ABSTRACT

NULL, KIMBERLY ANN. Ammonium Fluxes from Channel Deposits in the Neuse River Estuary, North Carolina: Implications for Ammonium Increase in Estuarine Waters. (Under the direction of Drs. Dave DeMaster and JoAnn Burkholder).

Sediment and porewater samples were collected from three nearshore sites and one mid-channel site in the Neuse River Estuary (NRE), North Carolina, USA to investigate advective and diffusive inorganic N fluxes from sediments. Ammonium (NH_4^+) fluxes were used to determine the significance of submarine groundwater discharge (SGD) in nearshore environments to the overall NH_4^+ dynamics in the water column. ^{222}Rn and NH_4^+ were measured in interstitial water at NRE nearshore sites to determine the advective flux of NH_4^+ from sediments to the overlying water column. Porewater samples were collected over an annual cycle from multi-level piezometers installed in nearshore sites. SGD was measured indirectly by using ^{222}Rn as a tracer and directly by using seepage meters. Maximum SGD occurred during spring at a rate of 13.6 ± 0.2 cm d^{-1} and was variable depending upon the sampling location. Shallow porewaters exhibited seasonal variations in NH_4^+ concentrations, which produced temporal changes in advective flux of NH_4^+ from the sediment. Seasonal trends in groundwater seepage rates and NH_4^+ concentrations suggest that groundwater is an important mechanism advecting nutrients from porewaters to the overlying water column, and that groundwater inputs are comparable to riverine NH_4^+ discharge.

NH_4^+, nitrate (NO_3^-), and dissolved oxygen (DO) diffusive fluxes across the sediment-water interface were measured in the shallow nearshore environments with sandy sediments and one mid-channel site with organic rich, fine-grained sediments. NH_4^+ was the major form of inorganic N in sediment porewaters and in the flux to the overlying water; NO_3^- fluxes were

small or not detected. NH_4^+ and DO fluxes showed significant seasonal variations at all sites. NH_4^+ diffusive flux was highly variable and ranged from –29.1 to 811 μmol m^{-2} hr^{-1} among the three sites, with the negative flux indicating flux into the sediments from the water column. Sediment experiments were also conducted at a nearshore and mid-channel site to measure the NH_4^+ production rates. The nearshore site demonstrated increasing NH_4^+ production with depth, down to 35 cm (0.004 μmol NH_4^+ cm^{-3} wet sediment d^{-1}), whereas the highest NH_4^+ production at the mid-channel site (0.001 μmol NH_4^+ cm^{-3} wet sediment d^{-1}) occurred in the 0-10 cm interval. SGD contributed significantly more NH_4^+ to the overlying water in the nearshore environment than the diffusive flux from organic rich mid-channel sediments at these sampling locations.

Data compiled from this study and multiple other studies conducted in the NRE were applied to a mass balance model to analyze seasonal variations in NH_4^+ sources and to investigate the increase of NH_4^+ concentration in the NRE water column. Many of the sources of NH_4^+ dynamics in the NRE are driven by temperature and climate, and therefore, demonstrate seasonal variability. Advection terms and other climate-related parameters, including SGD and resuspension events, were found to be of similar importance during the winter and summer periods. The advection term, including SGD, porewater exchange, and resuspension, represented >23% of the NH_4^+ inputs during the winter season and >21% during the summer. SGD and permeable porewater exchange were the dominant advection terms during both seasons. Sediments played a crucial role in NH_4^+ supply to the overlying water column. When sandy sediments and muddy sediments are included in the budget and the role of advection is considered, sediments may contribute more than 70% of the NH_4^+ to

the water column. The nearshore environment was relatively consistent between summer and winter when diffusive fluxes and advective fluxes from SGD were considered, 35% for summer and 24% for winter.

This study demonstrated that nearshore sediments of the NRE are sites with significant NH_4^+ production that can be important to benthic primary production and overall water column concentration in shallow waters. This study quantifies NH_4^+ production and flux from sediments, which is poorly understood in nearshore environments, and may help to explain an overall increase in water column NH_4^+ concentrations that has been documented in the NRE and certain other shallow, eutrophic estuaries. The data can provide valuable information important to management practices and future eutrophication mitigation studies.

Ammonium Fluxes from Channel Deposits in the Neuse River Estuary, North Carolina: Implications for Ammonium Increase in Estuarine Waters

by
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DEDICATION

I would like to dedicate my dissertation to my grandfather, William Locke, who passed away while I was writing my dissertation. I want to thank him for his constant support. My grandfather grew up poor and did not finish high school, but completed his GED, and always thought education was an important part of life. He led a very successful life full of love from his wife, son, grandchildren, and great grandchildren. I have always admired my grandfather for his simple, happy, family-oriented lifestyle. He worked hard at his job and loved my grandmother unconditionally.

My grandfather always told me that my education is something that can never be taken away from me. He always believed in me since I started school and encouraged me to continue if that is what I chose. Even when he was in the hospital he still told me that I would finish and find the job that I was seeking. Not once did he question the path I chose to stay in school and continue my education. I feel fortunate to have been able to spend all these years with him and wish I could have had more. I feel he has contributed to my success in school and has influenced my decisions in life. He always believed I would succeed, and I wish more than anything in the world that he could be here to see me graduate. I will miss him dearly.

BIOGRAPHY

Kimberly Ann Null was born on an Airforce base hospital in Montgomery, Alabama. She mostly grew up in Indiana where majority of her family resides. All her life she enjoyed the outdoors and playing in the mud. She spent 12 years doing gymnastics and loved every minute of it. Other sports she picked up in high school included volleyball and track. She lived in Lowell, IN during middle school and high school where she found much trouble to get into with her best friend, Jenny Stang. There are not too many sports she will not try. Unfortunately, three knee surgeries by the end of high school ended her sports career. She attended Purdue University in Lafayette, IN for three semesters after high school and transferred to Indiana University-Purdue University Indianapolis in hopes of alleviating the financial burdens of attending college. She finished her B.S. in Environmental Science and Public Health and immediately found a passion for geological sciences. She has always enjoyed the environmental issues, thanks to her 8th grade science teacher, Mrs. Downey. She continued her education at IUPUI and received a M.S. in geology focusing on sediment geochemistry. The ocean was always an interest to her so she decided to pursue her dreams in marine science at North Carolina State University. At NCSU, she combined her passion for environmental issues and marine sciences by studying groundwater nutrient supply in coastal environments. She had many unimaginable experiences at NCSU, including three Antarctic cruises and three cruises in the Gulf of Mexico. She

never thought she would see penguins in the wild! After all the field work in the Neuse Estuary and cruise work was over, she finally wrapped up her dissertation!

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1. INTRODUCTION

Nitrogen (N) over-enrichment in coastal waters is an important factor driving water quality degradation worldwide (Vitousek et al. 1997). Many coastal environments have sustained an increase in nutrient concentrations over the past decade due to densely populated coastlines and anthropogenic activities (Valiela et al. 1999, Howarth et al. 2002). As of a decade ago, an estimated 37% of the world's population resides within 100 km of a marine coast, with coastal population growth projected to continue to rapidly increase (Small et al. 2000). Sources of dissolved inorganic nitrogen (DIN) to coastal environments include runoff, point source discharges, atmospheric deposition, sediment regeneration, and groundwater discharge (Vitousek et al. 1997).

Submarine groundwater discharge (SGD) has been identified as an important mechanism for transporting constituents, including nutrients, heavy metals, and other contaminants, to marine coastal ecosystems (e.g. Moore 1996, Corbett et al. 1999, Krest et al. 2000, Charette and Buesseler 2004, Paytan et al. 2006). SGD has been studied by researchers in multiple disciplines and also by various methods. Thus, the definition of groundwater discharge varies across disciplines. Here SGD is defined as total advective discharge into a water body across the sediment-water interface, and includes subsurface terrestrial freshwater and recirculated seawater (Taniguchi et al. 2002). SGD and advection in permeable coastal environments can provide significant N loads to the overlying water column and stimulate primary production. As examples, SGD has been linked to algal

blooms along the coast of Long Island (LaRoche et al. 1997) and in coastal reef systems (Paytan et al. 2006).

Once nitrate (NO_3^-) and ammonium (NH_4^+) enter a coastal ecosystem, these inorganic forms of nitrogen (N_i) can undergo many processes and transformations depending on environmental conditions. In many coastal systems, the dominant form of biological N_i uptake is NH_4^+, and it can account for the majority of phytoplankton production (Glibert 1988, Nixon 1995, Twomey et al. 2005). At water column concentrations in excess of 2 μM, NH_4^+ is preferred over NO_3^- for assimilation by phytoplankton (McCarthy et al. 1977, Glibert 1988). Although NO_3^- generally has been considered to be the major "new" source of N_i added to coastal ecosystems (Dugdale and Goerring 1967), some anthropogenic sources such as sewage treatment plants and industrialized animal agriculture are adding substantial "new" NH_4^+ as well (Burkholder et al. 1997, Álvarez-Góngora and Herrera-Silveira 2006, Dugdale et al. 2007). Moreover, much of the N that supports productivity in estuaries is derived from remineralization and recycling from sediments and commonly is not "new" N, such as the N supplied by rivers and atmospheric deposition (Dugdale and Goerring 1967). Benthic recycling from sediments has been estimated to provide 20-80% of N requirement for phytoplankton in shallow estuarine waters (depth < 50 m; Nixon 1995, Boynton and Kemp 1985). Thus, regeneration and flux of NH_4^+ from sediments to the overlying water is a significant source of N to phytoplankton in shallow estuaries (Harrison 1980).

Increasing NH_4^+ in eutrophic estuaries can significantly alter overall system ecology. For example, Dugdale et al. (2007) reported that NO_3^- uptake by phytoplankton in San Francisco Bay can be limited by excessive NH_4^+ concentrations, leading to depressed fish

production. The ecological response to increasing nutrient concentrations varies among estuarine systems because of differences in tidal regime, mean water depth, freshwater input, and other factors (Cloern 2001). In the shallow lagoonal Neuse River Estuary (NRE), NH_4^+ has been linked to stimulation of certain harmful algal species (Rothenberger et al. 2009). Although coastal resource managers generally emphasize total N (TN) or total dissolved inorganic N (DIN), the above examples illustrate the importance of considering both bioavailable N_i forms separately. The NRE is an ideal estuarine system for examining the dynamics of individual chemical species of DIN and assessing the biogeochemical inputs of these important nutrients to a nitrogen-sensitive system.

The NRE has sustained accelerated eutrophication from increased nutrient loading and, over the past decade, water column NH_4^+ concentrations – but not NO_3^- concentrations – have increased about 500% in the mesohaline section while TN loading has decreased (Burkholder et al. 2006). Other estuaries, such as the Cape Fear, have also sustained significant increases in NH_4^+ concentrations over the past decade (Burkholder et al. 2006). While nutrient *loading* is an important consideration in management efforts to reduce coastal eutrophication, ambient water column *concentrations and forms* of N are key variables supporting algal assemblage shifts, excessive algal production, and associated adverse effects of eutrophication (Hecky and Kilham 1988, Glibert et al. 2006). The major sources of nutrient supply should be accounted for, including characterization of poorly known sources such as SGD.

Previous research to assess sediment nutrient contributions in the NRE mostly has focused on the organic-rich muddy sediments, which were believed to be the major source of

benthic nutrients to the overlying water column (Rizzo and Christian 1996, Haruthian 1997, Alperin et al. 2000). Because of their low organic content, sandy nearshore environments were thought to contribute minimal nutrient supplies to the overlying water by diffusional processes. Moreover, previous studies of benthic nutrient flux in the NRE were conducted prior to the documented increase in water column NH_4^+ concentrations. There are limited groundwater measurements in the NRE as well, and therefore limited data on advective flux of nutrients from nearshore sediments.

The focus of this study was to quantify NH_4^+ production and regeneration, considering both diffusive and advective fluxes, in the poorly characterized sandy nearshore environments of the mesohaline NRE. The overall objective was to assess the role of SGD and nearshore sediments in supplying NH_4^+ to the water column, and to develop a seasonal NH_4^+ budget for the mesohaline estuary. I hypothesized that the nearshore environments contribute NH_4^+ to the overlying water via diffusional processes and advection, such as SGD, and that advection (SGD) will produce higher NH_4^+ flux than molecular diffusion. Spatially, I expected nearshore environments to contribute comparable NH_4^+ flux to the overlying water as the organic-rich, mid-channel sediments.

Understanding nutrient inputs and outputs in coastal environments is critical for designing and implementing sustainable management practices (National Research Council 2000). Previous research in the Neuse system has contributed quantitative estimates of nutrient sources including atmospheric deposition (Walker et al. 2000, Aneja et al. 2003, Whitall et al. 2003), sedimentary processes (Haruthunian 1997, Alperin et al. 2000, Piehler et al. 2002, Fear et al. 2004), resuspension (Giffin and Corbett 2003), and groundwater (Bratton

2004, Fear et al. 2007, Spruill and Bratton 2008), but further research is needed to understand N dynamics and the striking increase of NH_4^+ over the past decade in this system. The NRE was an ideal system to study N cycling in a eutrophic estuary and the documented NH_4^+ increase in the NRE water column provided relevance that sparked interest to focus on NH_4^+ dynamics. This study contributes valuable information that quantifies previously unmeasured variables required for the scientific understanding of the dramatic increase in NH_4^+ in the NRE. The insights gained from this research also will be generally applicable to other shallow eutrophic estuaries that are also exhibiting significant increases in NH_4^+ concentrations.

Following this introduction, Chapter 2 of this dissertation explains the above described research divided into chapters for each component. Chapter 2 describes the measurements to estimate SGD and its associated ammonium flux. Chapter 3 explains the diffusive flux of nitrogen from the seabed in the NRE. Data from Chapter 2 and 3 are compiled in Chapter 4 to balance ammonium inputs and outputs to the NRE system. Finally, Chapter 5 summarizes the findings from all data collected during this study.

