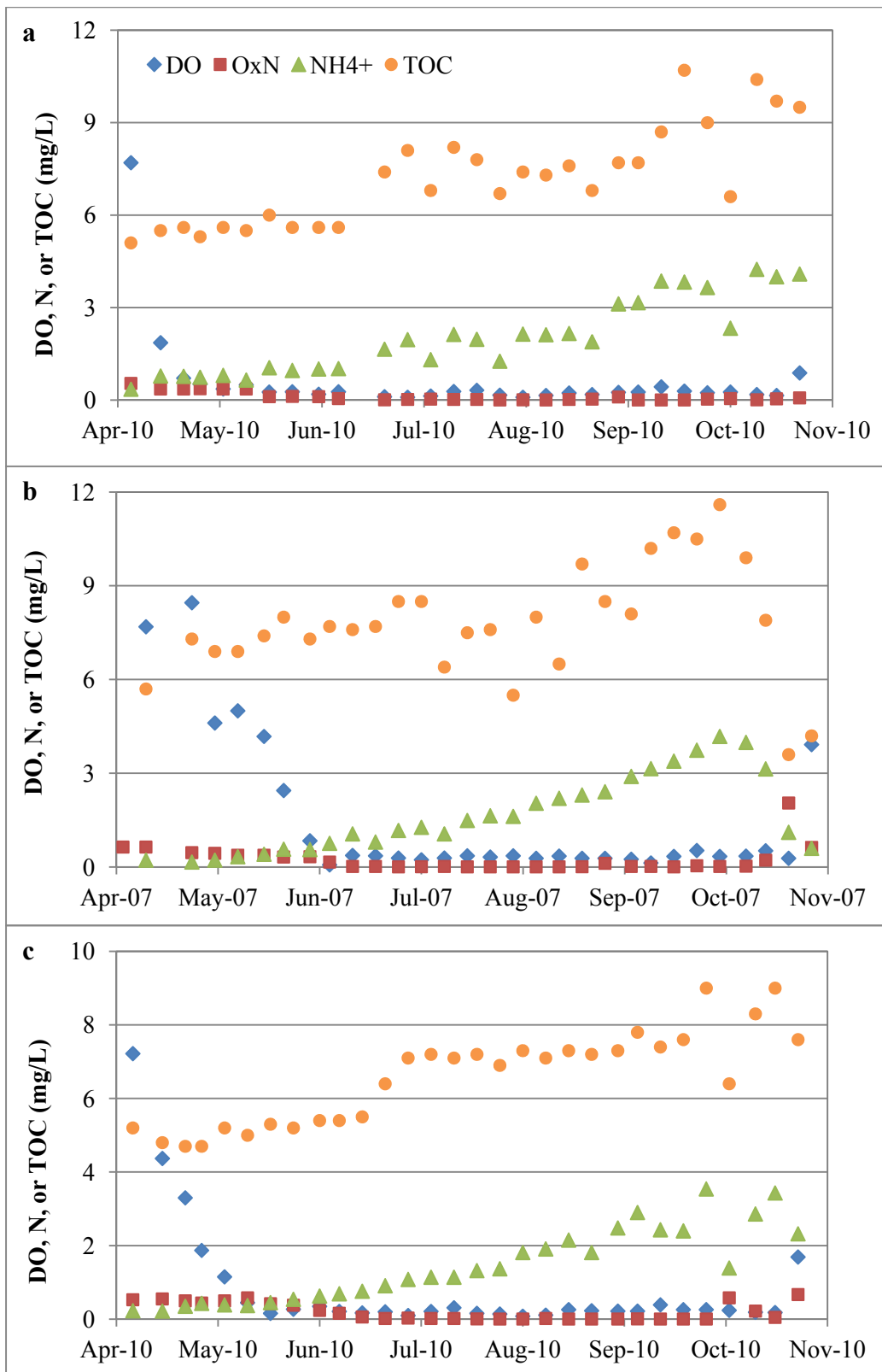
Figure 4-6. Correlation between TOC and NH_4^+ at the sediment-water interface during periods of hypolimnetic anoxia in the reservoir.
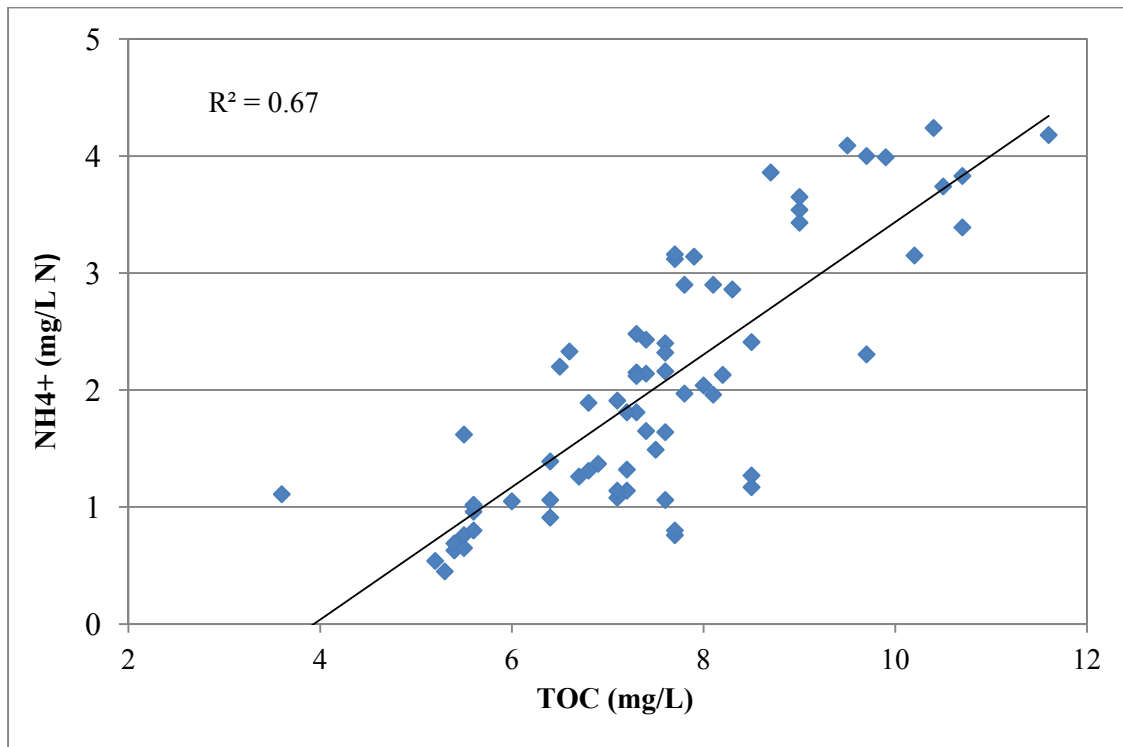
Figure 4-7. Time series for DO, OxN and NH$_4^+$ measured above the sediment-water interface of stations (a) RE02 2006, (b) RE10 2008, and (c) RE05 2009.