1.1. References

Alperin, M.J., Clesceri, E.J., Wells, J.T., Albert, D.B., McNinch, J.E., Martens, C.S., 2000. Sedimentary processes and benthic-pelagic coupling, pp. 63-105. In: R. A. Leuttich (ed.), Neuse River Estuary Modeling and Monitoring Project: Final Report – Monitoring Phase. Report. UNC Water Resources Research Institute, Raleigh.

Álvarez-Góngora, C., Herrera-Silveira, J.A., 2006. Variations of phytoplankton community structure related to water quality trends in a tropical karstic coastal zone. Mar. Pollut. Bull. 52, 48-60.

Aneja, V.P., Nelson, D.R., Roelle, P.A., Walker, J.T., 2003. Agricultural ammonia emissions and ammonium concentrations associated with aerosols and precipitation in the southeast United States. J. Geophys. Res. 108(D4), ACH12-1 – 12-11.

Boynton, W., Kemp, W., 1985. Nutrient regeneration and oxygen consumption by sediments along an estuarine salinity gradient. Mar. Ecol. Prog. Ser. 23, 45-55.

Bratton, J., 2004. Integrated science team deploys new tools to study submarine ground water in North Carolina. USGS, *Soundwaves*, Vol. FY2004, No. 62, 3-4.

Burkholder, J.M., Mallin, M.A., Glasgow, H.B., Larsen, L.M., McIver, M.R., Shank, G.C., Deamer-Melia, N., Briley, D.S., Springer, J., Touchette, B.W., Hannon, E.K., 1997. Impacts to a coastal river and estuary from rupture of a large swine waste holding lagoon. J. Environ. Qual. 26, 1451-1466.

Burkholder, J.M., Dickey, D.A., Kinder, C., Reed, R.E., Mallin, M.A., Melia, G., McIver, M.R., Cahoon, L.B., Brownie, C., Deamer, N., Springer, J., Glasgow, H., Toms, D., Smith, J., 2006. Comprehensive trend analysis of nutrients and related variables in a large eutrophic estuary: A decadal study of anthropogenic and climatic influences. Limnol. Oceanogr. 51, 463-487.

Charette, M.A., Buesseler, K.O., 2004. Submarine groundwater discharge of nutrients and copper to an urban subestuary of Chesapeake Bay (Elizabeth River). Limnol. Oceanogr. 49, 376-385.

Cloern, J.E., 2001. Our evolving conceptual model of the coastal eutrophications problem. Mar. Ecol. Prog. Ser. 210, 223-253.

Corbett, D.R., Chanton, J., Burnett, W., Dillon, K., Rutkowski, C., Fourqurean, J.W., 1999. Patterns of groundwater discharge into Florida Bay. Limnol. Oceanogr. 44, 1045-1055.

Dugdale, R.C., Goering, J.J., 1967. Uptake of new and regenerated forms of nitrogen in primary productivity. Limnol. Oceanogr. 12, 196-206.

Dugdale, R.C., Wilkerson, F.P., Hogue, V.E., Marchi, A., 2007. The role of ammonium and nitrate in spring bloom development in San Francisco Bay. Estuar. Coast. Shelf Sci. 73, 17-29.

Fear, J., Gallo, T., Hall, N., Loftin, J., Paerl, H., 2004. Predicting benthic microalgal oxygen and nutrient flux responses to a nutrient reduction management strategy for the eutrophic Neuse River Estuary, North Carolina, USA. Estuar. Coast. Shelf Sci. 61, 491-506.

Glibert, P. M., 1988. Primary productivity and pelagic nitrogen cycling, p. 3-31. In T. H. Blackburn and J. Sørensen [eds.], Nitrogen Cycling in Coastal Marine Environments. Scientific Committee on Problems of the Environment, of the International Council of Scientific Unions. SCOPE 33, John Wiley and Sons, New York.

Glibert, P.M., Burkholder, J.M., Parrow, M.W., Lewitus, A.J., Gustafson, D.E., 2006. Direct uptake of nitrogen by *Pfiesteria piscicida* and *Pfiesteria shumwayae*, and nitrogen nutritional preferences. Harmful Algae 5, 380-394.

Harrison, W.G., Platt, T., 1980. Variations in assimilation number of coastal marine phyto-phytoplankton: Effects of environmental co-variates. J. Plankton Res. 2, 249-260.

Haruthunian, 1997. Seasonal and Spatial Variations in Benthic Organic Nitrogen Remineralization in the Neuse River Estuary, North Carolina. M.S. Thesis, UNC Chapel Hill, 70 pp.

Hecky, R.E., Kilman, P., 1988. Nutrient limitation of phytoplankton in freshwater and marine environments: A review of recent evidence on the effects of enrichment. Limnol. Oceanogr. 33, 796-822.

Howarth, E., Boyer, W., Pabich, W.J., Galloway, J.N., 2002. Nitrogen use in the United States from 1961–2000 and potential future trends. Ambio 31, 88-96.

Krest, J.M., Moore, W.S., Gardner, L.R., Morris, J.T., 2000. Marsh nutrient export supplied by groundwater discharge: Evidence from radium measurements. Global Biogeochem. Cycles 14.

LaRoche, J., Nuzzi, R., Waters, R., Wyman, K., Falkowski, P., Wallace, D., 1997. Brown Tide blooms in Long Island's coastal waters linked to interannual variability in groundwater flow. Global Change Biol. 3, 397-410.

McCarthy, J.J., Rowland Taylor, W., Taft, J.L., 1977. Nitrogenous nutrition of the plankton in the Chesapeake Bay. 1. Nutrient availability and phytoplankton preferences. Limnol. Oceanogr. 22, 996-1011.

Moore, W., 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. Nature 380, 612-614.

[NRC] National Research Council, 2000. Clean Coastal Waters – Understanding and Reducing the Effects of Nutrient Pollution. National Academy Press, Washington, DC.

Nixon, S.W., 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia 41, 199-219.

Paytan, A., Shellenbarger, G.G., Street, J.H., Gonneea, M.E., Davis, K., Young, M.B., Moore, W.S., 2006. Submarine groundwater discharge: An important source of new inorganic nitrogen to coral reef ecosystems. Limnol. Oceanogr. 51, 343-348.

Piehler, M., Thompson, S., Dyble, J., Moisander, P., Fear, J., Paerl, H., 2002. Biologically mediated nitrogen dynamics in eutrophying estuaries. Assessing denitrification, N_2 fixation and primary productivity responses to proposed N loading reductions in the Neuse River Estuary. Water Resources Research Institute of the UNC Report, Report No. 339.

Rizzo, W., Christian, R., 1996. Significance of subtidal sediments to heterotrophically-mediated oxygen and nutrient dynamics in a temperate estuary. Estuaries 19, 475-487.

Rothenberger, M., Burkholder, J.M., Wentworth, T., 2009. Multivariate analysis of phytoplankton and environmental factors in a eutrophic estuary. Limnol. Oceanogr. 54, 2107-2127.

Small, C., Gornitz, V., Cohen, J.E., 2000. Coastal hazards and the global distribution of human population. Environmental Geosciences 7, 3-12.

Taniguchi, M., Burnett, W.C., Cable, J.E., Turner, J.V., 2002. Investigation of submarine groundwater discharge. Hydrol. Process. 16, 2115-2129.

Twomey, L., Piehler, M., Paerl, H., 2005. Phytoplankton uptake of ammonium, nitrate and urea in the Neuse River Estuary, NC, USA. Hydrobiologia 533, 123-134.

Valiela, I., Costa, J., Foreman, K., Teal, J., Howes, B., Aubrey, D., 1999. Transport of groundwater-borne nutrients from watersheds and their effects on coastal waters. Biodegradation 10, 177-197.

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.G., 1997. Human alteration of the global nitrogen cycle: Sources and consequences. Ecol. Appl. 7, 737-750.

Walker, J., Aneja, V., Dickey, D., 2000. Atmospheric transport and wet deposition of ammonium in North Carolina. Atmosphere and Environment 34, 3407-3418.

Whitall, D., Hendrickson, B., Paerl, H., 2003. Importance of atmospherically deposited nitrogen to the annual nitrogen budget of the Neuse River estuary, North Carolina. Environ. Int. 29, 393-399.

2. ^{222}RN-BASED ADVECTION OF AMMONIUM INTO THE NEUSE RIVER ESTUARY, NORTH CAROLINA, USA

2.1 Abstract

^{222}Rn and ammonium (NH_4^+) were measured in the interstitial waters of the Neuse River Estuary (NRE), North Carolina, USA to determine the advective flux of NH_4^+ from sediments to the overlying water column. Porewater samples were collected over an annual cycle from multi-level piezometers installed in nearshore sites. NH_4^+ concentrations in sandy environments of the NRE were ten-fold higher than concentrations in the overlying water column. Shallow porewaters exhibited seasonal variations in NH_4^+ concentrations, which produced temporal changes in NH_4^+ flux from the sediment. Submarine groundwater discharge (SGD) was measured indirectly by using ^{222}Rn as a tracer and directly by using seepage meters. The data indicated significant groundwater radon input to porewaters, with ^{222}Rn concentrations in the range of 400 – 3500 disintegrations per minute (dpm)·L^{-1} and variable discharge rates depending on the sampling location and season. The mean SGD at all sites for all seasons, estimated from ^{222}Rn measurements, was 9 ± 2 cm d^{-1}. Maximum SGD measured occurred during spring at a rate of 14 ± 0.2 cm d^{-1}. High porewater NH_4^+ concentrations in sandy nearshore sediments contributed NH_4^+ to the overlying water via groundwater discharge as an advective process. Seasonal trends in groundwater seepage rates and NH_4^+ concentrations suggest that groundwater is an important mechanism advecting nutrients from porewaters to the overlying waters, and that groundwater inputs are comparable to riverine NH_4^+ discharge. SGD N:P ratios (NH_4^+ as N) were >16:1, indicating that SGD is an important factor for phytoplankton growth and may influence the NRE

shifting toward a less N-limited system. The data from this study advance understanding concerning the role of ammonium in the progressive eutrophication of shallow estuarine ecosystems.

2.2 Introduction

Nitrogen over-enrichment in coastal waters is an important factor driving water quality degradation worldwide (Vitousek et al. 1997). Many coastal environments have sustained an increase in nutrient concentrations over the past decade due to densely populated coastlines and anthropogenic activities (Valiela et al. 1990, Howarth et al. 2002). Sources of dissolved inorganic nitrogen (DIN) to coastal environments include runoff, point-source discharges, atmospheric deposition, sediment regeneration, and groundwater discharge (Vitousek et al. 1997). Among these, submarine groundwater discharge (SGD) has been identified as an important mechanism for transporting constituents such as nutrients, heavy metals, and other contaminants to marine coastal ecosystems (e.g. Moore 1996, Krest et al. 2000, Charette and Buesseler 2004). SGD has been studied by researchers in multiple disciplines and also by various methods. Therefore, the definition of groundwater discharge varies across disciplines and may include only freshwater discharge, or both freshwater and recirculated seawater. For the purpose of this study, SGD is defined as total advective discharge into a water body across the sediment water interface, including subsurface terrestrial freshwater and recirculated seawater (Taniguchi et al. 2002).

SGD can be a significant source of nutrients to the overlying water (e.g. Capone and Bautista 1985, Valiela et al. 1990, Corbett et al. 1999, Paytan et al. 2006, Cable and Martin 2008), contributing to geochemical budgets and biological activity. Groundwater discharge has been linked to influence the presence of brown tide blooms along the coast of Long Island Sound (LaRoche et al. 1997). SGD also supplies various coral reef environments with

anthropogenically-derived nitrate (Paytan et al. 2006). Since interstitial water in sediments is often significantly higher in nutrients than overlying water, the porewaters, which are part of the broad groundwater definition used here, can play an important role in the eutrophication of estuaries. SGD can be a source of new and regenerated nutrients to overlying water and may contribute similar nutrient loads as riverine loads, especially nitrogen (Capone and Bautista 1985, Valiela et al. 1990, Reay et al. 1992). Climate and geology are important factors influencing SGD (Freeze 1969). Although groundwater discharge is ubiquitous along coasts worldwide, it is not accounted for in many locations because of measurement difficulties and spatial/temporal heterogeneity (Burnett et al. 2001). Therefore, the effects of SGD on coastal ecosystems are poorly understood in comparison to riverine influences.

The Neuse River Estuary (NRE), North Carolina, USA, like many other coastal environments, has sustained accelerated eutrophication over recent years (Paerl et al. 1995, Burkholder et al. 2006). The North Carolina General Assembly mandated a 30% reduction in N loading in the NRE in the late 1990s (15A NCAC 2B.0232). Although total nitrogen decreased in the past decade, there has been a concomitant ~500% increase in water-column ammonium (Burkholder et al. 2006). Nitrogen contamination in shallow groundwater (depth < 31 m) has become especially important and has been documented in the Coastal Plain of North Carolina within the past decade as a result of increased nitrogen supply from swine operations, agricultural fertilizers, and urbanization (Spruill et al. 1996, Mallin 2000). Limited SGD data are available for the NRE, and the role of SGD in the documented water-column ammonium increase is not well understood. The objectives of this study were to 1) estimate SGD in the NRE over an annual cycle using ^{222}Rn and seepage meters; 2)

investigate and quantify the SGD ammonium flux to the NRE; and 3) compare these findings with available information on SGD in the mesohaline NRE and evaluate its contribution to nutrient inputs.

Methods to estimate SGD along coasts have included various natural tracers (e.g. radium isotopes, ^{222}Rn, chloride, methane), seepage meters, piezometers, temperature, conductivity, water budgets, and modeling (Burnett et al. 2006). It is becoming common, in fact, to use multiple methods to measure groundwater discharge because of its complex nature and the discrepancies found among methods used at the same location (Burnett et al. 2006, Cable et al. 2004). The two methods selected for this study, ^{222}Rn and seepage meters, have been used to quantify groundwater discharge in many studies (e.g. Cable et al. 1996, 2004, Corbett et al., 1999, 2000, Holly et al. 2003, Burnett et al. 2006, Burnett and Dulaiova 2006, Martin et al. 2007, Fear et al. 2007, McCoy et al. 2007, Cable and Martin 2008, Smith et al. 2008, Spruill and Bratton 2008).