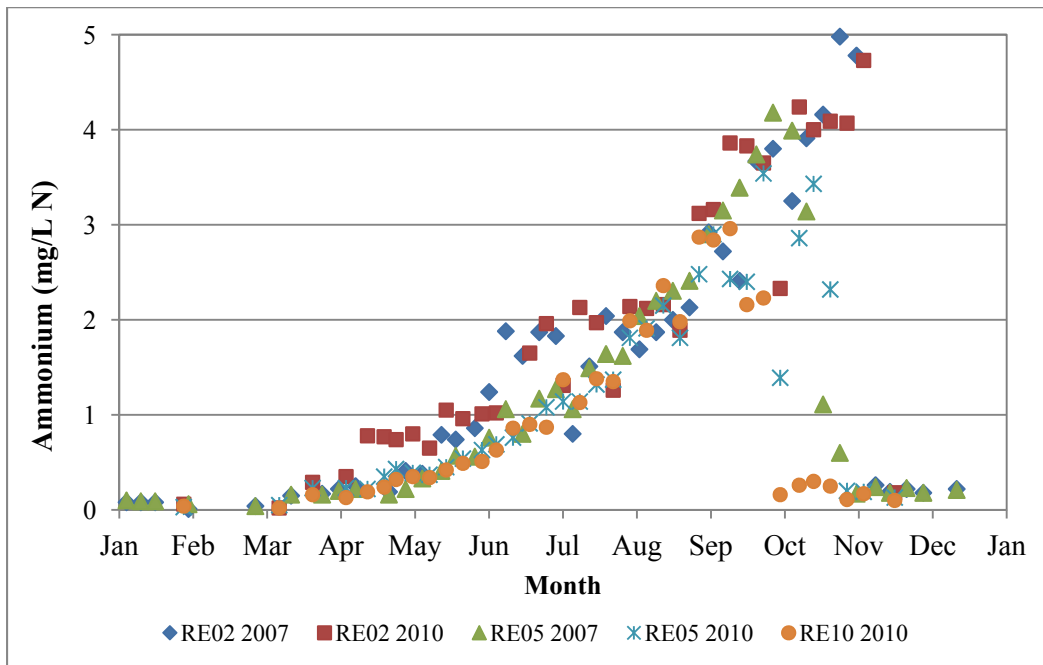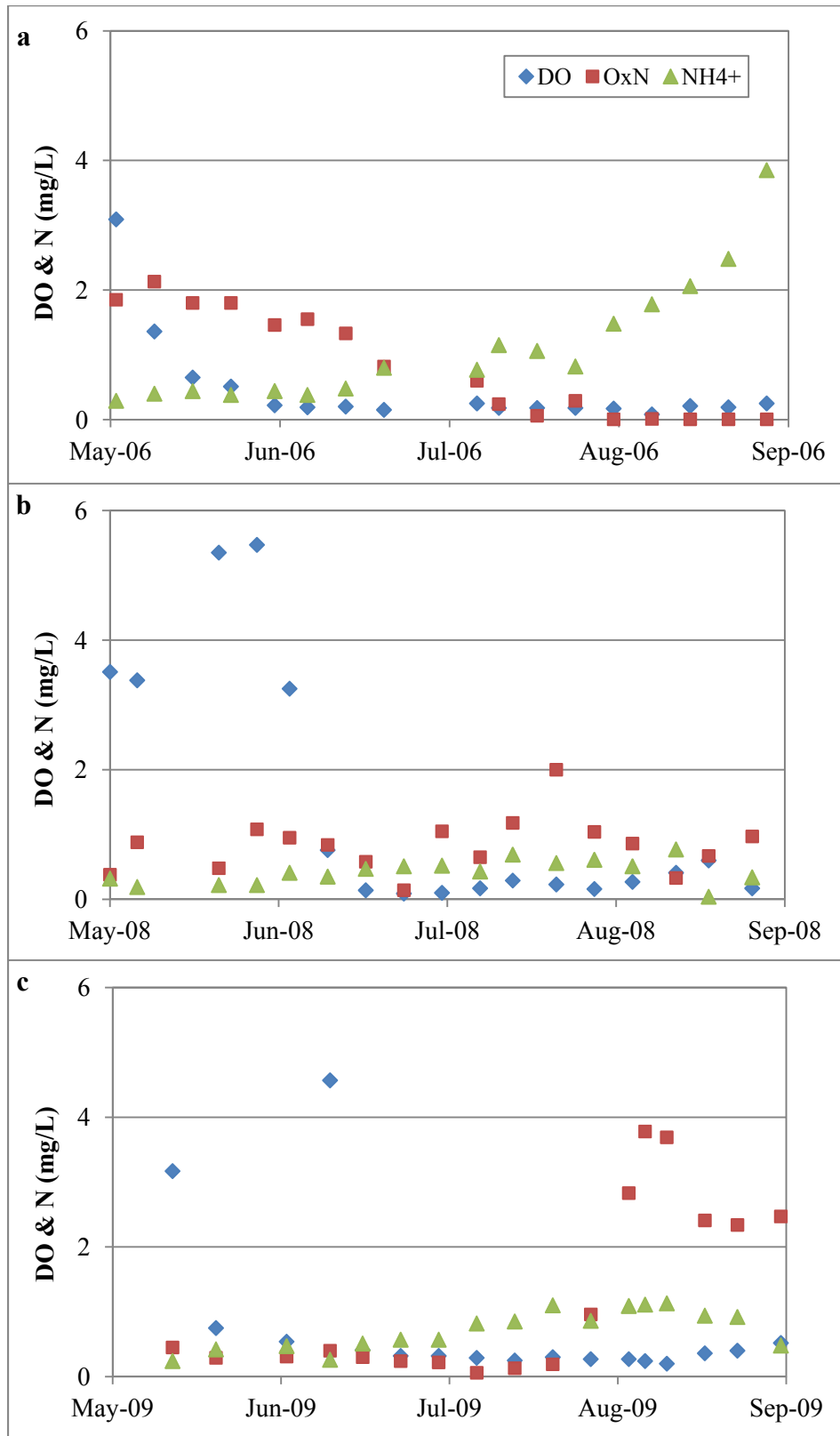**Figure 4-8.** Boxplot for ammonium concentration in selected years for station (a) RE02, (b) RE05. Their corresponding OxN concentrations are summarized in Table 2. Width of the box plot does not represent any aspect of the data.
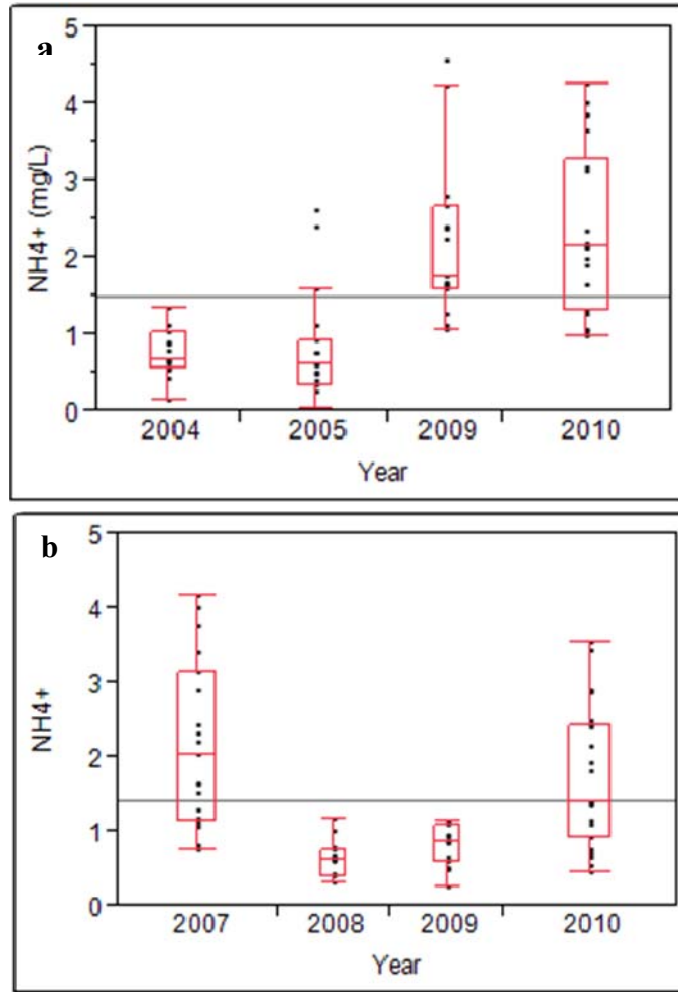
Figure 4-9. Time series for OxN and NH$_4^+$ measured above the sediment-water interface in microcosm studies using sediment from the Occoquan Reservoir. Results for reactors 1 and 2 are shown in Figure 4-9a and for reactors 3 and 4 in Figure 4-9b.
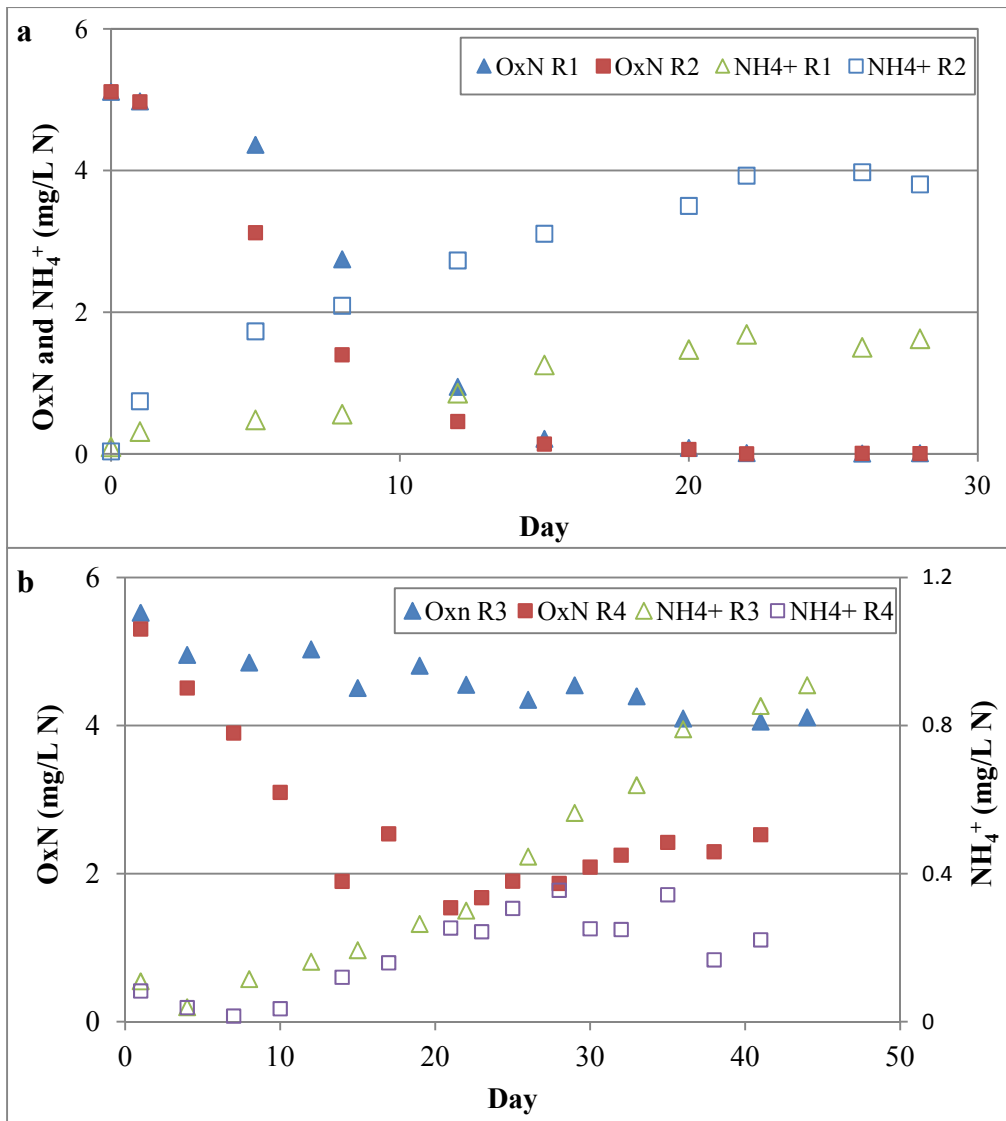
Figure 4-10. Time series for NH_4^+ concentration for laboratory experiment 2. R6 and R7 were operated under aerobic conditions and R8 and R9 were operated under anoxic conditions. R6 and R8 had a high C:N ratio and R7 and R9 had a low C:N ratio.
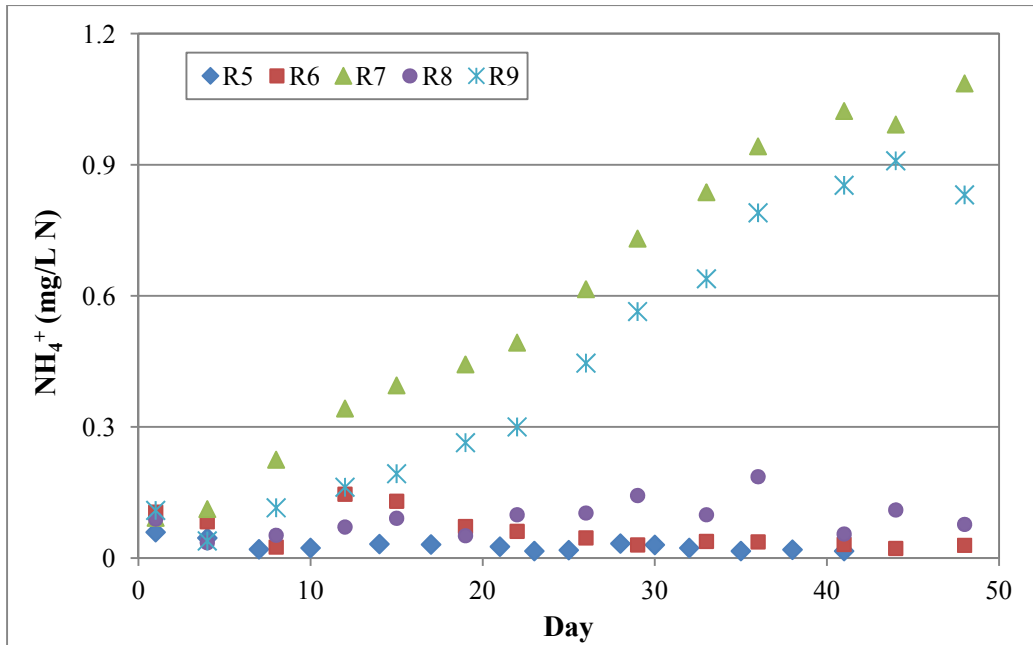
Figure 4-11. Time series for OP concentrations measured in R6 – R9 for experiment 2. R6 and R7 were operated under aerobic conditions and R8 and R9 were operated under anoxic conditions. R6 and R8 had a high C:N ratio and R7 and R9 had a low C:N ratio.
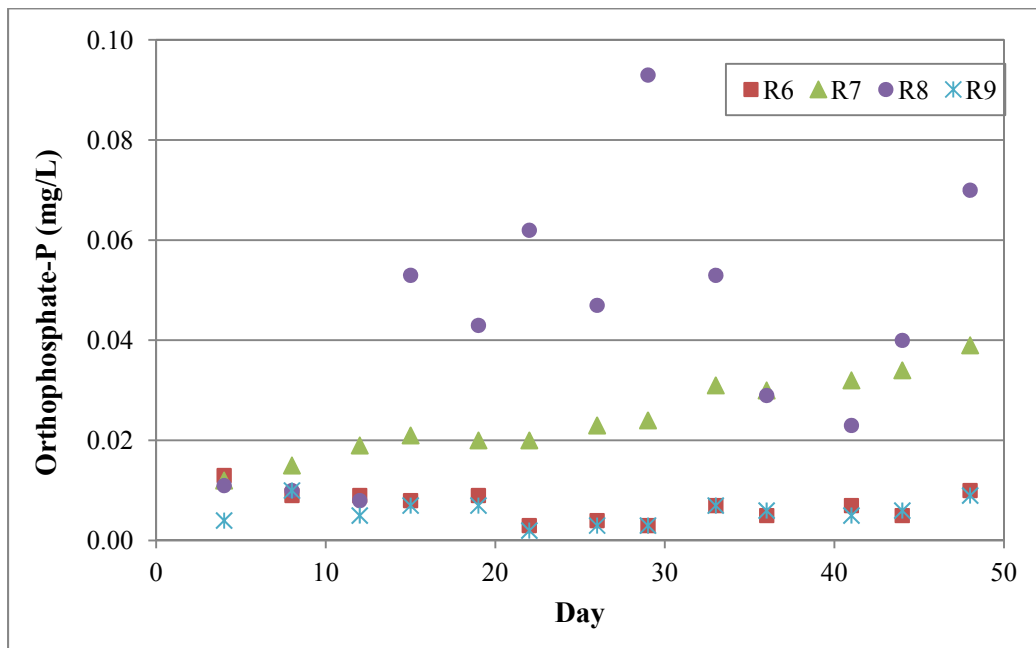
Chapter 5 - Effects of decreasing the nitrate input from an advanced water reclamation facility on the water quality of the Occoquan Reservoir