2.3 Study Area

The Neuse River watershed is approximately 16,000 km^2 with river flow direction from west to east (Matson and Brinson 1990). The Coastal Plain of North Carolina and the NRE are underlain by sedimentary formations ranging from Pleistocene in age to recent deposits (Winner and Coble 1996). The unconfined aquifers underlying the NRE receive approximately 53 cm of recharge from precipitation annually (Giese et al. 1991). The majority of the NRE is underlain by a surficial aquifer that is 10-30 m thick with a hydraulic gradient of 10 m d^{-1} (Winner and Coble 1996). Below the surficial aquifer are the Yorktown and Pungo River confining units. The Yorktown confining unit is approximately 3-10 m thick and limits the amount of water discharging into the estuary from the Yorktown aquifer, except through buried paleochannels near Cherry Point (Wrege and Jen 2004). The Yorktown and Castle Hayne aquifers are two important aquifers in the Coastal Plain (Giese et al. 1991). The Yorktown aquifer is composed of fine sands and shell beds and produces high yielding wells. The Castle Hayne aquifer is composed of limestone that has high hydraulic conductivity on the order of 60 m d^{-1} (Winner and Coble 1996).

The NRE, located along the eastern seaboard of North Carolina (Figure 2.1), covers an area of approximately 4.55×10^8 m^2 and drains into Pamlico Sound which, together with the Albemarle Sound, form the second largest estuarine system on the U.S. mainland in areal extent (Steel 1991). The average discharge of the Neuse River is approximately 113 m^3 s^{-1} with a range of 55 – 173 m^3 s^{-1} based on the United States Geological Survey (USGS) mean monthly discharge measurements near Fort Barnwell, NC since 1996 (Figure 2. 2) (Title:

USGS Surface-Water Monthly Statistics http://waterdata.usgs.gov/nwis/monthly?). The NRE is a shallow estuary with a mean water depth of 4.5 m (Roelofs and Bumpus 1953) and limited inputs from the ocean. Tidal influence is minimal, and winds are the important mixing force in this shallow system (Luettich et al. 2000, Reed et al. 2004). Based on the freshwater discharge and limited oceanic exchange, water residence times are on the order of 50-100 days, which contributes to extensive recycling of nutrients (Christian et al. 1991; Steel 1991). Consequently, the NRE has sustained excessive eutrophication over the past decade resulting in annual fish kills, harmful algal blooms, and overall poor water quality (Burkholder et al. 2006).

The mesohaline estuarine flow regime is surface outflow and bottom-water inflow (Reed et al. 2004). Stratification frequently occurs during late summer months when winds are reduced, but sometimes persists from April through October (Burkholder et al. 2006). Consequently, local strong winds can influence the oxygenation and nutrient distribution in the estuary. Winds play a significant role in sediment resuspension and nutrient release from the benthic environment (Giffin and Corbett 2003). Distinct sediment boundaries are present in the NRE and the different sediment regimes can be distinguished based on porosity, among other characteristics. The sediments of the central channel consist of organic rich, fine-grained silt and clay with a porosity > 0.8 (Alperin et al. 2000). The center of the channel collects fine-grained sediment because it is the deepest area of the estuary and wave energy is minimal during calm periods. Nearshore sediments are mainly fine- to medium-grained sand with a average porosity < 0.6 (Alperin et al. 2000).

This study was conducted at one upstream site, Mills Branch (MB), located in the oligohaline portion of the estuary, and two downstream sites, Cherry Point (CP) and Wilkinson Point (WP) (Figure 2.1). All sites were located in sandy nearshore environments with porosity <0.7 measured for this study. MB is located near a housing subdivision with a nearby boat ramp and wildlife area. The vegetation along the shoreline includes a few sparse cypress trees and wetland vegetation. CP is also located near a housing subdivision, but the beach area is protected by riprap. Very little vegetation is present at CP. WP is near a summer camp with a well-maintained lawn, and the shoreline vegetation is mostly tall grasses.

2.4 Methods

2.4.1 Piezometers

Three multi-level piezometers, design followed from Martin et al. (2003), were installed in perpendicular transects to the shoreline at each of the three study sites, Mills Branch (MB); Cherry Point (CP); and Wilkinson Point (WP), during July 2006. The piezometers at MB were identified as MB1, MB2, and MB3, and were 3, 6, and 9 m, respectively, from the shoreline. At CP, the piezometers were identified as CP2, CP3, and CP4, and were installed 10, 15, and 20 m, respectively, from the shoreline. The WP transect had two piezometers, WP1 and WP2, located 7 and 10 m, respectively, from the shore. The piezometers were between 150 cm to 230 cm in length and had screened ports every 10- to 30-cm. PVC tubing (3/8" diameter) ran from the intake port along the inside of the PVC pipe to the surface, allowing samples to be collected using a peristaltic pump (Global Waters Instrumentation Inc., Gold River, CA). Porewater samples were collected into an overflow container to measure physical/chemical parameters (temperature, salinity, conductivity, and dissolved oxygen ([DO]) once the abundances of these tracers stabilized. Piezometers were sampled along with complementary water column measurements approximately bi-monthly from June 2007 to September 2008. One site was sampled per week during each sampling month. MB was not sampled in October due to equipment malfunction, and WP was not sampled in January and April because of boat restrictions due to adverse weather conditions. Measurements were made using a handheld YSI-85 with [DO], conductivity, temperature, and salinity probes (YSI, Incorporated). After the initial chemical parameters were measured, nutrient samples were collected in acid-stripped polypropylene bottles for

ammonium (NH_4^+), nitrate+nitrite (NO_3^-+NO_2^-), and soluble reactive phosphate (SRP). The NH_4^+ and NO_3^-+NO_2^- samples were analyzed colorimetrically using an automated Quattro Continuous-Flow Analysis (CFA) system. SRP was analyzed on a Lachat 8000 series nutrient analyzer. Ten milliliters of sample were collected for ^{222}Rn analysis (see following section) from an overflow container using a glass syringe. ^{222}Rn was sampled to estimate the rate of SGD at three locations in the NRE (MB, CP, WP) during six individual months between June 2007 through September 2008.

2.4.2 Radon

^{222}Rn is a valuable tracer for measuring SGD in coastal environments because it is enriched in subsurface waters compared to overlying seawater and behaves conservatively (e.g. Cable et al. 1996, Corbett et al. 1999, 2000, McCoy et al. 2007, Martin et al. 2007, Burnett et al. 2008, Cable and Martin 2008). ^{222}Rn has a half-life of 3.8 days and its parent, ^{226}Ra, has a half-life of 1,622 years. This naturally occurring tracer is an inert gas, and therefore, we expect measured activities to be mostly influenced by sediment lithology and radium content. Sediment production of ^{222}Rn must be measured because production of ^{222}Rn from ^{226}Ra varies with different soil/sediment lithologies (Martin et al. 2007). As a result of radon mobilization in sediments and porewater, ^{222}Rn activities can be in disequilibrium with the parent isotope, and this signal can be used to quantify the amount of groundwater entering an estuarine or coastal environment.

Ten milliliters of porewater sampled from the multi-level piezometers were collected for ^{222}Rn analysis from an overflow container using a glass syringe. The 10-mL sample was transferred to vials that had been pre-filled with 10 mL scintillation cocktail (Sigma Aldrich) to eliminate contact with air. Porewater ^{222}Rn was analyzed on a Packard Tri-Carb liquid scintillation counter.

Sediment slurry experiments (Martens et al. 1980, Corbett et al. 1998, Cable et al. 2004) were conducted to estimate the sediment-supported levels of porewater ^{222}Rn at equilibrium with solid phase sediment. Sediment-supported ^{222}Rn (^{222}Rn produced from sedimentary ^{226}Ra) was determined by collecting vibracores down to 240 cm depth from nearshore sites near the multi-sampling piezometers. Two cores were collected from the

Cherry Point site and one core from Wilkinson Point. A core was not collected from Mills Branch because of logistics, equipment limitations, and limited boat time to travel to the oligohaline portion of the estuary. Approximately 300 g of wet sediment were collected at three to five depths close to the piezometer port depths of 10, 50, 110, 190, and 230 cm beneath the seafloor (cmbsf). Sediment subsections were placed in 6-L air-tight Nalgene containers with 4 L of seawater and the slurry was incubated for 30 days to allow for in-growth of ^{222}Rn. It was assumed that after 30 days, ^{222}Rn (3.8 d half life) in the water was equilibrated with ^{226}Ra production from the sediment. The Nalgene containers were then connected to the extraction lines, and ^{222}Rn was extracted using a cryogeni technique (Mathieu et al. 1988, Cable et al. 1996). Each sample from the 6-L Nalgene bottles was degassed using a recirculating stream of helium with the ^{222}Rn isolated from the extraction line in a cold trap. The resulting ^{222}Rn was transferred to Lucas cells and counted using a photomultiplier tube array. Porosity and grain size were measured and used to convert sample activity to porewater activity. The activity ratio (AR) between porewater ^{222}Rn activities and sediment-supported ^{222}Rn activities was used to determine whether equilibrium had been established (Smith et al. 2008).

2.4.3 SGD Rates from ^{222}Rn Measurements

The flux of ^{222}Rn from porewaters to the overlying water was based on the zone of ^{222}Rn deficiency in porewaters created by advection and diffusion processes (Smethie et al. 1981, Martin et al. 2007, Cable and Martin 2008). As porewater is transported through the sediments via advective processes, a deficit of ^{222}Rn develops relative to its production from its parent, ^{226}Ra. Sediment-supported ^{222}Rn was measured at several depths using a slurry test as described (Smethie et al. 1981, Corbett et al. 1998). Porewater ^{222}Rn activities were subtracted from the sediment-supported ^{222}Rn to estimate the zone of ^{222}Rn deficiency for CP and WP. MB sediment-supported ^{222}Rn was assumed to be equal to the highest porewater ^{222}Rn activity measured in that sediment column. The SGD rate was calculated for each site using the following equation (Martin et al. 2007, Cable and Martin 2008):

$$J_{export} = \lambda \int (P - \lambda C(z))dz \approx \lambda \sum (P - \lambda C(z))\Delta z \qquad (1)$$

wherein λ is the ^{222}Rn decay constant (0.1809 day^{-1}), z is depth in the sediment column, C(z) is the ^{222}Rn activity for each depth in dpm L^{-1} of wet sediment, and P is the measured sediment-supported ^{222}Rn concentration in dpm L^{-1} of wet sediment. The diffusion of porewater must be subtracted from the advective processes (J_{export}) (Martin and Cable 2008). Diffusion can be calculated using Fick's First Law:

$$J_{diff} = - \Phi D_s \, dC / dz \qquad (2)$$

wherein Φ is the sediment porosity, Ds is the sediment diffusion coefficient for radon corrected for tortuosity, z is depth, and dC/dz is the concentration gradient of ^{222}Rn. Then,

$$J_{net} = J_{export} - J_{diff} \qquad (3)$$

J_{net} divided by the shallowest ^{222}Rn concentration gives the advective rate for porewater exchange, or SGD. The SGD calculated in this study accounted for recirculated seawater and fresh groundwater in the total flux, since this approach measureed the entire zone of deficiency of ^{222}Rn.

2.4.4 Seepage Meters

Seepage meters were used to estimate SGD at the same sampling sites and at the same times when ^{222}Rn was measured in porewaters. Modified Lee-style seepage meters were designed from 19-L (5 gallon) drums that were cut in half (Lee 1977). The seepage meters were gently pushed into the sediments and allowed to stabilize for approximately 15 minutes before attaching collection bags (Cherkauer and McBride 1988, Landon et al. 2001). Four-liter collection bags were pre-filled with 1 L of de-ionized water to reduce artificial flux from bag effects (Shaw and Prepas 1989, Cable et al. 1997, Corbett and Cable 2003). De-ionized water was used in order to measure changes in nutrient concentrations in the collection bag. Seepage meters were left in place for a minimum of 100 min to minimize the effect of initial artificial influx of water (Cable et al. 1997). The collection bag was clamped and detached from the seepage meter after approximately 100-150 min so that the water in the collection bag could be measured using a graduated cylinder.

2.5 Results

2.5.1 Porewater Characteristics

A summary of ranges for physical/chemical parameters in porewaters at the three sampling sites is provided in Table 2.1 for the 1.5-year sampling period. Porewater temperatures showed seasonal variability throughout the entire depth profile at all three sampling sites. Overall, MB had the least variable dissolved oxygen [DO] profile and CP had the largest [DO] variability (Table 2.1). All sites had similar temperature profiles, with smaller temperature ranges at depth across the seasons (Figure 2.3 A-H). For example, at CP, porewater at 230 cmbsf showed the smallest temperature range across seasons (13.2-27.7^{o}C) compared to 5.2-32.4 ^{o}C at 10 cmbsf (Table 2.1, Figure 2.3F). During warmer months, porewater temperatures decreased with depth (Figure 2.3 A-H). Inversely, temperatures increased with depth during January, when surface waters were colder. No temperature trends were evident along the offshore transects at any of the three sites.

MB exhibited the lowest [DO] concentrations, typically < 1.0 mg L^{-1}, with the smallest change with depth (Figure 2.4 A-C). MB also demonstrated the smallest concentration range across sampling months (Table 2.1). CP showed the largest range in [DO] concentrations for the various sampling periods (Table 2.1). Porewater [DO] was highest at CP during most sampling months and increased in the piezometer farthest offshore (Figure 2.4 D-F). [DO] at CP decreased with depth and then slightly increased at 190 and 230 cmbsf in the piezometer CP4 20 m offshore (Figure 2.4 F). WP had porewater [DO] < 2.0 mg L^{-1} (Table 2.1) and typically decreased with depth (Figure 2.4 G-H).

Upstream site MB sustained the most freshwater riverine inputs, and therefore, had the lowest conductivity which ranged from 1.3-7.1 mS cm^{-1} at 10 cmbsf and decreased slightly with depth to 1.1-1.3 mS cm^{-1} (Table 2.1). Trends in conductivity were not evident with depth or distance offshore at MB (Figure 2.5 A-C). At CP, the range in conductivity across seasons was smaller with depth (190 and 230 cmbsf: 0.6-1.2 and 0.3-1.7 mS cm^{-1} respectively; 10 cmbsf: 7.3-26.7 mS cm^{-1}) (Table 2.1). Conductivity decreased with depth (Figure 2.5 D-F), and also decreased offshore at CP4, 20 m from the shoreline. WP demonstrated the least amount of change with depth across the sampling seasons, but WP did not include winter or early spring samples. Conductivity at WP decreased with depth down to 30 cmbsf, then remained constant or increased down to 150 cmbsf (Figure 2.5 G-H).

Porewater salinity was relatively constant with depth at the upstream MB site, ranging between 0.6 and 0.8 for all sampling trips (Table 2.1). CP porewater salinity ranged from 0.3 to18 and decreased with sediment depth (Table 2.1). WP porewater salinity ranged from 6 to 20 and was representative of freshwater / seawater mixing (Table 2.1). Salinity showed slight temporal variation at CP and WP, although WP did not demonstrate the same porewater salinity gradient as CP. WP porewater salinity was variable with salinity peaks often occurring at specific depths.

2.5.2 Porewater and Sediment-supported ^{222}Rn

At upstream station MB the ^{222}Rn distribution pattern with depth was similar to porewater salinity distribution, in that the ^{222}Rn activity was relatively constant (< 200 dpm L^{-1}) (Figure 2.6A). At CP, ^{222}Rn porewater activities increased with depth (to values > 4,000 dpm L^{-1}) (Figure 2.6B). There was significant variation at certain depths among some sampling dates, especially between January and warmer months, and between CP2 and CP4. $^{222}Radon$ activities at CP were inversely related to salinity (Figure 2.7). ^{222}Rn activity was maximal in the deepest porewater samples from the two downstream study sites (CP: 190 and 230 cmbsf; WP: 140 cmbsf). At WP, on the north side of the channel, ^{222}Rn activities increased slightly with depth, but values were significantly lower (< 500 dpm L^{-1}) than at CP (Figure 2.6C). Piezometer WP2 had higher ^{222}Rn activities in shallow sediments than the shallow sediments of piezometer WP1.

Vibracores from CP and WP showed significantly different sediment lithologies between sites (Figure 2.8 A-C). Sediment-supported ^{222}Rn from slurried sediment experiments increased with depth, with the maximum activity at 230 cmbsf at CP (Figure 2.9A). The maximum measured sediment-supported ^{222}Rn at the piezometers 15 m from shore at CP was 5,000 dpm L^{-1} at 140 cmbsf, and the maximum sediment supported ^{222}Rn offshore was 2,000 dpm L^{-1} at 230 cmbsf. Sediment-supported ^{222}Rn at CP ranged from 62 dpm L^{-1} at 10 cmbsf to 2056 dpm L^{-1} at 230 cmbsf for the piezometer located 20 m offshore. ^{222}Rn was in excess of sediment-supported ^{222}Rn at WP and 20 m offshore at CP. At WP, sediment-supported ^{222}Rn was highest at 80 cm depth out of the three sediment samples measured (Figure 2.9B).

2.5.3 SGD Estimates

The mean SGD based on ^{222}Rn distributions, was 5.1 cm d^{-1} for MB, 12.6 cm d^{-1} for CP, and 7.9 cm d^{-1} for WP (Table 2.2, Figure 2.10A). ^{222}Rn-based SGD estimates were lowest at MB and CP in January (Figure 2.10A). The mean SGD at all sites for all seasons, estimated from ^{222}Rn measurements, was 9.1 ± 1.5 cm d^{-1}. By comparison, the mean SGD for all seasons estimated from seepage meters was 0.8 cm d^{-1} for MB, 4.7 cm d^{-1} for CP, and 3.1 cm d^{-1} for WP (Table 2.2, Figure 2.10B). The mean SGD estimated from all sites and seasons using seepage meters was 3.0 ± 1.6 cm d^{-1}.

2.5.4 Nutrients

Nitrate ($NO_3^-+NO_2^-$) was typically not detected, or comprised less than 10% of the N found in porewaters at the three sites. At upstream site MB, $NO_3^-+NO_2^-$ was detected at 10 cmbsf at < 0.2 μM concentrations and 0.5 μM during January, when $NO_3^-+NO_2^-$ water-column concentrations were ~9 μM (Figure 2.11). $NO_3^-+NO_2^-$ was detected at less than 0.4 μM concentrations with depth at CP and was present only during October, January, and April. At CP, typically $NO_3^-+NO_2^-$ concentrations were undetectable in surface waters and increased with depth (Figure 2.11). At WP, $NO_3^-+NO_2^-$ concentrations were not detected in any of the porewater samples. $NO_3^-+NO_2^-$ concentrations in the shallow porewaters were at or near detection limits, therefore, only NH_4^+ concentrations were considered in the calculated fluxes. NH_4^+ was elevated in porewaters relative to surface water at all three sites (Figure 2.12), and all sites showed significant temporal variability in NH_4^+ porewater concentration between warm (August, September) and cold (January) months. At CP, but not at WP, NH_4^+ porewater concentrations decreased with depth. MB had the highest NH_4^+ concentrations among the three sites, with maximum porewater concentration at 150 cmbsf (> 200 μM), consistent across seasons.

Mean porewater SRP values decreased with depth, demonstrating higher concentrations at 10 cmbsf compared to > 140 cmbsf (Table 2.3). At MB, SRP concentrations increased slightly to 30 cmbsf and then decreased at greater depths. MB had higher SRP concentrations compared to CP and WP. At CP, SRP concentrations ranged from 0.9 to 12.1 μM at 10 cmbsf, and decreased with depth. SRP porewater concentrations were higher at WP and ranged from 4.5 to 18.2 μM at 10 cmbsf.

2.6 Discussion

2.6.1 SGD Rates: ^{222}Rn and Seepage Meters

The porewater physical and chemical characteristics suggested that infiltrated seawater plays a role in advective porewater exchange in shallow sediments of the NRE. Temperature, [DO], and conductivity showed strong gradients in porewaters < 30 cmbsf (Figures 2.3-2.5). Conductivity data indicated that the porewaters (< 30 cmbsf) at CP and WP were affected by seawater flushing and diffusive transport, as conductivity sharply increased toward the sediment-water interface. In addition to seawater infiltration in the shallow porewaters, physical parameters suggested a freshwater influence in deeper porewaters. Porewater salinity profiles also indicated mixing of freshwater and seawater at depth at CP and possibly a shallow fresher lens at WP (Table 2.1). At CP, the CP4 piezometer (20 m from shore), porewater salinity was < 0.5 below 110 cm, indicating a freshwater source.

Use of two separate methodologies, ^{222}Rn activities and seepage meters, provided evidence of significant SGD occurring at the one upstream site, MB, and at the two downstream sites, CP and WP, in this study. Overall SGD estimated from ^{222}Rn was three-fold higher than SGD estimated from seepage meters. Although large standard deviations characterized many of the seepage meter data, the SGD values measured by the two methods were significantly different (ANOVA; p-value = 0.0004), and the ^{222}Rn methodology consistently yielded higher SGD estimates than seepage meters (Figure 2.13). Despite the significant difference between the two methods, the data were comparable to reports from

previous studies in the NRE (Spruill and Bratton 2008) and other environments (e.g. Taniguchi et al. 2002).

Sources of ^{222}Rn include excess delivered via groundwater from other parts of the aquifer and *in situ* production from ^{226}Ra (Semkow 1990, Tricca 2001). ^{226}Ra can be bound to mineral lattices, adsorbed onto grain surfaces, or dissolved in porewaters. Dulaiova et al. (2008) reported that elevated ^{222}Rn is produced mostly by ^{226}Ra on mineral surfaces, and dissolved ^{226}Ra in porewaters alone could not account for measured ^{222}Rn activities in Waquoit Bay, Massachusetts. Although ^{222}Rn behaves conservatively, ^{226}Ra can be influenced by redox sensitive compounds such as manganese and iron oxides and hydroxides (Gonneea et al. 2008). In this study, ^{222}Rn production in sediments was assumed to be constant in time from the consistent sediment source, but ^{222}Rn levels can vary spatially and temporally from differences in groundwater flow regime. CP had elevated ^{222}Rn concentrations compared to other sites. Based on a comparison of sediment-supported ^{222}Rn activities to sediment characteristics of vibracore samples, it is hypothesized that manganese and/or iron-oxide rich sediment layers at CP are creating zones that adsorb ^{226}Ra and produce high amounts of ^{222}Rn (Gonneea et al. 2008). The sediment-supported ^{222}Rn in core CP2 was higher than the total ^{222}Rn at the three depths sampled in the nearshore piezometer CP2 (10 m offshore), indicating that ^{222}Rn activity 10 m offshore is influenced by sediment production and horizontal transport or transport from depth. The activity ratio (AR) between sediment-supported ^{222}Rn for a core and measured porewater ^{222}Rn activity can be used to determine whether equilibrium (AR=1) had been established for a given depth interval (Smith et al. 2008). ARs ranged from 0.3 to 14.9 at CP and from 1.4 to 6.6 at WP, with averages of 4.7

and 4.4, respectively. The high ARs at both sites suggest that disequilibrium existed between ^{222}Rn and sediment-supported ^{222}Rn, and upward advection and diffusion of Rn exists.

Seepage meters can be used to estimate total SGD, which includes both groundwater flux and recirculated seawater. Seepage meter performance has been assessed by many scientists because of substantial variability in measurements and significant artifacts in seepage rates (Shaw and Prepas 1989, Cable et al. 1997, Corbett and Cable 2003). Cable et al. (1997) found that longer deployment of seepage meters (30-60 minutes) and pre-filling the collection bag minimized an initial short-term influx of seepage. Both of these techniques were applied in this study. The two previous studies conducted by Fear et al. (2007) and Spruill and Bratton (2008) in the mesohaline NRE reported slightly different mean SGD rates, 1 cm d^{-1} and 9 cm d^{-1} respectively. The difference in estimates of SGD between Fear et al. (2007) and Spruill and Bratton (2008) may have resulted from variability in application of seepage meters or SGD heterogeneity. Spruill and Bratton (2008) did not pre-fill the seepage meter collection bags, and Fear et al. (2007) placed seepage meters farther offshore where SGD is likely to be lower. In this study, seepage meter SGD rates were lower than calculated ^{222}Rn rates, but values were still within a factor of 3 or 4 of SGD rate estimated from ^{222}Rn. Spruill and Bratton (2008) reported a mean of 9 cm d^{-1} in SGD measurements with considerable variability (<1 - 43 cm d^{-1}). We estimated a similar average SGD at 9.1 cm d^{-1} using ^{222}Rn as a tracer, and 3.0 cm d^{-1} using seepage meters but with significantly less variability.

2.6.2 Ammonium Flux from SGD

Organic matter remineralization and other subsurface diagenetic processes are important in determining the nature of chemical species discharging through an aquifer, including groundwater transport through sediments. The processes control the chemical flux across the sediment-water interface, which can be a significant source of nutrients for estuarine primary production (e.g., Boynton and Kemp 1985, Hammond et al. 1985, Rizzo et al. 1996). The shallow nearshore environments are impacted by physical (advective flux) and biological processes (bioturbation) that may enhance remineralization rates and nutrient flux. Mixing of saltwater and fresh groundwater occurs along shorelines creating a subterranean estuary (Moore 1999), where nitrogen species can be transformed or removed depending on the oxidation-reduction regime of the pore fluid (Charette et al. 2005, Kroeger and Charette 2008). Subterranean estuaries typically have low carbon concentrations because of high mineralization rates from continual advection (Beer et al. 2005), but they are still biogeochemically active and can be significant in decreasing or transforming nitrogen before it is released to the overlying water column (Kroeger and Charette 2008).

In the sediment porewaters of the NRE, NO_3^-+NO_2^- was rarely detected, and only at depth, indicating removal of NO_3^-+NO_2 before entering the overlying water column (Figure 2.12). High overlying water NO_3^-+NO_2 concentrations upstream may have contributed to NO_3^-+NO_2 infiltration in shallow porewaters at MB. NO_3^-+NO_2 was not detected in shallow porewaters (< 100 cmbsf) at downstream sites CP and WP, except during January at CP. It is possible NO_3^-+NO_2 was transformed before fluxing from the sediment to the overlying water.

The location of the mixing zone depends on tidal influence, sea level, and potentiometric pressure. Chemical transformations at the mixing zone can be affected by sea level rise, as well as groundwater withdrawal, which can enhance saltwater intrusion and also increase groundwater nutrient loads by increasing the local oxygen concentrations (Krest et al. 2000, Slomp and Van Capellen 2004). The status of present subsurface conditions can serve as a baseline for interpreting future perturbations of the system, such as groundwater withdrawal and sea level rise.

Many factors potentially can influence NH_4^+ flux from the sediment to the water column, including sediment porosity, grain size, organic carbon content, as well as porewater dissolved oxygen content and salinity. Processes influencing NH_4^+ flux from sediments include various microbial processes such as nitrification, denitrification, and anaerobic ammonium oxidation. In addition to these factors and processes, other factors such as diffusive flux, tidal pumping, wave interaction, bioturbation, and groundwater discharge impact the release of NH_4^+ from porewaters to the overlying water. It is important to investigate nearshore sites where groundwater discharge occurs because the oxic/anoxic boundary and saltwater/freshwater boundary significantly affect the nature of organic matter degradation, NH_4^+ production, and other redox reactions (Spiteri et al 2008).