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5.1 Abstract

The Occoquan Reservoir is part of an indirect potable reuse system where reclaimed wastewater supplements the drinking water yield. To improve water quality in the reservoir, the water reclamation facility (WRF) discharges a nitrified product water that helps reduce the release of undesirable substances from the sediments during periods of hypolimnetic anoxia. Field sampling showed that when the oxidized nitrogen (OxN) concentration input to the reservoir was lower than 5 mg/L N during periods of thermal stratification, nitrate was depleted in the upstream areas of the reservoir, resulting in the release of ammonium and orthophosphate (OP) from the sediments downstream near the dam. When the OxN input to the reservoir was operationally increased to a concentration greater than 10 mg/L N, OP release was suppressed. Introducing OxN to the system decreased sediment ammonium release but it did not eliminate it. By discharging reclaimed water that contained nitrate levels greater than 10 mg/L N, reservoir water quality was protected and the discharged nitrate was converted to nitrogen gas as it moved through the reservoir.

Keywords: water reuse, nitrate, iron and phosphorus release, lake and reservoir management, sediments

5.2 Introduction

The Occoquan Reservoir in Northern Virginia is an artificial impoundment that is part of an indirect potable reuse system where an advanced WRF discharges high quality water into one of the two main tributaries to the impoundment, increasing the drinking water safe yield. The reservoir is a eutrophic system that undergoes an annual thermal stratification, and like many moderately deep, productive lakes, it experiences extended periods of hypolimnetic anoxia (Wetzel 2001). The resulting conditions increase the release of undesirable substances from the

deposited sediments, including ammonium, phosphorus and soluble metals, which decrease the water quality of the system (Cubas et al. 2012b).

To prevent the development of anaerobic conditions, the authorities managing the reservoir cooperate in using the WRF discharge to improve water quality in the reservoir. Depending on conditions in the reservoir, the WRF may be operated to discharge reclaimed water that is either low in nitrogen or highly nitrified. After the onset of thermal stratification in the reservoir, the WRF discharges water containing high concentrations of nitrate to maintain a relatively oxidized environment in the bottom waters. After the depletion of molecular oxygen, nitrate poises the oxidation reduction potential (ORP) to a level that prevents the release of phosphorus and reduced iron from the deposited sediments (Andersen 1982, Mortimer 1941, Prestigiacomo et al. 2009, Ripl 1976, Thirunavukkarasu et al. 2000). In the case of ammonium, there is some evidence that nitrate can decrease release from the sediments, but the mechanisms remain unclear (Cubas et al. 2012a). Although the use of nitrate as a restoration technique has been previously reported, the fact that it originates at a water reclamation facility and the manner by which it is transported to the bottom waters of the Occoquan Reservoir make the system unique.

Most lake and reservoir management approaches focus on decreasing external nutrient loads originating in the watershed (Hemond and Lin 2010). For this reason, stringent regulations are typically enforced for point and nonpoint pollution sources. The general consensus from a lake management point of view is that reducing the nitrogen load to a system is always beneficial. However, this concept is valid only if nitrogen is viewed solely as a nutrient without considering the properties of specific nitrogen species. For instance, nitrate contributes to the oxidation capacity of the water and plays an important role in lake acidity by increasing alkalinity when denitrification occurs (Hemond and Lin 2010, Stumm and Morgan 1996). Furthermore, decreasing the external nitrate input can result in phosphorus release from the sediments, thereby increasing internal phosphorus loading.

The stringent regulations on nitrogen discharges arise because some nitrogen species have the potential to stimulate phytoplankton productivity and exacerbate eutrophication, especially in nitrogen limited ecosystems (Beutel 2006). Another reason may be that some nitrogen species under certain conditions are toxic to aquatic organisms and humans (Camargo et al. 2005, Lewis

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and Morris 1986, Matthews et al. 2000). Therefore, a more complete understanding of the effects of nitrogen on aquatic systems is needed before implementation of any restoration technique aimed at increasing or decreasing nitrogen loads to a reservoir or lake system.

The physical properties of the Occoquan Reservoir favor high rates of denitrification, which control removal of oxidized nitrogen in the reservoir (Cubas et al. 2012b, Randall and Grizzard 1995). The physical properties that affect the denitrification rates are controlled by the morphology of the reservoir. Changes in the morphology of lakes and streams are known to cause changes in the physical and biochemical properties of aquatic systems, thereby altering the processes that occur in them (Wetzel 2001). For example, the shape of a lake or reservoir can directly affect the nature of the flow which subsequently affects the hydraulic retention time (HRT), mixing regimes and the transport of substances within the system (Rueda et al. 2007). In the Occoquan Reservoir, the morphology of the reservoir, together with temperature and density gradients that develop during the summer months, enhance the transport of nitrate to the anoxic bottom waters where denitrification occurs (Cubas et al. 2012c). This phenomenon, combined with the high inflow concentrations of nitrate, cause a gradual change in the rates of denitrification along the entire length of the reservoir (Banchuen 2003). Therefore, higher denitrification rates are observed in the upper reaches of the reservoir compared to those observed downstream. As a consequence of the unique morphology of the Occoquan Reservoir, most of the nitrate that enters the system is depleted before it reaches the dam, resulting in low nitrogen concentrations in the outflow.

The purpose of this study is to characterize the transport and consumption of nitrate in the Occoquan Reservoir between the point of entrance and the point of release at the dam. From this, it should be possible to determine if the amount of nitrate necessary to maintain an oxidized environment in the bottom waters. The benefits of using nitrate as a management technique are quantified in this study. By assessing the effects on nitrate on nutrient cycling in the reservoir, the consequences of using nitrate from a WRP as a management strategy can be determined.

5.3 Study Area

The Occoquan Watershed is located in the northern region of the state of Virginia, southwest of the city of Washington D.C., United States. The watershed is 1530 km^2 in size and is about 54%

forest, 28% urban and 18% of the land is divided between agricultural and pasture fields. The watershed is formed by four main headwater basins as shown in Figure 5-1. The Cedar Run and Broad Run sub-basins in the southwestern part of the watershed drain to Occoquan Creek. In the northern part of the watershed, Cub Run drains into Bull Run. The hydrologic characteristics of the watershed are described elsewhere (Xu et al. 2007). Together, Occoquan Creek and Bull Run form the two main tributaries of the Occoquan Reservoir, which serves as a public water supply and as recreational resource for more than 1.8 million people (OWML 2005). The physical characteristics of the reservoir are described elsewhere (Cubas et al. 2012b). The Occoquan Reservoir discharges to an embayment of the Potomac River, which is one of the principal tributaries of the Chesapeake Bay.

In the early 1960s, rapid development in the watershed, characterized by increasing transformations of rural areas to urban land uses resulted in high loads of both point and non-point pollution sources reaching the Occoquan Reservoir (Randall and Grizzard 1995). The subsequent deterioration of the reservoir water quality, coupled with the critical nature of the water supply, resulted in the development of a strategic water quality management plan by the state regulatory authority (SWCB 1971). This plan, which has come to be known as *The Occoquan Policy*, represented a milestone in water quality management, and also recognized the importance of reclaimed water as a resource. The policy resulted in the creation of the Upper Occoquan Service Authority (UOSA) water reclamation facility (WRF) which replaced 11 existing outdated water treatment plants. The UOSA WRF discharges into Bull Run approximately 10 km upstream of the confluence with Occoquan Creek (Figure 5-1). The WRF has the capacity for biological nitrogen removal and discharges a very high quality reclaimed water with low organic matter and phosphorus concentrations. During periods of hypolimnetic anoxia following the development of thermal stratification, the UOSA WRF is operated to provide a nitrified discharge that is used to prevent the onset of anaerobic conditions in the reservoir. During colder months when the reservoir waters are fully oxygenated, the WRF is operated to remove nitrogen and comply with existing regulations regarding point source nitrogen loads.

5.4 Materials and Methods

This study focused on the effects of nitrate on the water quality of the reservoir as well as the transport of oxidized nitrogen (OxN) from the point where it enters the reservoir (station RE30) to the downstream area near the dam (station RE02). For this study, the reservoir was divided into 5 segments where the sampling stations were used as the boundaries for each segment. The reservoir sampling stations used were RE02, RE05, RE10, and RE20 (confluence of Bull Run and Occoquan Creek), as shown in Figure 5-2. Station ST40 was used to measure the concentration of OxN that entered the reservoir through the Bull Run arm (Figure 5-1). Water quality data collected by the Occoquan Watershed Monitoring Laboratory (OWML) in 2009 were used to characterize the effects of nitrate on the water quality of the reservoir and to observe how nitrate was transported along the reservoir. Field sampling in the reservoir was performed weekly as part of the extensive water quality program conducted by OWML staff.

Water samples were taken in the hypolimnion approximately 30 cm above the sediment-water interface. Profiles of temperature and dissolved oxygen (DO) concentrations were created by making measurements at 0.75 m increments for the first 3 m from the surface, and at 1.5 m increments thereafter until reaching 30 cm above the sediment-water interface. To focus on periods of hypolimnetic anoxia which developed after the onset of the thermal stratification, the data used were obtained from the April to October period.

A YSI 600 XL Sonde® was used to measure temperature and DO. Oxidized nitrogen (NO_3^- + NO_2^-) (4500-NO_3-F), ammonia nitrogen (4500-NH_3 G), and Orthophosphate (4500-P-F) were analyzed in accordance with Standard Methods (AWWA et al. 2005). Previous nitrogen studies performed by the OWML have found that nitrite (NO_2^-) concentrations are very low compared to nitrate concentrations, therefore the measured OxN concentrations represent mostly nitrate.

5.5 Results and Discussion

The Occoquan Reservoir undergoes an annual thermal stratification during the warmer months of the year. To illustrate this, the vertical temperature and DO profiles taken from the deepest waters of station RE02 at various times during the year 2009 are shown in Figure 5-3. During the colder months, from November – March, the water column was well-mixed with little

vertical variation in temperature. Beginning in April, surface water warming initiated the establishment of thermal stratification and the epilimnetic layer progressively thickened through the summer, reaching a maximum value in early September. By October, cooling of the air mass in contact with the reservoir surface, coupled with less direct solar radiation and less resistance to wind mixing in the water column, resulted in the breaking of the stratification and the waters again became vertically mixed. By mid-November, the entire water column had cooled, with temperatures dropping below 13°C as seen in Figure 5-3a.

The effects of the annual thermal stratification on vertical profiles of DO in the reservoir are shown in Figure 5-3b. During the stratification period, the cooler layer of higher density water of the hypolimnion cannot be replenished with oxygen from the atmosphere because the density differential forms an effective barrier to the transfer of DO between the layers (Matthews and Effler 2006, Wetzel 2001). The oxygen supply available for biological activity in the hypolimnion is then progressively depleted until the concentration approaches zero and cannot be replenished until the reservoir is again thermally homogenous. In Figure 5-3b, it may be seen that the reduction of DO concentrations in the bottom waters began between the months of April and May. By June, oxygen was absent from the deep waters, and by the month of July, little oxygen was present below a depth of about 5 meters. Oxygen penetration was observed in deeper water of the reservoir in early October and complete disruption of the thermal stratification occurred in the month of November.

After the development of the thermal stratification, the loss of DO in the hypolimnion due to different process (i.e. organic matter mineralization, microbial respiration, and nitrification) was followed by the establishment of anaerobic conditions. Periods of anaerobic conditions in lakes and reservoirs promote the release of undesirable substances from the deposited sediments, including reduced metals such as iron and manganese, and nutrients such as nitrogen, mostly in the form of ammonium, and phosphorus in the form of orthophosphate (OP) (Beutel 2006, Correll 1998, Mortimer 1941). In the Occoquan Reservoir, the authorities managing the reservoir take advantage of the nitrate originating at the WRF as an alternate electron acceptor to prevent the development of anaerobic conditions in the deep waters of the reservoir. This management alternative has been proven to be effective in preventing the release of phosphorus, ammonium, iron, and manganese from the deposited sediments as long as a concentration of

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approximately 1 mg/L N of oxidized nitrogen (OxN) is maintained just above the sediment-water interface (Cubas et al. 2012b, Randall and Grizzard 1995).

Figure 5-4 shows the monthly variation in the OxN concentrations entering and leaving the main body of the reservoir through the year 2009, as affected by the operational mode of the WRF. Most of the nitrate that entered the reservoir was transported from UOSA and entered the impoundment through Bull Run at station ST40. During the months of January – March and October – December, the nitrate input to the reservoir from Bull Run was relatively low and never exceeded 5 mg/L N. During the same months, the WRF was operated in a nitrification/denitrification mode to decrease total nitrogen input to the reservoir. OxN concentrations measured at ST40 began to decrease after the month of April and remained low until the month of June, just before the nitrate input to the reservoir from the WRF increased. It was possible that during these months denitrification was taking place in the bottom waters of the stream. High rates of organic matter degradation typical of the warmer months resulted in areas of low DO concentration at the sediment-water interface. These areas of low DO may have enhanced the denitrification process thereby reducing the concentration of nitrate in Bull Run, consistent with the observations made by other researchers regarding denitrification in streams (Birgand et al. 2007, Tomaszek and Czerwieniec 2003).

During the months of August – October, when the hypolimnetic waters of the reservoir were anaerobic, the WRF was operated to discharge nitrified water that would provide nitrate to the bottom waters and reestablish an oxidized environment. During this time period, the OxN concentration measured in Bull Run (ST40) ranged from 6 – 13 mg/L N. The monthly mean OxN concentration measured in Occoquan Creek (ST10) was very low throughout the whole year, and the total contribution of nitrate was considered negligible. The OxN concentration measured in Occoquan Creek was low because the nitrate input from watershed sources is generally low. Also, during extended periods of low precipitation in the watershed typical of the summer months, the inflow from Occoquan Creek is greatly reduced and most of the water that enters the reservoir originates at the WRF.

One of the features that can be deduced from Figure 5-4 is the capability of the reservoir to consume most of the nitrate that entered the system. Figure 5-4 shows that the OxN

concentration measured at the outlet of the reservoir (ST01) never exceeded 2.5 mg/L N even though the OxN concentration in the input exceeded 10 mg/L N. The nitrate depletion along the length of the reservoir is attributed to high denitrification rates, which are favored by high concentrations of organic matter and low DO concentrations at the sediment-water interface (Randall and Grizzard 1995).

During periods of thermal stratification in the reservoir, the flowing waters of Bull Run, shaded by trees, are generally at a lower temperature than the surface waters of the impoundment. One consequence of this temperature difference is that, on entering the reservoir, the stream waters tend to plunge until they encounter waters of similar temperature and density. As a result, the Bull Run inflow during the summer months migrates towards the bottom waters of the reservoir. This plunging and migrating phenomenon is of great importance because the inflow from Bull Run, containing high concentrations of nitrate during the summer months, is preferentially delivered to the bottom waters of the upper reservoir (OWML 2005). However, not all the nitrate entering the reservoir migrated to the bottom. Cubas et al. (2012c) calculated that, during the years 2006 and 2007, approximately 15% of the nitrate that entered the reservoir from Bull Run was directed towards the epilimnion during the summer months. The plunging phenomenon, combined with the geomorphology of the reservoir and the high nitrate input, favors high rates of denitrification in the upper reaches of the reservoir. Therefore, most of the nitrate that entered the system was depleted before it reached the downstream waters near the dam.

Figure 5-5 illustrates the variation of DO and OxN concentrations during 2009 at the confluence of Bull Run and Occoquan Creek (station RE20). The reservoir was saturated with respect to DO during the months of February and March. By mid-April, after the onset of thermal stratification, DO concentrations began to decrease as the water temperature increased (Figure 5-3). By the month of June, the DO was near zero at the bottom waters and remained low until late August. By early September, oxygen began to penetrate to the bottom waters as a result of the stratification disruption and mixing of the water column and the DO concentration increased until it exceeded 8 mg/L N by the month of October.

From February to early March, the OxN concentration remained constant at approximately 4 mg/L N. Near the end of March, the OxN concentration began to decrease, most likely due to denitrification that occurred in segment 5 of the reservoir. By early April, the OxN concentration decreased to approximately 1 mg/L N and remained low through the end of June. During July and August, when the WRF increased nitrate input to the reservoir and the OxN concentration measured at RE20 increased until it reached approximately 5 mg/L N. The input of OxN to the reservoir was high during these two months (> 7 mg/L N) but, as previously explained, denitrification upstream in the Bull Run arm decreased the OxN concentration that reached this station. The decrease in OxN concentrations in early August was the result of high rates of denitrification which are typical in the upper reaches of the reservoir during the warmer months of the year. In September, the DO began to penetrate the bottom waters resulting in lower denitrification rates at station RE20 and upstream. As a result, OxN accumulated in the water column because of the continued high input to Bull Run from the WRF. Beginning in October, when the WRF restarted the denitrification process, the nitrate input to the reservoir decreased, thereby reducing the OxN concentrations reaching the reservoir for the remainder of the year.

The addition of WRF-derived nitrate to oxygen-depleted waters produced an oxidized environment in the deep waters of the reservoir, and was an effective strategy to reduce the release of undesirable substances from the deposited sediments. To illustrate this, time series data for DO, OxN, orthophosphate (OP), and ammonium (NH_4^+) measured at the bottom waters of stations RE10, RE05, and RE02 during the months of April – October are shown in Figure 5-6. Figure 5-6a shows that at station RE10, DO was depleted by the end of June and remained low until early September. At station RE05 (downstream from RE10), DO was depleted from the bottom waters by the end of May and remained low until the end of the summer (Figure 5-6b). The OxN concentration measured at both stations was low from late April to early July when nitrate input to the reservoir was also low. During the month of June, when the concentrations of both DO and OxN were very low above the sediment-water interface, OP began to accumulate in the water column as it was released from the sediments at both stations. OP reached a maximum concentration of 0.06 mg/L P at both stations, although the maximum value was observed approximately three weeks earlier at station RE05 than in RE10. OxN concentration began to increase by mid-July at station RE10, and by the end of July at station

RE05 after the WRF increased the nitrate input to the reservoir. When the OxN concentration increased to a value greater than 2 mg/L N, phosphorus release from the sediments ceased and the OP concentration in the water column decreased to less than 0.01 mg/L P in these two stations.

At station RE02 near the dam, both DO and OxN were depleted from the water column by early June as seen in Figure 5-6c. At this station, the OxN concentration reached a value close to zero during the months of June, July and mid-August. Sediment OP release began immediately after OxN was depleted above the sediment-water interface in early June. OP accumulation in the water column was observed throughout the whole anaerobic period and the maximum concentration measured was 0.22 mg/L P which was more than 3 times the maximum values measured at RE05 and RE10. The difference in OP concentrations may have been because at station RE02 the anaerobic period extended for a longer period of time than in the two stations upstream. The OP concentration at the end of the summer began to decrease before OxN was observed in the water column. It was possible that the nitrate from the WRF reached this station at the same date when OP concentration began to decrease and that denitrification occurred although OxN was not observed in the water column until approximately two weeks later. By the end of August when OxN had again accumulated in the water column, the OP concentration decreased to values below 0.01 mg/L P.

Nitrate is used as an alternate electron acceptor by certain microorganisms to harness the energy released in the oxidation of organic compounds following the thermodynamic constraints of microbially-mediated redox processes (Madigan et al. 2003, Stumm and Morgan 1996). Nitrate is then capable of poising the ORP at a sufficiently high level which prevents OP release. According to the classical explanation of phosphorus release from sediments, OP is tightly bound to iron (III) particles in the sediments when the system is in an oxidized state. When both DO and nitrate are depleted from an aquatic system, the ORP decreases as organisms shift to less desirable electron acceptors, and iron (III) is reduced to iron (II), causing the iron to become soluble. When this happens, the OP bound to the iron is released to the water column (Søndergaard et al. 1999, Wauer et al. 2005, Weston et al. 2005).

It has been suggested by some authors that a nitrate concentration of 1 mg/L N is sufficient to poise the ORP at a level that will prevent the release of OP from the sediments (Andersen 1982). The difference between the OP concentrations measured at station RE02 and at stations RE05 and RE10 during the summer months may be due to the different concentrations of nitrate that existed in each station. For example, in the reservoir, higher values of OxN resulted in lower concentrations of OP in the water column. For instance, at station RE10, the OxN concentration never reached a value of zero while at station RE02 the OxN concentration was almost zero, and was associated with higher accumulation of OP at RE02 than at RE10. This results are in agreement with some researchers who suggested that phosphorus release from sediments progressively decreased as the nitrate input increased until it was totally suppressed at high concentrations of nitrate (Cubas et al. 2012b, Foy 1986). This suggests that the amount of nitrate that ultimately reaches each segment of the reservoir will have an impact on the amount of phosphorus released from the sediments.