NRE sediments have been shown to be an important source of nutrients, specifically NH_4^+, to the overlying water (Haruthian 1997, Fisher et al. 1982, Alperin et al. 2000), but previous studies mostly focused on diffusive flux as opposed to advective flux (such as SGD) and targeted the organic rich mid-channel sediments. SGD can be an important vector for nutrient transport from sediments to the overlying water column (Capone and Bautista 1985,

Valiela et al. 1990, Corbett et al. 1999, Charette and Buesseler 2004, Slomp and Van Cappellen 2004, Paytan et al. 2006) and is commonly estimated by multiplying the shallowest porewater nutrient concentration by the advective component. Nutrient flux calculated by this method assumes that the nutrient behaves conservatively from the sediment depth measured to the sediment-water interface. This study focused on NH_4^+ because its documented increase in the NRE (Burkholder et al. 2006) and the fact that few data are available regarding NH_4^+ flux in sandy environments. NH_4^+ flux was calculated by multiplying the NH_4^+ concentration at 10 cmbsf by the SGD for each site seasonally. The average NH_4^+ flux at the three nearshore sites of the NRE over all seasons was 11.2 ± 2.0 mmol NH_4^+ m^{-2} d^{-1} (Table 2.4). MB exhibited the highest NH_4^+ flux, possibly due to higher organic degradation and the rate of flow (Spiteri et al. 2008). MB showed the highest NH_4^+ flux during September 2008 (39.9 mmol m^{-2} d^{-1}), and this flux was driven by the high NH_4^+ concentration at 10 cmbsf. In contrast, CP had higher SGD rates and lower NH_4^+ concentrations, resulting in lower NH_4^+ flux. The NH_4^+ fluxes in the nearshore environments were temporally and spatially variable. Based on the SGD and nutrient flux measurements, these data indicate that NH_4^+ can be an important source of nutrients from the sediments to the overlying waters in nearshore estuarine environments.

2.6.3 Implications of SGD on Nutrient Budgets

The volumn of water associated with SGD is often lower than river discharge, but SGD typically has higher nutrient concentrations than the associated riverine end member (Valeila 1990, Moore 1999). In other studies, SGD had higher or comparable values of nutrient loads compared to riverine loads, including New England bays (Valeila et al. 1990), Kahana Bay, Hawaii (Garrison et al. 2003), a South Carolina salt marsh (Krest et al. 2000), Tomales Bay, CA (Oberdorfer et al. 1999), and Florida Bay (Corbett et al. 1999). Thus, groundwater inputs can be a significant source of bioavailable N to coastal sediments, contributing 20% or more of the N inputs to receiving waters (e.g. Capone and Bautista 1985, Valiela et al. 1990).

The various forms of bio-reactive N often are grouped together as total dissolved inorganic nitrogen (NO_3^-, NO_2^-, NH_4^+), and upstream river discharge is typically the primary focus for estuarine nutrient loading and phytoplankton response. NO_3^- is the dominant form of DIN in many oceanic and coastal waters because NH_4^+ is oxidized to NO_3^- (Codispoti and Christensen 1985), but in the past two decades, dramatic increases in NH_4^+ have been documented in the NRE and other systems (Smith et al. 1999, Boesch et al. 2001, Cloern 2001, Burkholder et al. 2006, Dugdale et al. 2007, Jassby 2008, P. Glibert unpubl. data for Maryland's Coastal Bays). In this study, SGD contributed more NH_4^+ than riverine discharge during 4 of 6 months sampled (Figure 2.14). The SGD NH_4^+ flux was > 40 ± 7.4 mol d^{-1} during June, August, and September and was twice as much as the riverine flux during June, August, and October (Figure 2.14). River discharge peaked during late winter and early spring (January - May) and provided substantial riverine NH_4^+ during that period

(Figures 2.2 and 2.14). SGD was an important source of NH_4^+, especially during summer and fall when river discharge was lowest (Figure 2.14). Advective fluxes occur year-round to the overlying water but, based on these data, SGD can provide significant NH_4^+ for late summer blooms, when phytoplankton productivity is maximal (Mallin 1991, 1994).

In studies that focused on total DIN inputs rather than separately considering NH_4^+, groundwater was described as a minor contributor of the N and P loading to the NRE (Fear et al. 2007, Spruill and Bratton 2008). Using Lee-type seepage meters, Fear et al. (2007) estimated that groundwater contributed only 0.8% of N loading and 1.0% of P loading to the NRE, and Spruill and Bratton (2008) estimated that ~6% of N and P inputs were from groundwater. Productivity in the NRE is hydrologically influenced (Arhonditsis et al. 2007, Rothenberger et al. 2009a), but the role of SGD as a nutrient source to the NRE had not been considered extensively in previous studies. This research emphasizes the importance of investigating N forms individually, and indicates that SGD may be more important to water column NH_4^+ budget and phytoplankton productivity than previously estimated using DIN.

As an additional consideration, NH_4^+ is the preferred form of N over NO_3^- by phytoplankton (Middleburg and Niewenhuize 2000, Twomey et al. 2005). In the NRE, NH_4^+ uptake can account for approximately half of total N taken up by phytoplankton (Twomey et al. 2005). Rothenberger et al. (2009a) related the increase in water-column NH_4^+ in the NRE to higher abundance of certain harmful algal species such as *Heterosigma akashiwo*, which is known to prefer NH_4^+ as a N source (Herndon and Cochlan 2006). With new understanding of uptake rates and preferences of the pelagic community in relation to different N forms, it is useful to express the importance of N sources considering these different N forms.

Riverine nutrient cycling and loading are different than the processes associated with groundwater discharge. The chemical reactions that occur in the subsurface may produce different ratios of nutrients compared to river discharge. The nitrogen and phosphorus ratio (N:P) of marine pelagic phytoplankton is on the order of 16:1 (Redfield 1934) and global riverine dissolved reactive N:P is similar with a value of 18:1 (Meybeck 1982). Typically N is limiting in estuarine environments, but in high groundwater discharge locations the N:P of the discharging water may influence the nature of nutrient limitation. Estuarine N:P can be highly variable ranging from < 1.0 to > 200 (Day 1989) and can be lower than Redfield ratio during peak phytoplankton productivity, leading to N limitation (Nixon and Pilson 1983). SGD often has higher N:P ratios than overlying water because regenerated P adsorbs onto sediment particle surfaces in oxic sediments and is fairly immobilized relative to N (LaPointe 1990). Consequently, the N:P ratio in SGD can be dependent on the groundwater flow rates, the form and supply of N and P, and the redox conditions of the environment (Slomp and Van Cappellen 2004). In the subsurface mixing zone of oxic freshwater and anoxic saline groundwater, removal of phosphorus through iron and calcium bound P minerals can occur in the sediments (Slomp and Van Cappellen 2004). The ratio of N and P in the SGD is important because it may influence the phytoplankton assemblage and the limiting nutrient for phytoplankton growth.

The entire Neuse River system is eutrophic (Rothenberger et al. 2009b), and is classified by the North Carolina Department of Environment and Natural Resources (NC DENR 1997) as Nutrient-Sensitive Waters, prone to algal blooms, oxygen deficits and fish kills from excessive nutrient enrichment. The NRE is considered N-limited, although

seasonally it can be co-limited by both N and P (Rudek et al. 1991, Lin et al. 2007). NH_4^+, the dominant N form in porewaters at all three sites in this study, was used to calculate N:P ratios in the SGD: 73:1 at CP, 46:1 at WP, and 42:1 at MB averaged over all sampling months. These values were within the range of N:P ratios for SGD at other locations. Slomp and Van Cappellen (2004), for example, reported a range of 3 to 519, with higher N:P ratios indicating possible immobilization of P in the sediments by sorption to Fe-oxides or co-precipitation with Al, Ca, or Fe. The greater flux of N relative to P may also be important in shifting this estuary toward a P-limited system over time, or toward a N and P co-limited system, which would considerably alter the ecological dynamics.

2.7 Conclusions

Based on ^{222}Rn activities and seepage meter measurements collected between June 2007 and September 2008, SGD is an important component in nearshore environments of the NRE. The SGD rates estimated in this study were comparable to other rates found in coastal environments. Nearshore environments were an important source of NH_4^+ to the overlying water, and showed a strong temporal and spatial variability that was highly dependent on porewater NH_4^+ concentrations. NH_4^+ flux from SGD contributed substantially more NH_4^+ to the overlying water compared to riverine discharge four of the six months sampled. In fact, during three of the six sampling months, SGD contributed twice as much NH_4^+ than the riverine flux. SGD was shown to be an important source of NH_4^+ to phytoplankton during summer and fall when river discharge is low and productivity is maximal. This study underscores the importance of investigating N forms separately from total DIN, because emphasis only on total DIN inputs may underestimate the importance of SGD contributions to phytoplankton productivity. In addition, the higher flux of N relative to P in SGD estimates suggests that SGD could play an important role in shifting the NRE toward a P-limited system or N+P co-limitation over time, away from its N-limited present status.

The water column of the NRE has sustained a ~500% increase in NH_4^+ over the past decade, and the major N form in SGD is NH_4^+. This study advances understanding about N sources to the NRE and, more generally, about SGD in shallow estuaries under accelerated eutrophication, which characterizes many estuaries throughout the world (National Research Council 2000). SGD in coastal environments and ecosystems such as the NRE is important to consider by coastal resource managers because it contributes substantial nutrients and

other constituents from sediments and aquifers into nearshore environments. Many estuarine and coastal environments are economically important to fisheries and tourism, and the demand for resources from these environments increases as coastal population grows. As coastal environments become more adversely affected by this demand, factors influencing water quality, such as SGD, need to be targeted as a source for contaminants. Once a baseline of SGD and its contribution of constituents to the overlying water column are established in a particular system, resource managers can derive more accurate estimates of nutrient sources and budgets. The insights from these data will help to define the role of SGD in N fluxes to coastal ecosystems, and provide a baseline for assessing the effects of future perturbations such as sea level rise, fresh groundwater withdrawal, and urbanization.

2.8 References

Alperin, M.J., Clesceri, E.J., Wells, J.T., Albert, D.B., McNinch, J.E., Martens, C.S., 2000. Sedimentary processes and benthic-pelagic coupling, pp. 63-105. In: R. A. Leuttich (ed.), Neuse River Estuary Modeling and Monitoring Project: Final Report – Monitoring Phase. Report. UNC Water Resources Research Institute, Raleigh.

Arhonditsis, G. B., C. A. Stow, H. W. Paerl, L. M. Valdes-Weaver, L. J. Steinberg, and K. H. Reckhow. 2007. Delineation of the role of nutrient dynamics and hydrologic forcing on phytoplankton patterns along a freshwater-marine continuum. Ecological Modeling 208, 230-246.

Beer, D., Wenzhöfer, F., Ferdelman, T.G., Boehme, S.E., Huettel, M., Beusekom, J.E.E.v., Böttcher, M.E., Musat, N., Dubilier, N., 2005. Transport and Mineralization Rates in North Sea Sandy Intertidal Sediments, Sylt-Rømø Basin, Wadden Sea. Limnol. Oceanogr. 50, 113-127.

Boesch, D.F., Brinsfield, R.B., Magnien, R.E., 2001. Chesapeake Bay Eutrophication: Scientific Understanding, Ecosystem Restoration, and Challenges for Agriculture. J. Environ. Qual. 30, 303-320.

Boynton, W., Kemp, W., 1985. Nutrient regeneration and oxygen consumption by sediments along an estuarine salinity gradient. Mar. Ecol. Prog. Ser. 23, 45-55.

Burkholder, J.M., Dickey, D.A., Kinder, C., Reed, R.E., Mallin, M.A., Melia, G., McIver, M.R., Cahoon, L.B., Brownie, C., Deamer, N., Springer, J., Glasgow, H., Toms, D., Smith, J., 2006. Comprehensive trend analysis of nutrients and related variables in a large eutrophic estuary: A decadal study of anthropogenic and climatic influences. Limnol. Oceanogr. 51, 463-487.

Burnett, W.C., Taniguchi, M., Oberdorfer, J., 2001. Measurement and significance of the direct discharge of groundwater into the coastal zone. J. of Sea Research 46, 109-116.

Burnett, W.C., Aggarwal, P.K., Aureli, A., Bokuniewicz, H., Cable, J.E., Charette, M.A., Kontar, E., Krupa, S., Kulkarni, K.M., Loveless, A., Moore, W.S., Oberdorfer, J.A., Oliveira, J., Ozyurt, N., Povinec, P., Privitera, A.M.G., Rajar, R., Ramessur, R.T., Scholten, J., Stieglitz, T., Taniguchi, M., Turner, J.V., 2006. Quantifying submarine groundwater discharge in the coastal zone via multiple methods. Sci. Total Environ. 367, 498-543.

Cable, J.E., Martin, J.B., 2008. In situ evaluation of nearshore marine and fresh porewater transport into Flamengo Bay, Brazil. Estuar. Coast. Shelf Sci. 76, 473-483.

Cable, J.E., Martin, J.B., Swarzenski, P.W., Lindenberg, M.K., Steward, J., 2004. Advection Within Shallow Porewaters of a Coastal Lagoon, Florida. Ground Water 42, 1011-1020.

Cable, J.E., Bugna, G.C., Burnett, W.C., Chanton, J.P., 1996. Application of 222Rn and CH4 for Assessment of Groundwater Discharge to the Coastal Ocean. Limnol. Oceanogr. 41, 1347-1353.

Cable, J.E., Burnett, W.C., Chanton, J.P., 1997. Magnitude and variations of groundwater seepage along a Florida marine shoreline. Biogeochem. 38, 189-205.

Capone, D.G., Bautista, M.F., 1985. A groundwater source of nitrate in nearshore marine sediments. Nature 313, 214-216.

Capone, D., Slater, J., 1999. Interannual patterns of water table height and groundwater derived nitrate in nearshore sediments. Biodegradation 10, 277-288.

Charette, M.A., Sholkovitz, E.R., Hansel, C.M., 2005. Trace element cycling in a subterranean estuary: Part 1. Geochemistry of the permeable sediments. Geochim. Cosmochim. Acta 69, 2095-2109.