Figures 5-6a and b show that at stations RE05 and RE10, ammonium began to accumulate in the water column when the DO and OxN concentrations were low. When OxN was reintroduced into the system, sediment ammonium release decreased and the concentrations measured in the water column remained at their maximum values of 0.75 and 1.1 mg/L N, at stations RE10 and RE05, respectively. The difference in ammonium concentrations between these two stations was probably because the OxN concentrations were lower in station RE05 during the month of July. The lower OxN increased sediment ammonium release at station RE05 and resulted in a higher concentration of ammonium in the water column. At station RE02, ammonium began to accumulate in the water column by late May after both DO and OxN were depleted (Figure 5-6c). The ammonium concentrations fluctuated around a value of 2 mg/L N and several measurements exceeded 4 mg/L N. Ammonium concentrations in the water column did not decrease when nitrate reached the bottom waters of this station by mid-August. In fact, ammonium only disappeared when the DO concentration began to increase in the water column at the onset of the fall overturn.

Ammonium inputs from the watershed were low throughout 2009, while the concentrations measured in the water column of the reservoir during the anaerobic periods were high, suggesting that the likely source of ammonium was the sediment. When DO was present in the

water column before June and after September, ammonium accumulation was low because conditions were satisfactory for rapid biological oxidation of ammonium to nitrate. When OxN was present in the water column after DO depletion, sediment ammonium release was low and the concentration above the sediment-water interface never exceeded 1.0 mg/L N. When OxN concentrations declined to values near zero, sediment ammonium release became more evident and the water column concentrations were between 2-4 times higher than when OxN was present. These results suggested that the presence of nitrate in the water column was able to reduce sediment ammonium release but was not able to completely prevent it.

It is important to note that when the input OxN concentrations were low (< 5 mg/L N), only a very small amount of nitrate reached the downstream area of the reservoir. During the months of April – June after the onset of thermal stratification when the inputs of nitrate from the WRF were low and the denitrification rates were high, only a small fraction of the nitrate reached station RE10 and RE05 and practically no nitrate reached station RE02. When the WRF increased the nitrate input to the reservoir after the month of July, the fraction of nitrate that reached the lower areas of the impoundment increased. Following the change in WRF operations, a spike in the OxN concentration was observed at stations RE10 and RE05 by the end of July but no spike was observed at station RE02. The OxN concentration at RE10 began to increase 15 days after the high nitrate inflow entered the reservoir. This value is very close to the average retention time of 12 days between the inlet of the reservoir and station RE10 typical for the summer month when the inflow is low. In the days following the maximum OxN value in July, concentrations decreased and reached 2 mg/L N at RE10 and RE05 by the end of August. Finally, during the month of September prior to the fall overturn and when the OxN concentration entering the reservoir was higher than 10 mg/L N, the concentration of OxN that reached RE10 and RE05 was approximately 2 mg/L N and was lower than 2 mg/L N at station RE02. It appears that for this reservoir system, when using nitrate to maintain an oxidized environment in the bottom waters of the downstream area of the reservoir, a concentration of at least 10 mg/L N is needed at the inlet of the reservoir.

An additional benefit obtained when using nitrate to maintain an oxidized environment is the production of alkalinity from denitrification. Figure 5-7 shows that, during the month of April, the deep water alkalinity at stations RE05 and RE10 decreased by nearly half. During this

month, decomposition of organic matter was high, as evidenced by the rapid depletion of DO. A high rate of organic matter degradation produces excess CO_2 in the water column and the excess CO_2 may be expected to consume some of the natural alkalinity (Stumm and Morgan 1996). After the depletion of DO, and in the presence of OxN, biological denitrification was observed, with the expected production of bicarbonate serving to increase the alkalinity in the water column.

5.5.1 Water quality implications

The Occoquan Reservoir plays a unique role with respect to public water supply and indirect potable reuse of reclaimed water. During the summer, the high quality discharge from the UOSA WRF serves as a valuable management tool. The presence of nitrate prevents the release of undesirable substances from the deposited sediments during periods of thermal stratification and hypolimnetic anoxia in the reservoir. Because this unique approach to nutrient management has been a key component in the successful management and water quality improvement in the Occoquan Reservoir, several questions have been raised about the effects of implementing stringent nitrogen removal regulations in wastewater treatment plant effluents. Currently, point source nutrient control requirements mandate the UOSA WRF remove total nitrogen to an annual average of 8 mg/L in the plant discharge at an annual average flow of approximately 160 $\times$ 10^3 m^3/day (OWML 2005). Because of the need to avoid discharging excessive nitrogen to estuarine tributaries of the Chesapeake Bay, regulatory agencies are considering even more stringent regulations regarding total nitrogen discharge from the WRF. Data collected by the OWML in the last 40 years and results from experimental analysis have demonstrated that there is a well understood water quality benefit derived from the maintenance of oxidized nitrogen in the deep waters of the reservoir during certain periods of the year (Banchuen 2003, Cubas et al. 2012b, Randall and Grizzard 1995). Therefore, it seems prudent to assess the water chemistry and properties of the overall system prior to initiating any major changes in WRF operation and management protocols.

It has been shown in this study that low nitrate inputs have resulted in extended period of anaerobic conditions which enhanced the release of nutrients from the sediment in the deep waters of the downstream areas of the reservoir. The nutrient release is detrimental to water quality and may actually cause a net increase in nutrient discharges to the receiving waters

downstream of the reservoir. In the case of the Occoquan Reservoir, decreasing nitrate inputs in order to reduce the total nitrogen discharge from the reservoir may have the unintended consequence of increasing nitrogen releases by promoting extended periods of anaerobic conditions in the bottom waters of the reservoir (Cubas et al. 2012a). The potential for such increased releases of sediment ammonium must be considered when determining the overall effects of point source nitrogen control as a means of reducing nutrient fluxes through the reservoir and into the Chesapeake Bay. In addition, anaerobic conditions in the reservoir may result in the release of OP, iron, manganese, organic matter, sulfur and other substances that may be detrimental to water quality and cause difficulties in water treatment operations. Finally, it has been shown in this study and in others (Cubas et al. 2012c) that the reservoir has the capacity to remove most of the nitrate that enters the system without having an increase in the amount of nitrogen in the discharge.

5.6 Conclusions

For nearly 34 years, in addition to supplementing the safe drinking water yield of the Occoquan Reservoir, nitrified flows from the UOSA WRF have served to prevent the release of undesirable substances from the deposited sediments during periods of thermal stratification. When periods of hypolimnetic anoxia prevail, delivery of nitrates originating from the WRF discharge, serve to maintain an oxidized environment in the bottom waters at a relatively low cost. Results suggest that decreasing nitrate inputs to the reservoir will result in a noticeable increase in the release of phosphorus from the sediments during periods of thermal stratification. It was demonstrated that the reservoir itself had the capacity to remove most of the nitrate input via the denitrification process which had the additional benefit of increasing the alkalinity of the water. Decreasing the nitrate input may result in higher concentrations of nitrogen and other unwanted constituents originating from the deposited sediments.

5.7 References

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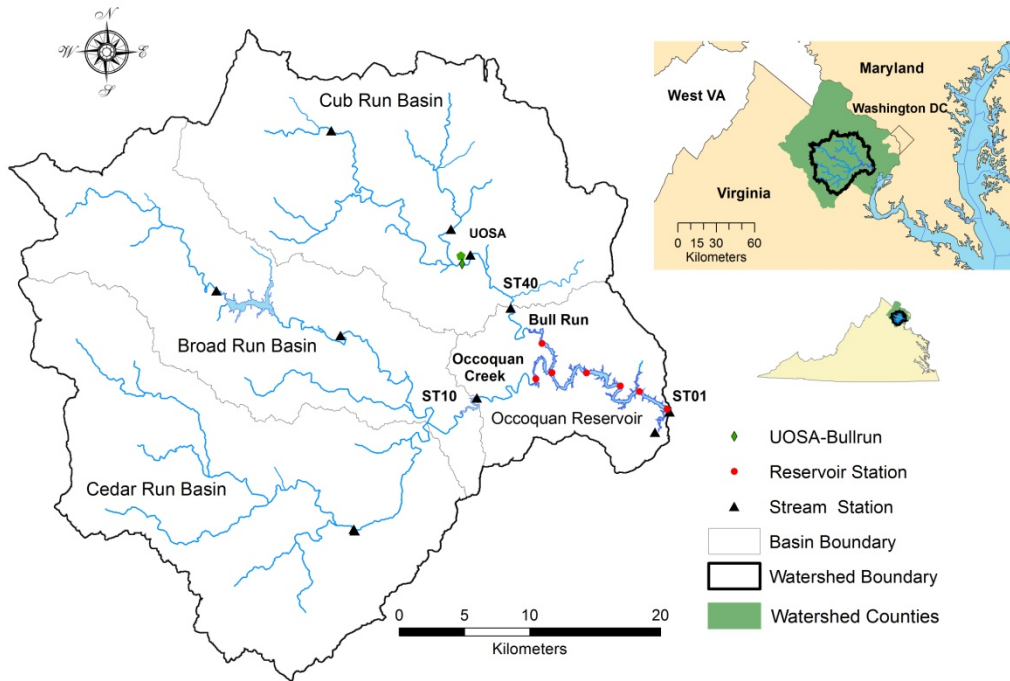
Figure 5-1. The Occoquan Watershed and Reservoir.