Charette, M.A., Buesseler, K.O., 2004. Submarine Groundwater Discharge of Nutrients and Copper to an Urban Subestuary of Chesapeake Bay (Elizabeth River). Limnol. Oceanogr. 49, 376-385.

Cherkauer, D., McBride, J., 1988. A remotely operated seepage meter for use in large lakes and rivers. Groundwater 26, 165-171.

Christian, R.R., Boyer, J.N., Stanley, D.W., 1991. Multi-year distribution patterns of nutrients within the Neuse River Estuary, North Carolina. Mar. Ecol. Prog. Ser. 71, 259-274.

Cloern, J.E. 2001. Our evolving conceptual model of the coastal eutrophication problem. Mar. Ecol. Prog. Ser. 210, 223-253.

Codispoti, L.A., Christensen, J.P., 1985. Nitrification, denitrification and nitrous oxide cycling in the eastern tropical South Pacific Ocean. Mar. Chem. 16, 277-300.

Corbett, D.R., Dillon, K., Burnett, W., Chanton, J., 2000. Estimating the Groundwater Contribution into Florida Bay via Natural Tracers, 222Rn and CH4. Limnol. Oceanogr. 45, 1546-1557.

Corbett, D.R., Chanton, J., Burnett, W., Dillon, K., Rutkowski, C., Fourqurean, J.W., 1999. Patterns of Groundwater Discharge into Florida Bay. Limnol. Oceanogr. 44, 1045-1055.

Corbett, R., Cable, J.E., 2003. Seepage meters and advective transport in coastal environments: comments on "Seepage meters and Bernoulli's revenge" by Shinn, Reich and Hickey. Estuaries 26, 1383-1389.

Day, J.W., Hall, C., Kemp, W., Yanez-Arancibia, A. (Eds),1989. Estuarine Ecology. John Wiley and Sons, Inc.

Dugdale, R.C., Wilkerson, F.P., Hogue, V.E., Marchi, A., 2007. The role of ammonium and nitrate in spring bloom development in San Francisco Bay. Estuar. Coast. Shelf Sci. 73, 17-29.

Dulaiova, H., Gonneea, M.E., Henderson, P.B., Charette, M.A., 2008. Geochemical and physical sources of radon variation in a subterranean estuary – Implications for groundwater radon activities in submarine groundwater discharge studies. Marine Chemistry 110, 120-127.

Fear, J., Paerl, H., Braddy, J., 2007. Importance of submarine groundwater discharge as a source of nutrients for the Neuse River Estuary, North Carolina. Estuaries and Coasts 30, 1027-1033.

Fisher, T.R., Carlson, P.R., Barber, R.T., 1982. Sediment nutrient regeneration in three North Carolina estuaries. Estuar. Coast. Shelf Sci. 14, 101-116.

Freeze, A. 1969. The mechanism of natural groundwater recharge and discharge-1. one-dimensional, vertical, unsteady, unsaturated flow above a recharging or discharging groundwater flow system. Water Resources Res. 5, 153-171.

Garrison, G.H., Glenn, C.R., McMurtry, G.M., 2003. Measurement of submarine groundwater discharge in Kahana Bay, O'ahu, Hawaii. Limnol. Ocean 48, 920-928.

Giese, G.L, Eimers, J.L., Coble, R.W., 1991. Simulation of Ground-Water Flow in the Coastal Plain Aquifer System of North Carolina. USGS Open-File Report 90-372, 178 p.

Giffin, D., Corbett, D.R., 2003. Evaluation of sediment dynamics in coastal systems via short-lived radioisotopes. J. Mar. Syst. 42, 83-96.

Gonneea, M.E., Morris, P.J., Dulaiova, H., Charette, M.A., 2008. New perspectives on radium behavior within a subterranean estuary. Mar. Chem. 109, 250-267.

Hammond, D.E., Fuller, C., Harmon, D., Hartman, B., Korosec, M., Miller, L.G., Rea, R., Warren, S., Berelson, W., Hager, S.W., 1985. Benthic fluxes in San Francisco Bay. Hydrobiologia 129, 69-90.

Haruthunian, 1997. Seasonal and Spatial Variations in Benthic Organic Nitrogen Remineralization in the Neuse River Estuary, North Carolina. M.S. Thesis, UNC Chapel Hill.

Herndon, J., Cochlan, W.P., 2006. Nitrogen utilization by the raphidophyte *Heterosigma akashiwo*: Growth and uptake kinetics in laboratory cultures. Harmful Algae 6, 260-270.

Howarth, R.W., Boyer, E.W., Pabich, W.J., Galloway, J.N., 2002. Nitrogen use in the United States from 1961-2000 and potential future trends. Ambio 31, 88-96.

Jassby, A. 2008. Phytoplankton in the Upper San Francisco Estuary: Recent biomass trends, their causes and their trophic significance. San Francisco Estuary and Watershed Science 6, Article 2.

Krest, J.M., Moore, W.S., Gardner, L.R., Morris, J.T., 2000. Marsh Nutrient Export Supplied by Groundwater Discharge: Evidence From Radium Measurements. Global Biogeochem. Cycles 14, 167-176.

Kroeger, K.D., Charette, M.A., 2008. Nitrogen biogeochemistry of submarine groundwater discharge. Limnol. Ocean. 53, 1025-1039.

Landon, M., Rus, D., Harvey, F., 2001. Comparison of instream methods for measuring hydraulic conductivity in sandy sediments. Groundwater 39, 870-885.

Lapointe, B., Clark, M., 1992. Nutrient inputs from the watershed and coastal eutrophication in the Florida keys. Estuaries and Coasts 15, 465-476.

LaRoche, J., Nuzzi, R., Waters, R., Wyman, K., Falkowski, P., Wallace, D., 1997. Brown Tide blooms in Long Island's coastal waters linked to interannual variability in groundwater flow. Global Change Biol. 3, 397-410.

Lee, D., 1977. A device for measuring seepage flux in lakes and estuaries. Limnol. Oceanogr. 22, 140-147.

Lin, J., Lian, X., Pietrafesa, L.J., Ramus, J.S., Paerl, H.W., 2007. Water quality gradients across the Albemarle-Pamlico Estuarine system: Seasonal variations and model applications. J. Coastal Res. 23, 213-229.

Luettich 2000 Leuttich, R., McNinch, J., Paerl, H., Peterson, C., Wells, J., Alperin, M., Martens, C., Pinckney, J., 2000. Neuse River Estuary Modeling and Monitoring Project Stage 1: Hydrography and Circulation, Water Column Nutrients and Productivity, Sedimentary Processes and Benthic-Pelagic Coupling, and Benthic Ecology. Report No. 325-B. UNC Water Resources Research Institute, Raleigh.

Luettich, R.A., Carr, S.D., Reynolds-Fleming, J.V., Fulcher, C.W., McNinch, J.E., 2002. Semi-diurnal seiching in a shallow, micro-tidal lagoonal estuary. Cont. Shelf Res. 22, 1669-1681.

Mallin, M.A., Paerl, H.W., Rudek, J., 1991. Seasonal phytoplankton composition, productivity and biomass in the Neuse River Estuary, North Carolina. Estuar. Coast. Shelf Sci. 32, 609-623.

Mallin, M.A., 1994. Phytoplankton ecology of North Carolina estuaries. Estuaries, 17, 561-574.

Mallin, M.A., 2000. Impacts of industrial-scale swine and poultry production on rivers and estuaries. Am. Sci. 88, 26-37.

Martens, C.S., Kipphut, G.W., Val Klump, J., 1980. Sediment-water chemical exchange in the coastal zone traced by in situ Radon-222 flux measurements. Science 208, 285-288.

Martin, J., Cable, J., Smith, C., Roy, M., Cherrier, J., 2007. Magnitudes of submarine groundwater discharge from marine and terrestrial sources: Indian River Lagoon, Florida. Water Resour. Res. 43, W05440, 1-15.

Martin, J.B., Cable, J.E., Swarzenski, P.W., Lindenberg, M.K., 2004. Enhanced submarine ground water discharge from mixing of porewater and estuarine water. Ground Water 42, 1000-1010.

Martin, J.B., Hartl, K.M., Corbett, D.R., Swarzenski, P.W., Cable, J.E., 2003. A multi-level pore-water sampler for permeable sediments. J. of Sed. Res. 73, 128-132.

Mathieu, G., Lubpton, R., Hammond, D., 1988. System for measurement of 222-Rn at low levels in natural waters. Health Phys. 55, 989-992.

Matson, E.A., Brinson, M.M., 1990. Stable Carbon Isotopes and the C: N ratio in the estuaries of the Pamlico and Neuse Rivers, North Carolina. Limnol. Oceanogr. 35, 1290-1300.

McCoy, C.A., Corbett, D.R., McKee, B.A., Top, Z., 2007. An evaluation of submarine groundwater discharge along the continental shelf of Louisiana using a multiple tracer approach. J. Geophys. Res. 112, C03013, 1-13.

Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers. Am. J. Sci. 282, 401-450.

Middelburg, J.J., Nieuwenhuize, J., 2001. Nitrogen isotope tracing of dissolved inorganic nitrogen behaviour in tidal estuaries. Estuar. Coast. Shelf. Sci. 53, 385-391.

Moore, W., 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. Nature 380, 612-614.

Moore, W., 1998. Application of ^{226}Ra, ^{228}Ra, ^{223}Ra, and ^{224}Ra in coastal waters to assessing coastal mixing rates and groundwater discharge to oceans. Journal of Earth System Science 107, 343-349.

Moore, W.S., de Oliveira, J., 2008. Determination of residence time and mixing processes of the Ubatuba, Brazil, inner shelf waters using natural Ra isotopes. Estuar. Coast. Shelf Sci. 76, 512-521.

Moore, W.S., 1999. The subterranean estuary: a reaction zone of ground water and sea water. Mar. Chem. 65, 111-125.

Nixon, S.W. and Pilson, M.E., 1983. Nitrogen in estuarine and coastal marine ecosystems, pp. 565-648. In E.J. Carpenter and D.G. Capone [eds.], Nitrogen in the Marine Environment. New York: Academic Press.

Nixon, S.W., 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia 41, 199-219.

North Carolina Department of Environment and Natural Resources (NC DENR). 1997. Neuse River Nutrient-Sensitive Waters (NSW) Management Strategy. NC DENR, Raleigh.

Oberdorfer, J., Valentino, M., Smith, S., 1999. Groundwater contribution to the nutrient budget of Tomales Bay, California. Biodegradation 10, 199-216.

Oberdorfer, J.A., Charette, M., Allen, M., Martin, J.B., Cable, J.E., 2008. Hydrogeology and geochemistry of near-shore submarine groundwater discharge at Flamengo Bay, Ubatuba, Brazil. Estuar. Coast. Shelf Sci. 76, 457-465.

Paerl, H., Mallin, M., Donahue, C., Go, M., Peierls, B., 1995. Nitrogen Loading Sources and Eutrophication of the Neuse River Estuary, North Carolina: Direct and Indirect Roles of Atmospheric Deposition. Report No. 291. UNC Water Resources Research Institute, Raleigh.

Paytan, A., Shellenbarger, G.G., Street, J.H., Gonneea, M.E., Davis, K., Young, M.B., Moore, W.S. 2006. Submarine groundwater discharge: An important source of new inorganic nitrogen to coral reef ecosystems. Limnol. Oceanogr. 51, 343-348.

Reay, W.G., Gallagher, D.L., Simmons, G.M. Jr., 1992. Groundwater discharge and its impact on surface water quality in a Chesapeake Bay inlet. J. Am. Water Resour. Assoc. 28, 1121-1134.

Redfield, A.C., 1934. On the proportions of organic derivatives in seawater and their relation to the composition of plankton, pp. 177-192. In: R.J. Daniel [ed.], James Johnson Memorial Volume. Liverpool Univ. Press, Liverpool, UK.

Reed, R.E., Glasgow, H.B., Burkholder, J.M., Brownie, C., 2004. Seasonal physical–chemical structure and acoustic Doppler current profiler flow patterns over multiple years in a shallow, stratified estuary, with implications for lateral variability. Estuar. Coast. Shelf Sci. 60, 549-566.

Rizzo, W., Christian, R., 1996. Significance of subtidal sediments to heterotrophically-mediated oxygen and nutrient dynamics in a temperate estuary. Estuaries 19, 475-487.

Roelofs, E.W., Bumpus, D.F., 1953. The hydrography of Pamlico Sound. Bulletin Marine Science of the Gulf and the Caribbean 3, 181-205.

Rothenberger, M., J.M. Burkholder, T. Wentworth, 2009a. Multivariate analysis of phytoplankton and environmental factors in a eutrophic estuary. Limnol. Oceanogr. 54, 2107-2127.

Rothenberger, M., Burkholder, J.M., Brownie, C., 2009b. Long-term effects of changing land use practices on surface water quality in a major lagoonal estuary. Environmental Management 44, 505-523.

Rudek, J., Paerl, H.W., Mallin, M.A., Bates, P.W., 1991. Seasonal and hydrological control of phytoplankton nutrient limitation in the lower Neuse River Estuary, North Carolina. Mar. Ecol. Prog. Ser. 75, 133-142.

Semkow, T.M., 1990. Recoil-emanation theory applied to radon release from mineral grains. Geochim. Cosmochim. Acta 54, 425-440.

Shaw, R.D., Prepas, E.E., 1989. Anomalous, short-term influx of water into seepage meters. Limnol. Oceanogr. 34, 1343-1351.

Slomp, C.P., Van Cappellen, P., 2004. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. Journal of Hydrology 295, 64-86.

Smethie, W.M., Nittrouer, C.A., Self, R.F., 1981. The use of radon-222 as a tracer of sediment irrigation and mixing on the Washington continental shelf. Marine Geology 42, 173-200.

Smith, C.G., Cable, J.E., Martin, J.B., Roy, M., 2008. Evaluating the source and seasonality of submarine groundwater discharge using a radon-222 porewater transport model. Earth Planet. Sci. Lett. 273, 312-322.