Figure 5-2. Segments of the Occoquan Reservoir and sampling stations used for water quality analysis.
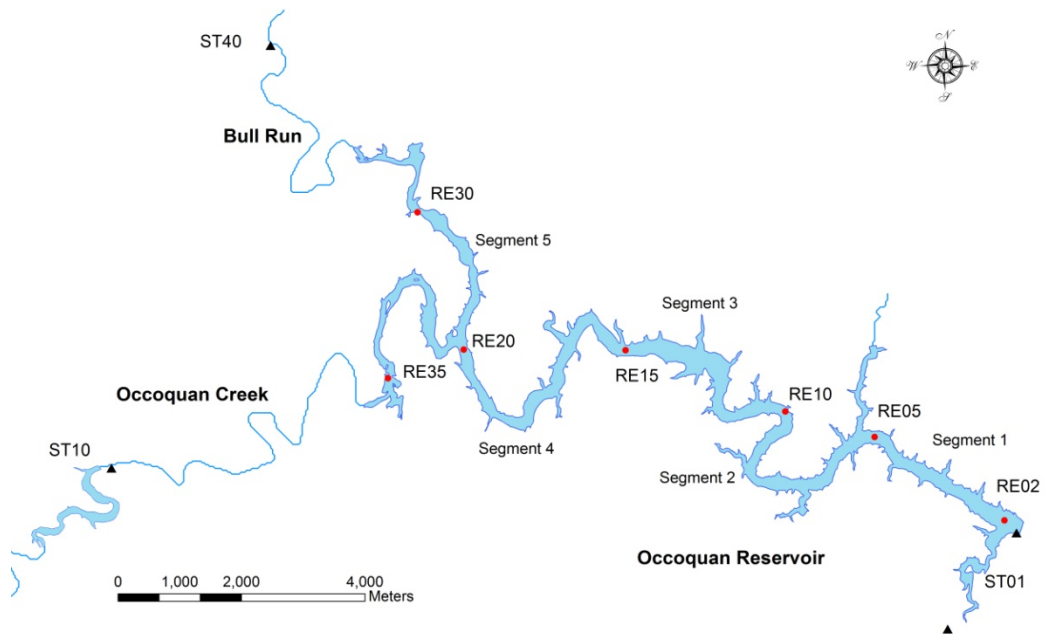
Figure 5-3. 2009 vertical (a) temperature and (b) DO profiles for the Occoquan Reservoir station RE02.
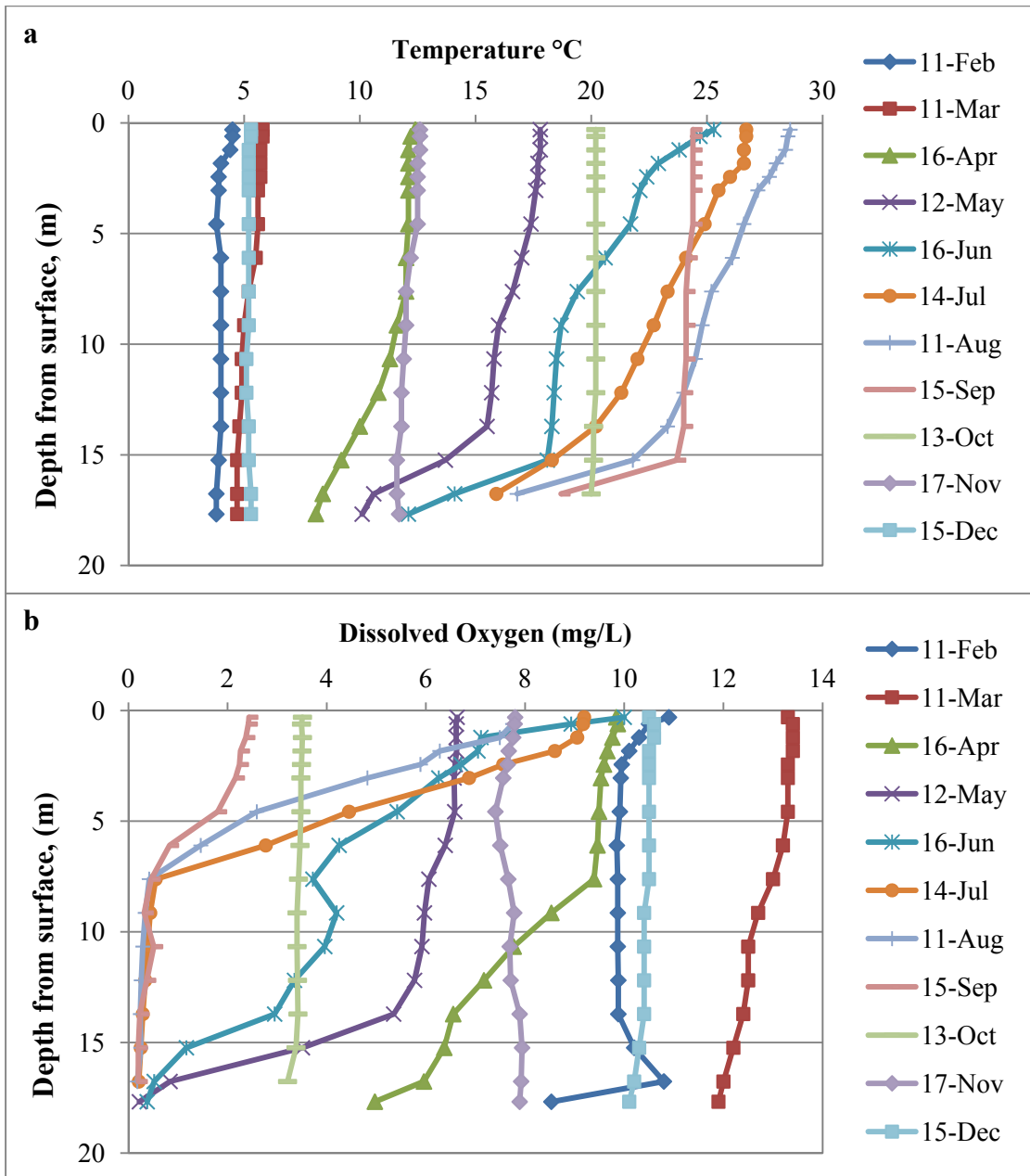
Figure 5-4. Monthly mean OxN concentrations entering and leaving the reservoir in the year 2009. St40 and ST10 are located in Bull Run and Occoquan Creek, respectively. ST01 is located in the outlet of the reservoir.
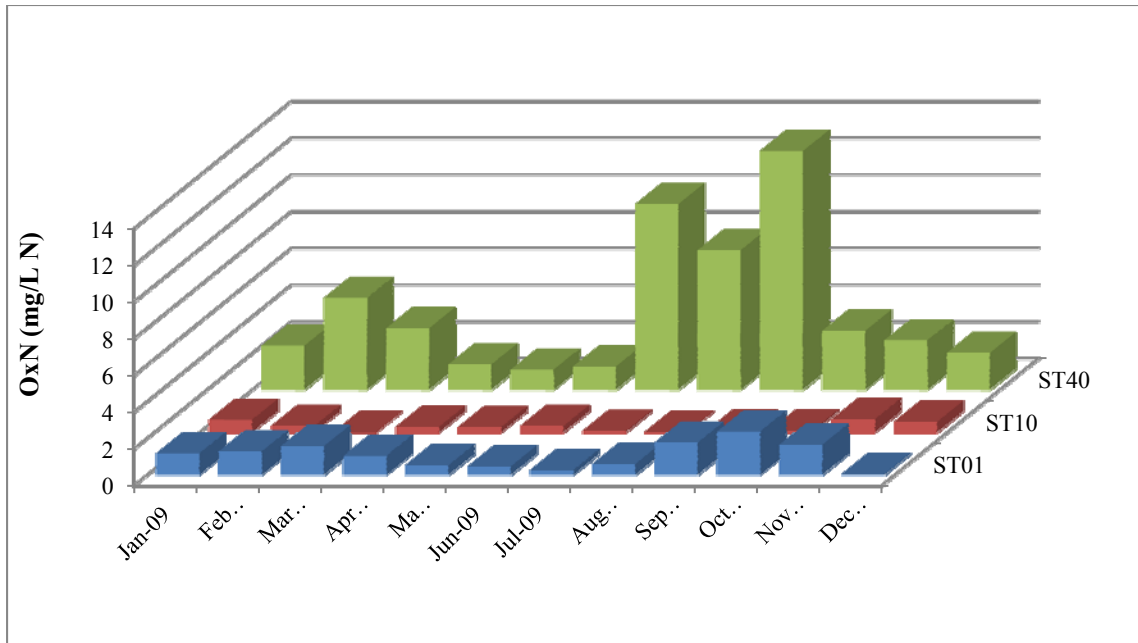

Figure 5-5. Time series for DO and OxN measured above the sediment-water interface of station RE20 of the Occoquan Reservoir.
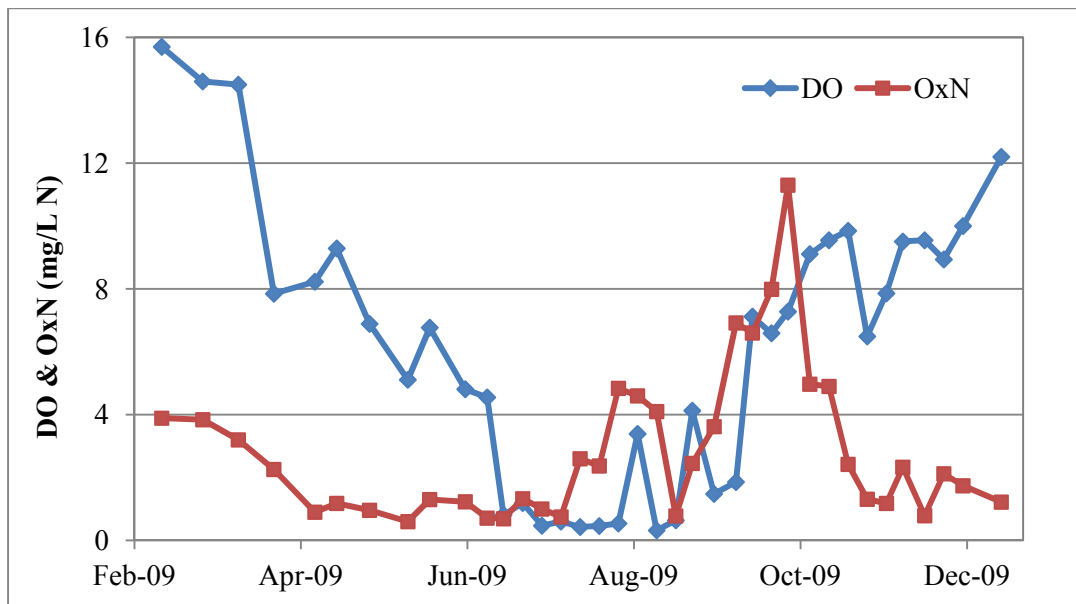
Figure 5-6. Time series for DO, OxN, OP, and NH_4^+ above the sediment-water interface at stations (a) RE10, (b) RE05, and (c) RE02.
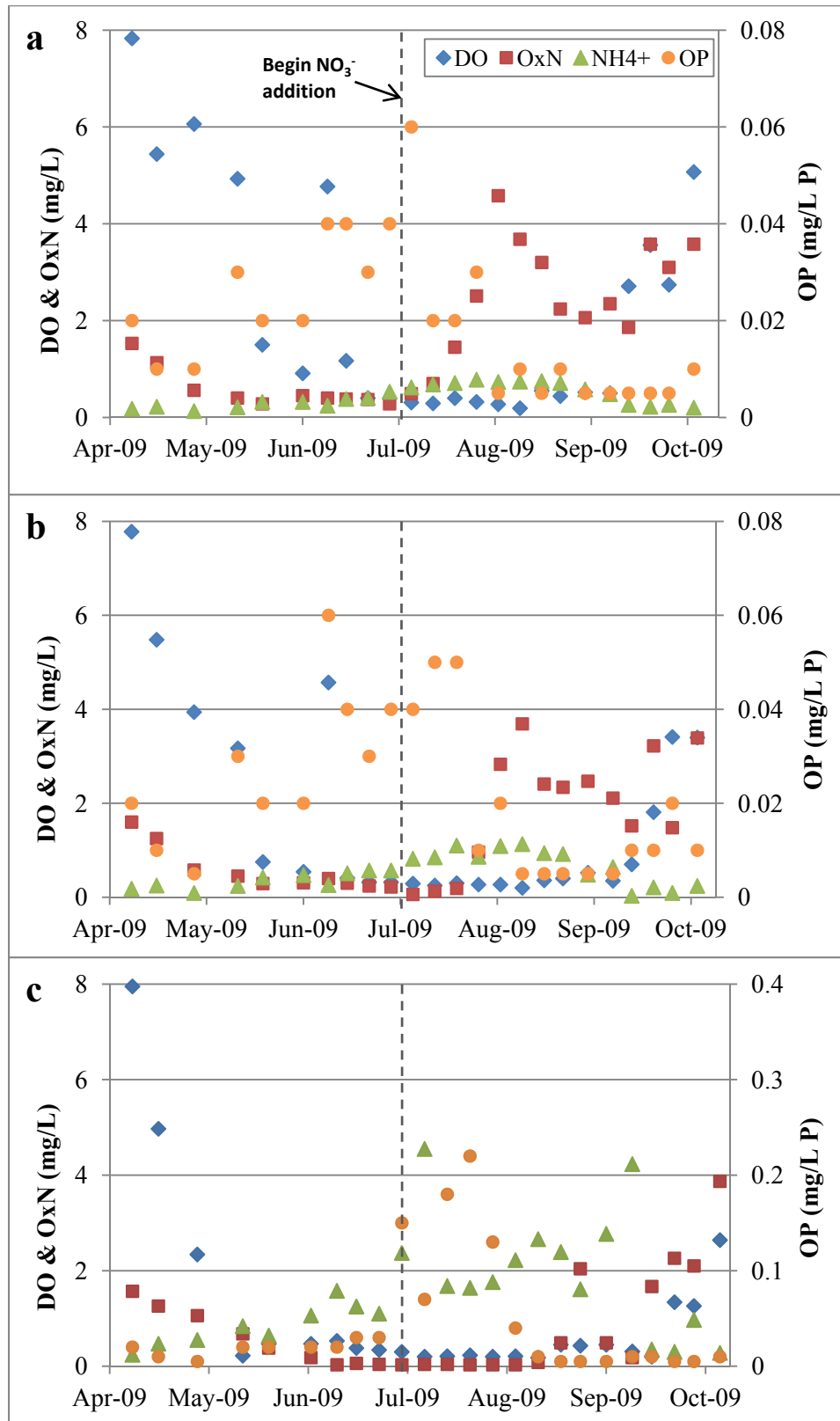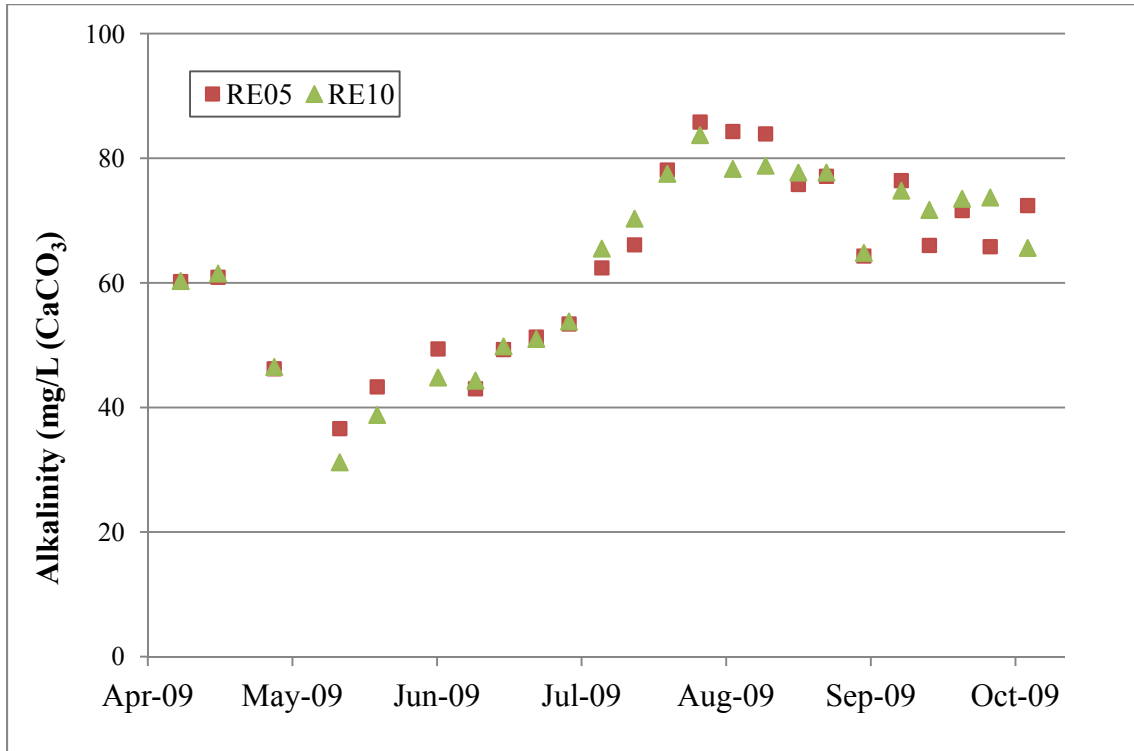
Figure 5-7. Time series for alkalinity production measured in the bottom waters of stations RE05 and RE10.

Chapter 6 – Recommendations for future studies – Characterization of organic matter released from the sediments of the Occoquan Reservoir

6.1 Introduction

The Occoquan Reservoir, a constructed impoundment located in northern Virginia and used as a source for drinking water, has recently experienced an increase in organic matter (OM). Increases in dissolved organic carbon (DOC) concentrations in rivers and other surface waters have been observed in the northern parts of Europe and North America over the last few years (de Wit et al. 2007). Observed DOC concentration increases have raised concerns due to the potential for negative impacts on water bodies used as sources for drinking water.

Dissolved organic matter (DOM) in aquatic systems is a heterogeneous mixture resulting from the breakdown of bacteria, algal, and higher plant organic material, and can range in molecular weight from a few hundred to 100,000 daltons (Da) (Leenheer and Croué 2003). Sources of DOM to surface waters include: (1) the flushing of humic DOM from catchment soils and vegetation, (2) the release of non-humic microbial exudates, and (3) the production of microbially-derived humic DOM from biomass (Miller et al. 2009). The source, composition, and amount of OM are critical factors that will affect the mobility and fate of organic carbon in aquatic systems (Leenheer and Croué 2003).

OM is widely known to play a major role in aquatic systems, including reservoirs, and influences many of the processes that take place in the water column and at the sediment-water interface. High concentrations of OM in reservoirs are of great concern because of the many problems created in water treatment processes, including those related to the formation of disinfection byproducts when OM reacts with strong oxidants. The presence of high concentration of OM also increases the demand for oxidizers, and may affect other treatment processes, such as manganese removal by oxidation. Organic matter also has an impact on aesthetic factors such as color, taste and odor, thereby increasing costs in water treatment plants (Fellman et al. 2010, Letterman and American Water Works 1999).

In aquatic ecosystems, OM also influences the speciation, transport, and bioavailability of nutrients, metals and many inorganic pollutants that are sorbed to organic-rich sediments. DOM

is either a product or a reactant (or both) in most natural biochemical processes, serving as a carbon and energy source for organisms which influence the concentrations of dissolved oxygen, nutrients, and numerous trace metals in aquatic systems (Aguilar and Thibodeaux 2005). Finally, OM affects light attenuation, and plays a role in controlling the depth of the photic zone, which directly affects photochemical processes and primary production in lake and streams (Cory and McKnight 2005).

6.2 Justification

The Occoquan Reservoir is a well-characterized impoundment that plays a unique role with respect to indirect potable reuse. An advanced water reclamation facility (WRF) discharges high quality reclaimed water into one of the major tributaries, thereby increasing the safe drinking water yield of the system. The monitoring program implemented in the Occoquan System has occasionally detected episodes of high concentrations of OM during the summer season when the reservoir becomes anaerobic.

Figure 6-1 shows a subset of the field observations from the bottom waters of the reservoir at a sampling station near the Occoquan Dam (RE02) during the stratification period for two different years (2006 and 2009). A unique feature of the data in the plots is that the OM, measured as total organic carbon (TOC), was observed to increase after both dissolved oxygen (DO) and oxidized nitrogen (OxN) were depleted in the reservoir. The increase in TOC was also accompanied by an increase in the ammonium ion (NH_4^+) concentration. Before the onset of the thermal stratification, and before DO began to decrease in the water column, the OM concentration was relatively constant with average concentrations ranging from $4-6$ mg/L as TOC (data not shown). Shortly after the onset of anaerobic conditions in the bottom waters near the dam, TOC began to accumulate in the water column, with the likely source being the sediments. During this period, the TOC concentration for the summer of 2006 and 2009 peaked to a value of approximately 12 mg/L, which was 3 times the concentration measured before DO and OxN were depleted from the water column.
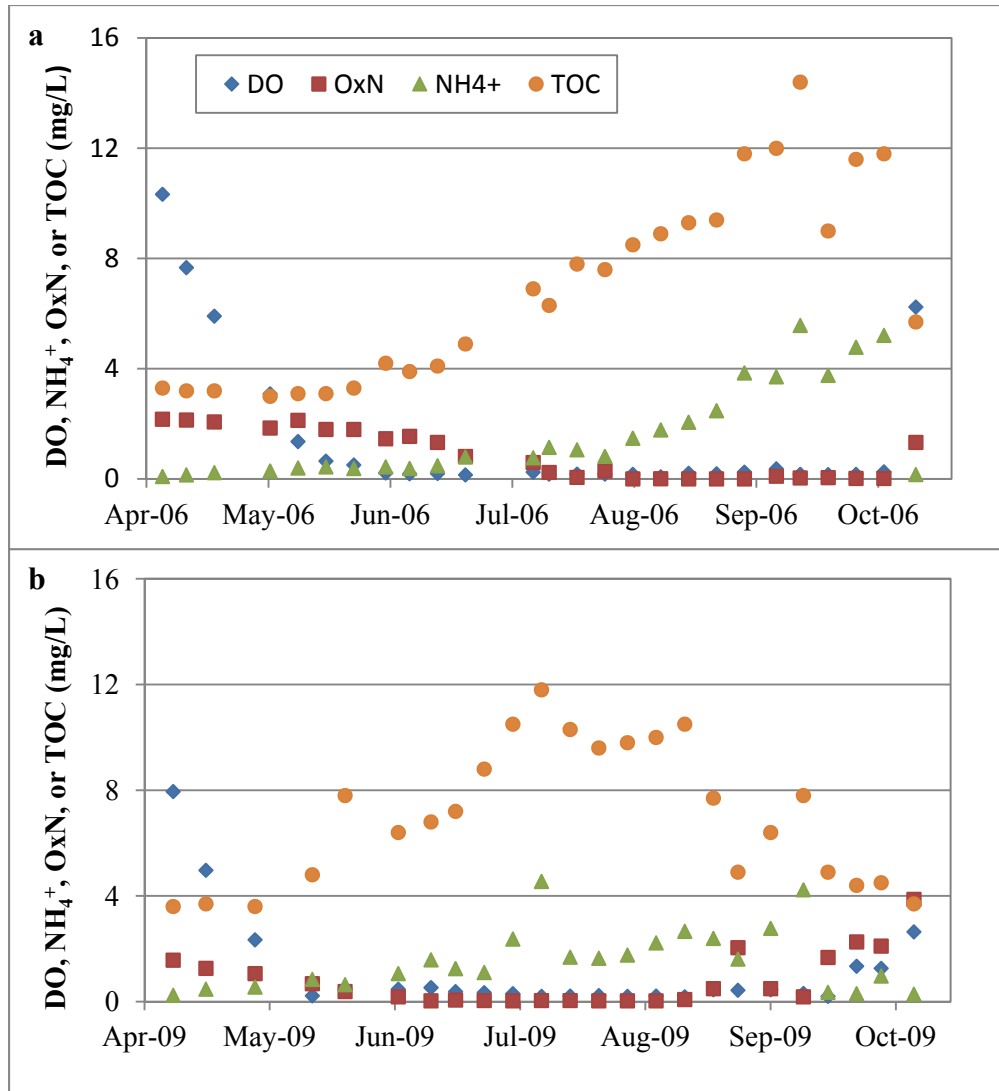
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Figure 6-1. Occoquan Reservoir time series for DO, OxN, NH_4^+ and OM at station RE02 above the sediment-water interface for (a) 2006 and (b) 2009.