Smith, V.H., Tilman, G.D., Nekola, J.C., 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. Environmental Pollution 100, 179-196.

Spiteri, C., Slomp, C.P., Tuncay, K., Meile, C., 2008. Modeling biogeochemical processes in subterranean estuaries: Effect of flow dynamics and redox conditions on submarine groundwater discharge of nutrients. Water Resour. Res. 44, 1-18, W02430, doi:10.1029/2007WR006071.

Spruill, T., Bratton, J., 2008. Estimation of groundwater and nutrient fluxes to the Neuse River Estuary, North Carolina. Estuaries and Coasts 31, 501-520.

Spruill, T., Eimers, J., Morey, A., 1996. Nitrate-Nitrogen Concentrations in Shallow Ground Water of the Coastal Plain of the Albemarle-Pamlico Drainage Study Unit, North Carolina and Virginia. USGS Fact Sheet 241-96, USGS, Raleigh.

Steel, J. [ed.], 1991. Albemarle-Pamlico Estuarine System - Technical Analysis of Status and Trends. A/P Estuarine Study Report 90-01, Albemarle-Pamlico Estuarine Study, U.S. Environmental Protection Agency and the North Carolina Department of Environment, Health and Natural Resources, Raleigh.

Taniguchi, M., Burnett, W.C., Cable, J.E., Turner, J.V., 2002. Investigation of submarine groundwater discharge. Hydrological Processes 16, 2115-2129.

Twomey, L., Piehler, M., Paerl, H., 2005. Phytoplankton uptake of ammonium, nitrate and urea in the Neuse River Estuary, NC, USA. Hydrobiologia 533, 123-134.

Valiela, I., Costa, J., Foreman, K., Teal, J., Howes, B., Aubrey, D., 1990. Transport of groundwater-borne nutrients from watersheds and their effects on coastal waters. Biodegradation 10, 177-197.

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.G., 1997. Human alteration of the global nitrogen cycle: Sources and consequences. Ecol. Appl. 7, 737-750.

Winner, M.D., and Coble, R.W., 1996. Hydrogeologic Framework of the North Carolina Coastal Plain. USGS Professional Paper 1404-I, 106 p.

Wrege, B.M., and Jen, P.S., 2004. Data from Stratigraphic Test Holes Drilled at the U.S. Marine Corps Air Station, Cherry Point, North Carolina, 1994-2001, and Periodic Water Levels, 2000-2003. USGS Open-File Report 2004-1434. USGS, Reston (VA).

Table 2.1. Range in physical/chemical parameters and dissolved oxygen (DO) concentrations for porewaters at each depth sampled at the three study sites in the Neuse River Estuary. Porewaters were sampled during six individual months between June 2007 and September 2008.

Site	Depth (cmbsf)	Temperature (^{o}C)	DO (mg L^{-1})	Conductivity (mS cm^{-1})	Salinity
Mills Branch	10	13.6 - 29.6	0.1 - 1.0	1.3 - 7.1	0.6 - 3.9
	20	13.5 - 29.4	0.1 - 0.9	1.3 - 3.2	0.6 - 1.7
	30	13.9 - 29.0	0.2 - 1.0	1.3 - 4.9	0.6 - 1.3
	50	14.9 - 27.7	0.2 - 1.2	1.2 - 1.6	0.6 - 0.8
	80	15.7 - 27.4	0.2 - 0.9	1.2 - 1.8	0.6 - 0.8
	110	16.2 - 26.7	0.4 - 0.9	1.3 - 1.5	0.6 - 0.8
	140	16.4 - 26.4	0.3 - 1.0	1.1 - 1.5	0.6 - 0.8
	210	17.6 - 22.5	0.2 - 0.7	1.1 - 1.3	0.6 - 0.6
Cherry Point	10	5.2 - 32.4	0.3 - 6.6	7.3 - 26.7	4.0 - 17.5
	20	5.8 - 30.8	0.3 - 4.3	13.0 - 26.8	7.1 - 16.3
	30	7.3 - 30.6	0.2 - 3.0	1.3 - 27.5	0.7 - 13.6
	50	8.6 - 30.1	0.3 - 2.8	4.4 - 28.8	2.3 - 17.8
	80	9.8 - 29.3	0.3 - 2.5	3.8 - 23.2	1.2 - 14.0
	110	10.9 - 28.8	0.4 - 3.0	0.8 - 23.8	0.4 - 14.4
	150	13.9 - 27.0	0.6 - 3.3	0.6 - 18.1	0.3 - 10.7
	190	14.5 - 26.4	1.3 - 4.0	0.6 - 1.2	0.3 - 0.6
	230	13.2 - 27.7	0.3 - 4.7	0.3 - 1.7	0.2 - 0.8
Wilkinson Point	10	19.7 -29.6	0.5 - 2.2	15.7 - 29.0	8.5 - 17.9
	20	19.6 - 28.5	0.3 - 1.4	13.8 - 27.3	7.4 - 16.7
	30	20.1 - 27.2	0.2 - 1.1	13.1 - 28.0	7.1 - 17.1
	50	20.8 - 27.0	0.6 - 1.6	14.6 - 28.2	8.2 - 17.3
	80	21.5 - 27.0	0.6 - 1.1	13.5 - 29.1	7.6 - 18.0
	110	21.6 - 27.0	0.2 - 1.0	12.7 - 31.9	7.3 - 19.8
	150	21.7 - 27.7	0.2 - 1.0	13.6 - 32.6	8.2 - 20.3

Table 2.2. Mean SGD for all sampling trips for each site (Mills Branch, MB; Cherry Point, CP; Wilkinson Point, WP) using ^{222}Rn as a tracer and seepage meters.

	^{222}Rn		Meter	
	cm d^{-1}	Std. Dev.	cm d^{-1}	Std. Dev.
MB	5.1	2.9	0.8	0.9
CP	12.6	0.5	4.7	1.9
WP	7.9	1.5	3.1	2.6

Table 2.3. Ranges of porewater soluble reactive phosphate (SRP) over all sampling months at the three study sites, Mills Branch, Cherry Point, and Wilkinson Point.

Site	Depth (cmbsf)	SRP (μM)
Mills Branch	10	3.6 - 20.5
	20	9.3 - 23.5
	30	9.3 - 19.9
	50	5.1 - 27.6
	80	7.1 - 54.5
	110	9.4 - 15.9
	140	9.1 - 16.6
	210	7.9 - 12.6
Cherry Point	10	0.9 - 12.1
	20	0.8 - 5.1
	30	0.6 - 5.4
	50	0.2 - 2.9
	80	0.4 - 1.3
	110	0.3 - 1.1
	150	0.5 - 1.4
	190	0.4 - 1.0
	230	0.5 - 1.1
Wilkinson Point	10	4.5 - 18.2
	20	7.8 - 17.7
	30	4.9 - 14.8
	50	7.2 - 16.8
	80	7.8 - 18.5
	110	7.9 - 13.3
	140	8.9 - 12.5

Table 2.4. Seasonal comparison of NH_4^+ flux (mmol m^{-2} d^{-1}) at Mills Branch (MB), Cherry Point (CP), and Wilkinson Point (WP) based on SGD measurements from ^{222}Rn and seepage meters. NH_4^+ concentrations were based on samples collected from 10 cmbsf (ND = data not available).

	^{222}Rn		Mean	Meter		Mean
	NH_4^+ Flux	**SD**	**by Site**	**NH_4^+ Flux**	**SD**	**by Site**
MB						
June	23.7			-4.2	-2.4	
Aug	24.0	1.4		1.1	3.6	
Oct	ND			ND		
Jan	2.5	4.7		3.5	0.7	
April	11.0	2.6		0.2	2.6	
Sept	39.9	13.7	**20.2**	14.7	8.4	**3.1**
CP						
June	9.2	0.4		6.9	1.6	
Aug	12.6	0.5		3.1	2.0	
Oct	3.5	0.4		0.2	0.5	
Jan	1.1	1.01		0.8	0.3	
April	4.2	0.2		1.1	0.4	
Sept	1.6	0.3	**5.4**	0.4	0.1	**2.1**
WP						
June	5.1	1.4		1.5	1.5	
Aug	5.0	1.6		2.6	1.7	
Oct	ND			ND		
Jan	ND			ND		
April	ND			ND		
Sept	12.8	2.3	**7.6**	5.6	6.2	**3.2**
Overall Mean:	**11.2**	**1.5**		**3.0**	**1.9**	

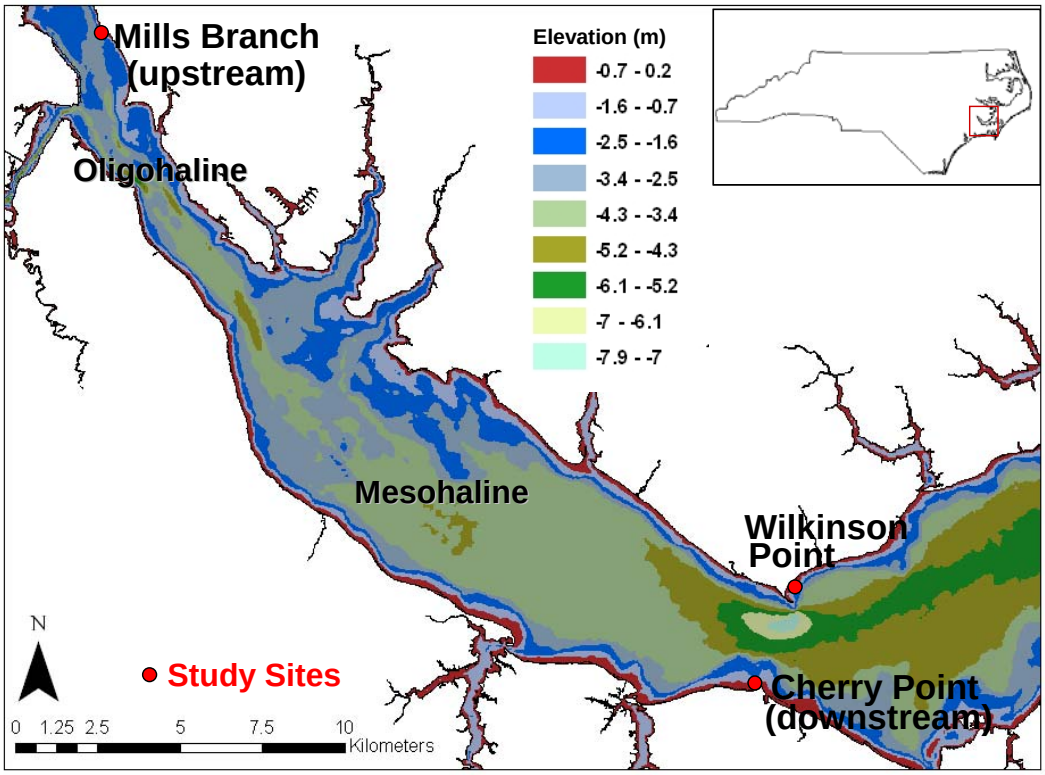


Figure 2.1. Bathymetric map of the Neuse River Estuary, North Carolina and location of sampling sites. The three study sites are Mills Branch (MB), Cherry Point (CP), and Wilkinson Point (WP).

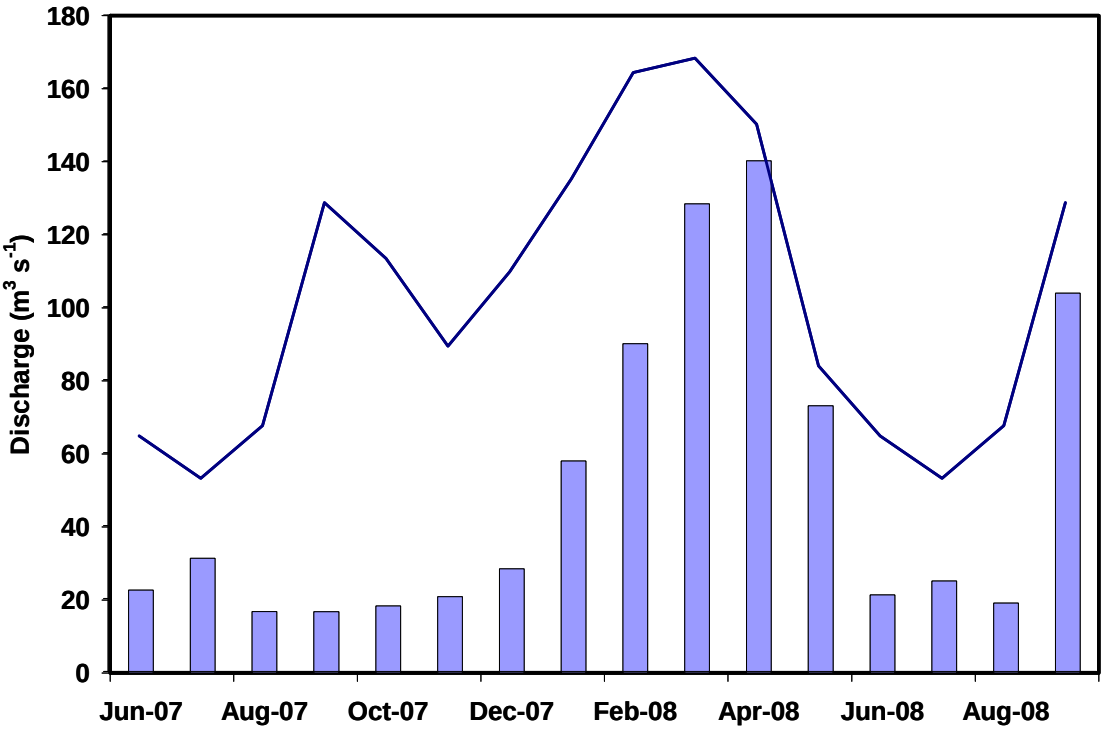


Figure 2.2. Average monthly discharge of the Neuse River at Fort Barnwell, ~ 30 km above the most upstream site (MB), during the sampling period. The line indicates the 13-year average discharge (1996-2009). Source: United States Geological Survey [USGS] (http://waterdata.usgs.gov/nwis/monthly?).