When sufficient OxN was present in the hypolimnetic waters to delay the onset of anaerobic conditions, TOC release from the sediments was low compared to periods when the system was completely anaerobic. Figure 6-2 shows that while the OxN concentration was greater than 1 mg/L N above the sediment-water interface, the TOC concentration did not exceed 6 mg/L. As was shown previously in Figure 6-1, when the system was nitrate-depleted (anaerobic) the TOC concentration reached over 12 mg/L. These results, along with other data related to stream loads from the tributary sub-basins, suggest that most of the OM observed during the summer season was produced in the reservoir.

If the OM observed in the reservoir may be shown to be autochthonous in nature, then there appear to be two possible sources. The first one might be related to what is known as internal production. In-lake primary production by phytoplankton can be a dominant source of autochthonous non-humic DOC which can be related to chlorophyll a (Miller et al. 2009). Data from the reservoir reveals that when the hypolimnetic waters become anaerobic, there is evidence of nutrient (nitrogen and phosphorous) release from the sediment to the water column. If conditions exist to allow nutrients in the hypolimnion to overcome the water density gradient, then most of these nutrients may become available for phytoplankton growth. As phytoplankton completes their life cycle, the particulate organic detritus may settle directly to the bottom of the reservoir, thereby increasing the amount of DOC measured in the sediment-water interface.

A second source for OM might be direct release from the sediment, although the mechanisms are still unknown. Some researchers hypothesize that DOC production in the sediments is the result of microbial respiration and fermentation processes which break down the complex organic compounds that make up decaying plant matter. Decomposition of organic matter when the sediments are rich in organic content results in the release of particulate and dissolved organic matter into the water column (Geurts et al. 2010). In other cases, rapid release of bacterial DOM is usually associated with mechanisms linked to cell division (Kawasaki and Benner 2006). During anaerobic decomposition, there are a series of microbially-mediated reactions where the product is lower molecular weight OM. During these reactions, intermediate compounds are formed which contribute to the DOC pool in interstitial waters (Aguilar and Thibodeaux 2005).
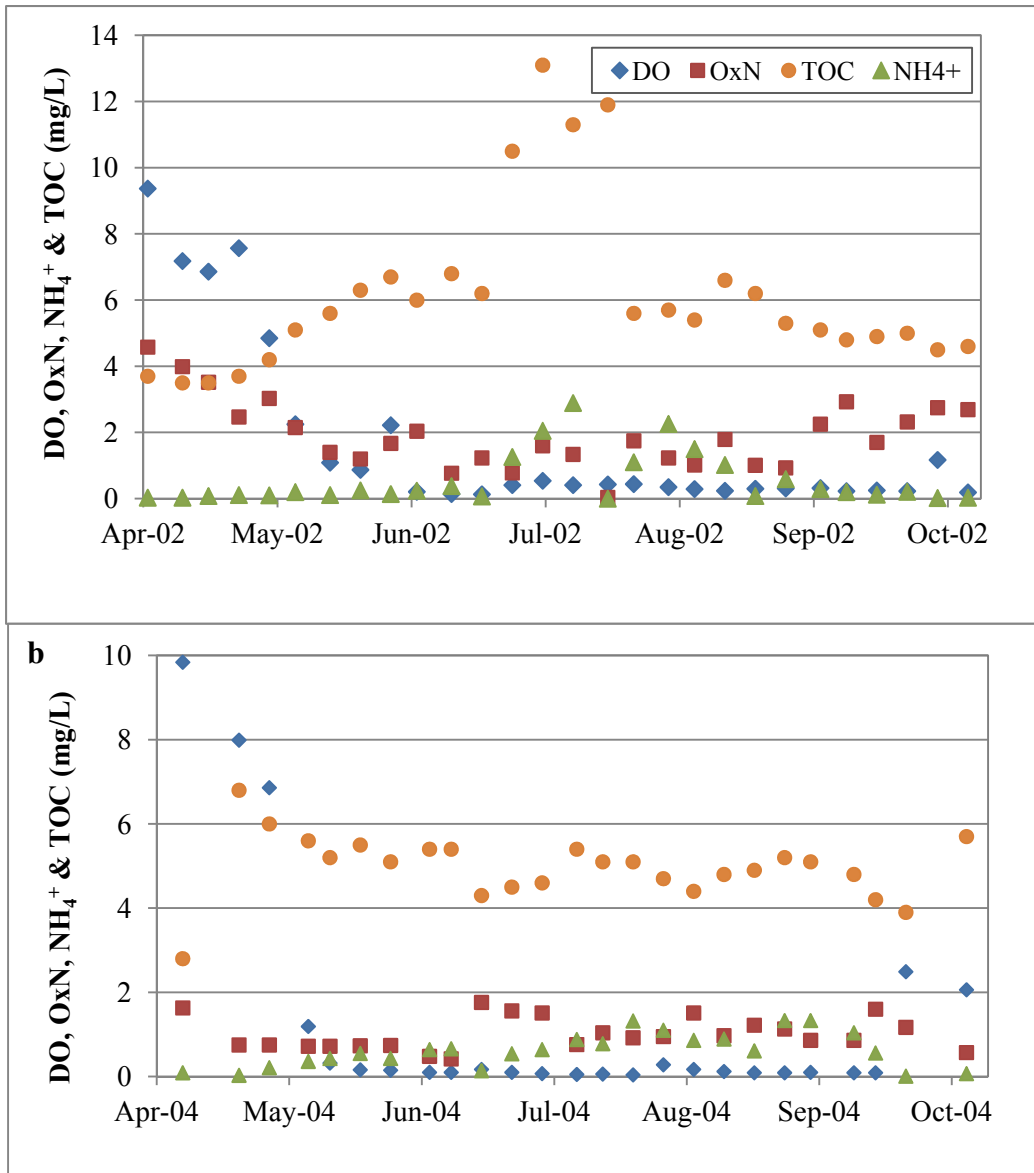
Figure 6-2. Occoquan Reservoir time series for DO, OxN, NH_4^+ and OM at station RE02 above the sediment-water interface for (a) 2002 and (b) 2004.

Better characterization of OM should be done before drawing conclusions about the mechanisms that control the observed water column increases. Characterization of DOM can give specific information about precursors (lignins, tannins, proteins, amino sugars), the processes that produce DOM (biodegradation, condensation reactions, photolysis), and reactive structures in DOM (disinfection byproduct [DBP] precursors) (Leenheer and Croué 2003). Previous studies

done in the Occoquan Watershed have characterized and differentiated the type and sources of OM entering the reservoir. Using florescence spectroscopy, Holbrook et al. (2005) were able to indentify three different fluorescent components in water samples that resolved differences in catchment land-use during summer baseflow conditions. The same approach might be used to identify similarities and differences between the characteristics of OM measured in the lower Reservoir (RE02) and those measured at upstream stations in previous studies (Holbrook et al. 2006). By comparing these characteristics, it may be possible to determine if the OM measured at the station closest to the dam is of allochthonous or autochthonous origin.

6.2.1 Objective

The objective of this proposed study is to characterize OM at a location in the reservoir near the drinking water intake with the goal of identifying the source(s) during the summer season under anaerobic conditions. The characterization and data analysis will be done using fluorescence spectroscopy and the methods described in previous studies performed in the Occoquan Reservoir (Holbrook et al. 2005, Holbrook et al. 2006). The analysis should be able to determine if the observed OM is allochthonous (high MW OM originating from watershed sources), or autochthonous (low MW OM produced by microbial activity within the reservoir). By evaluating the fluorescence spectra from water samples, precursors of OM will be identified. Total and dissolved measurements of organic carbon, nitrogen, and phosphorus, along with chlorophyll a, and sediment nitrogen and carbon analysis will be performed on the same samples in order to complement the fluorescence spectroscopy data.

The results obtained will also be compared to specific UV absorbance (SUVA) values collected by the Occoquan Watershed Monitoring Laboratory and Fairfax Water. Recent studies have demonstrated that SUVA values can often be related to fluorescence indices (Leenheer and Croué 2003, Weishaar et al. 2003). The aromatic carbon content and the absorbance of UV light, which are general characteristics of the pool of molecules that comprise DOC, are important indicators of DOC reactivity in a number of environmental processes. Similarly, the reactivity of DOC and aquatic humic substances with oxidants such as chlorine and ozone, is strongly dependent on the aromaticity of the organic matter (Weishaar et al. 2003). Aquatic humic substances within the DOC pool are generally thought to be the primary precursors of THM and

many other DBPs. Aquatic humic substances comprise the aromatic fraction of DOC and are amenable to removal from water by coagulation (McKnight et al. 2001, Weishaar et al. 2003). The amount of removal required depends on the chemical characteristics of the raw water, including the specific UV absorbance, SUVA 254. This may be of great importance because if a strong relationship between SUVA and fluorescence values is found, then drinking water treatment plant operators may make conclusions about the OM present in source waters by doing regular SUVA analysis.

Finally, to further expand the characterization of water column OM near the drinking water intake, analyses related to biodegradation of organic matter will be done. Inoculations of reservoir water into microbial cultures from the sediments will be done to determine if the DOC measured in the water column is readily biodegradable. Biodegradable organic matter (BOM) may be measured with operationally defined protocols, such as biodegradation over a given time (Leenheer and Croué 2003). The BOM content of rivers varies with the origin of the NOM. Autochthonous NOM, which is produced from macrophytes, algae, and bacteria, is more biodegradable than allochthonous NOM, which has a pedogenic origin.

6.3 Possible outcome

The investigation should provide insights into the sources of OM present in the reservoir water column. A preponderance of low MW compounds would point to microbial sources, while a prevalence of high MW molecules such as fulvic or humic substances would be associated with terrestrial origins. In the case of an abundance of low MW substances, it would be probable that the OM consists mostly of amino acids, polysaccharides or other simpler molecules that may be easily degraded. However, if the results suggest that heavier molecules exist, then it would be more likely that the measured OM is a product of the breakdown of large complex molecules of humic origin. In the latter case, such OM would be expected to be more resistant to further microbial degradation. In any case, knowledge of the OM source may be expected to be useful in determining treatment processes and coagulant dose to be used in drinking water treatment.

Finally, extending OM characterization from the compound-class level to the specific compound level and synthesizing standards are the present research challenges. Thus, the information from expensive DOM fractionations with spectral characterizations may be transferred to

interpretations with inexpensive methods. Improved understanding of the structural chemistry of DOM components may be useful in designing new (or optimizing existing) water treatment processes to remove these components. It has been generally accepted that hydrophobic DOM represents the major source of DBP precursor sites, but certain hydrophilic DOM components not removed by conventional water treatment have been found to react with disinfecting agents to produce undesirable DBPs.

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