Figure 2.3. Porewater temperature depth profiles at three nearshore sites in the Neuse River Estuary. Mills Branch piezometer MB1(A) 3 m from shore, MB2(B) 6 m from shore, and MB3 (C) 9 m from shore. Cherry Point piezometer CP2(D) 10 m from shore, CP3 (E) 15 m from shore, and CP4(F) 20 m from shore. Wilkinson Point piezometer WP1(G) 7 m from shoreline and WP2(H) 10 m from shore. Each symbol represents different sampling dates: June 2007 ◆ August 2007 ◇ October 2007 ▲ January 2008 △ April 2008 ● September 2008 ○

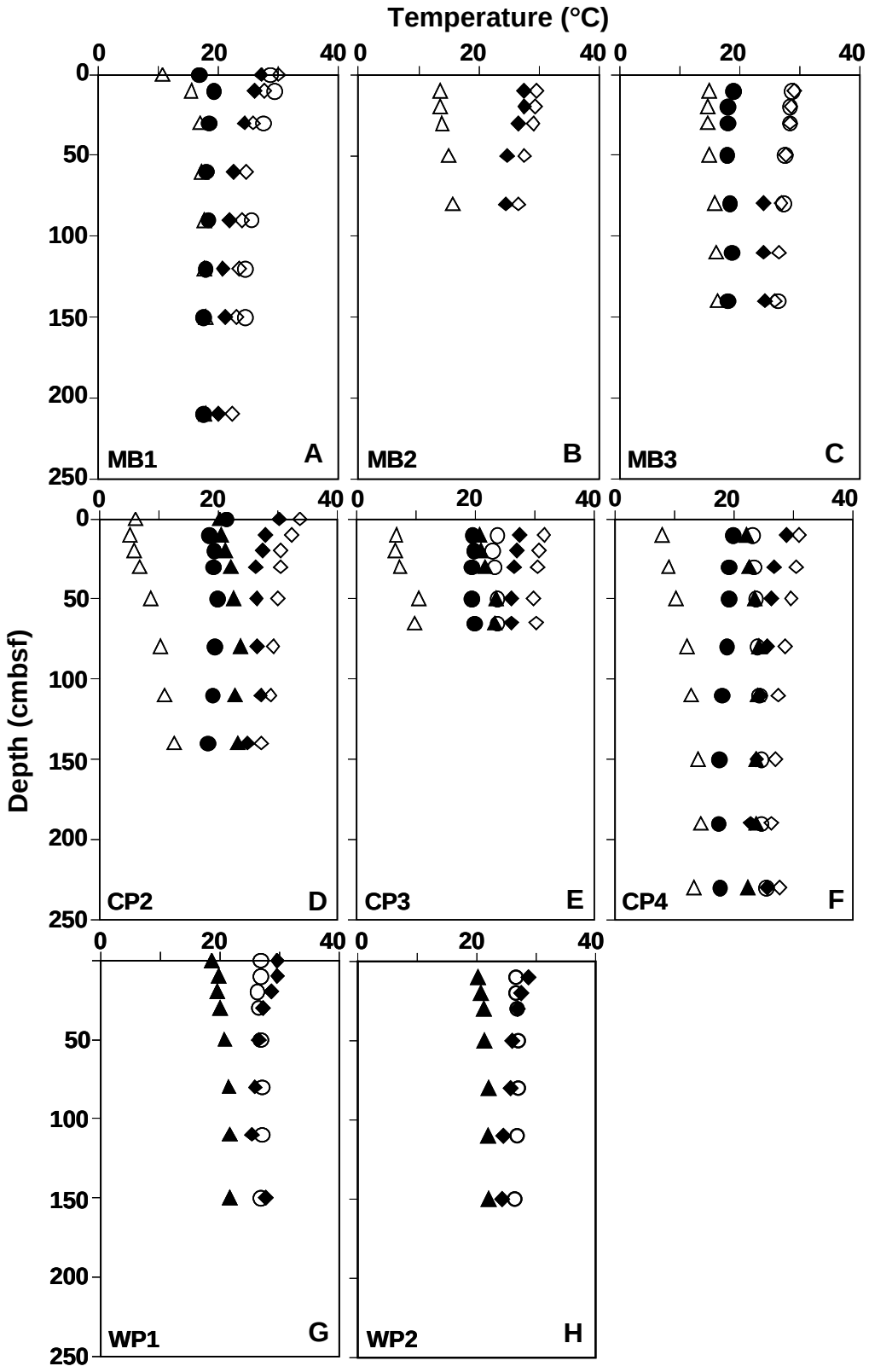

Temperature (°C)
Depth (cmbsf)
0
20
40
50
100
150
200
250
MB1
A
MB2
B
MB3
C
CP2
D
CP3
E
CP4
F
WP1
G
WP2
H

Figure 2.4. Porewater dissolved oxygen [DO] (mg L^{-1}) depth profiles at three nearshore sites in the Neuse River Estuary. Mills Branch piezometer MB1(A) 3 m from shore, MB2(B) 6 m from shore, and MB3 (C) 9 m from shore. Cherry Point piezometer CP2(D) 10 m from shore, CP3 (E) 15 m from shore, and CP4(F) 20 m from shore. Wilkinson Point piezometer WP1(G) 7 m from shoreline and WP2(H) 10 m from shore. Each symbol represents different sampling dates: June 2007 ◆ August 2007 ◇ October 2007 ▲ January 2008 △ April 2008 ● September 2008 ○

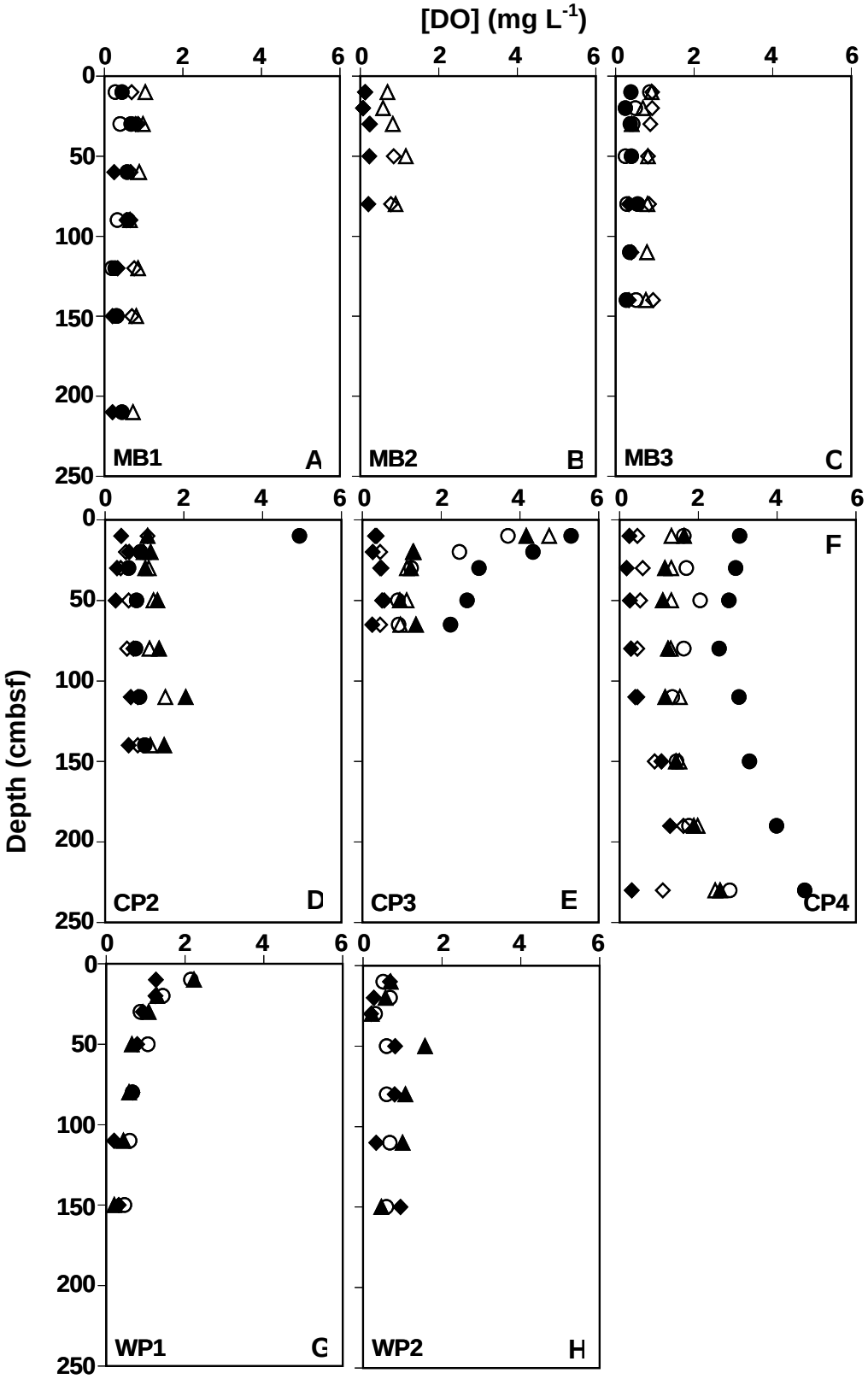

[DO] (mg L-1)
Depth (cmbsf)
MB1
A
MB2
B
MB3
C
CP2
D
CP3
E
F
CP4
WP1
G
WP2
H

Figure 2.5. Porewater conductivity (mS cm^{-1}) depth profiles at three nearshore sites in the Neuse River Estuary. Mills Branch piezometer MB1(A) 3 m from shore, MB2(B) 6 m from shore, and MB3 (C) 9 m from shore. Cherry Point piezometer CP2(D) 10 m from shore, CP3 (E) 15 m from shore, and CP4(F) 20 m from shore. Wilkinson Point piezometer WP1(G) 7 m from shoreline and WP2(H) 10 m from shore. Each symbol represents different sampling dates: June 2007 ◆ August 2007 ◇ October 2007 ▲ January 2008 △ April 2008 ● September 2008 ○

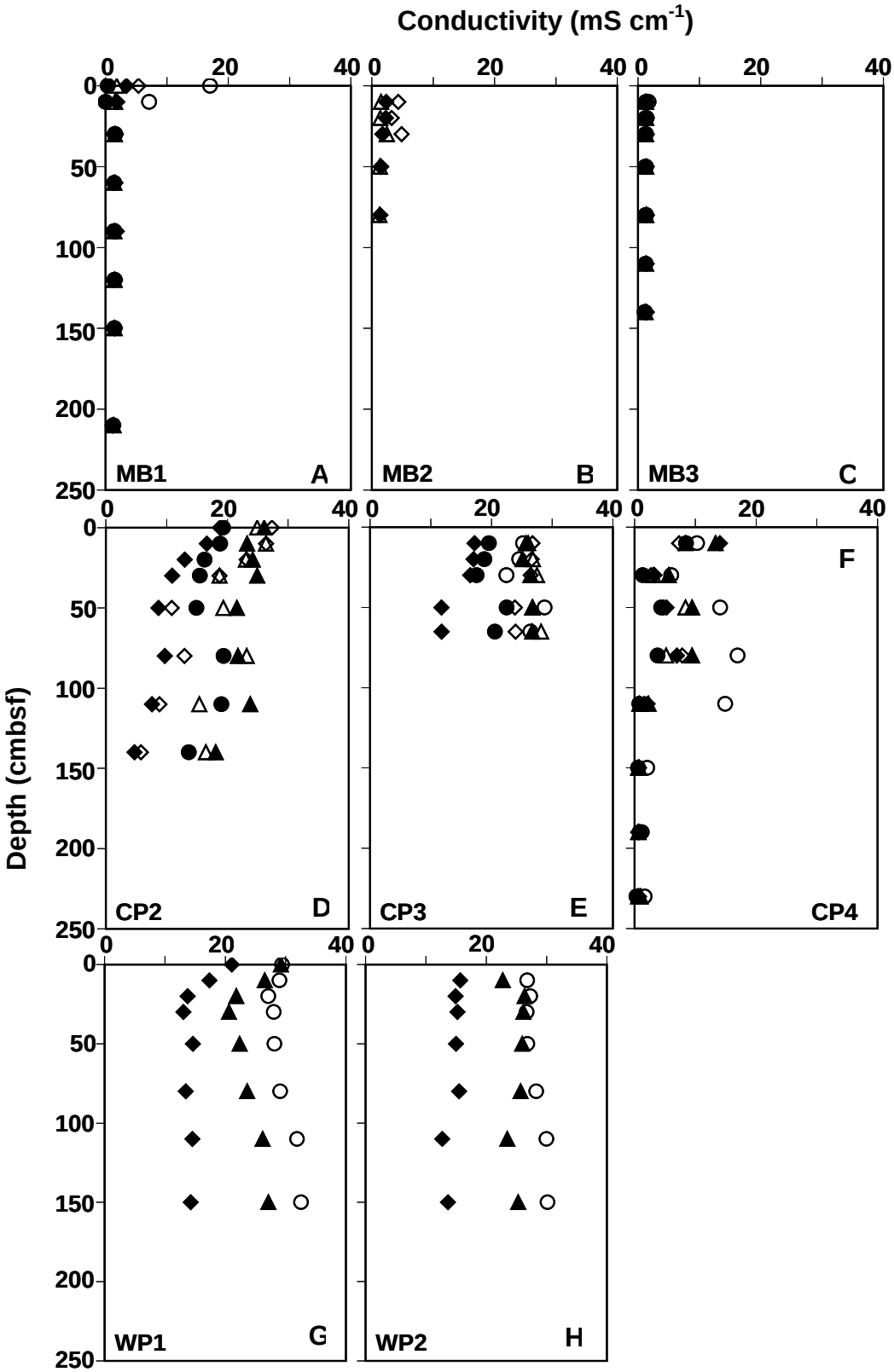
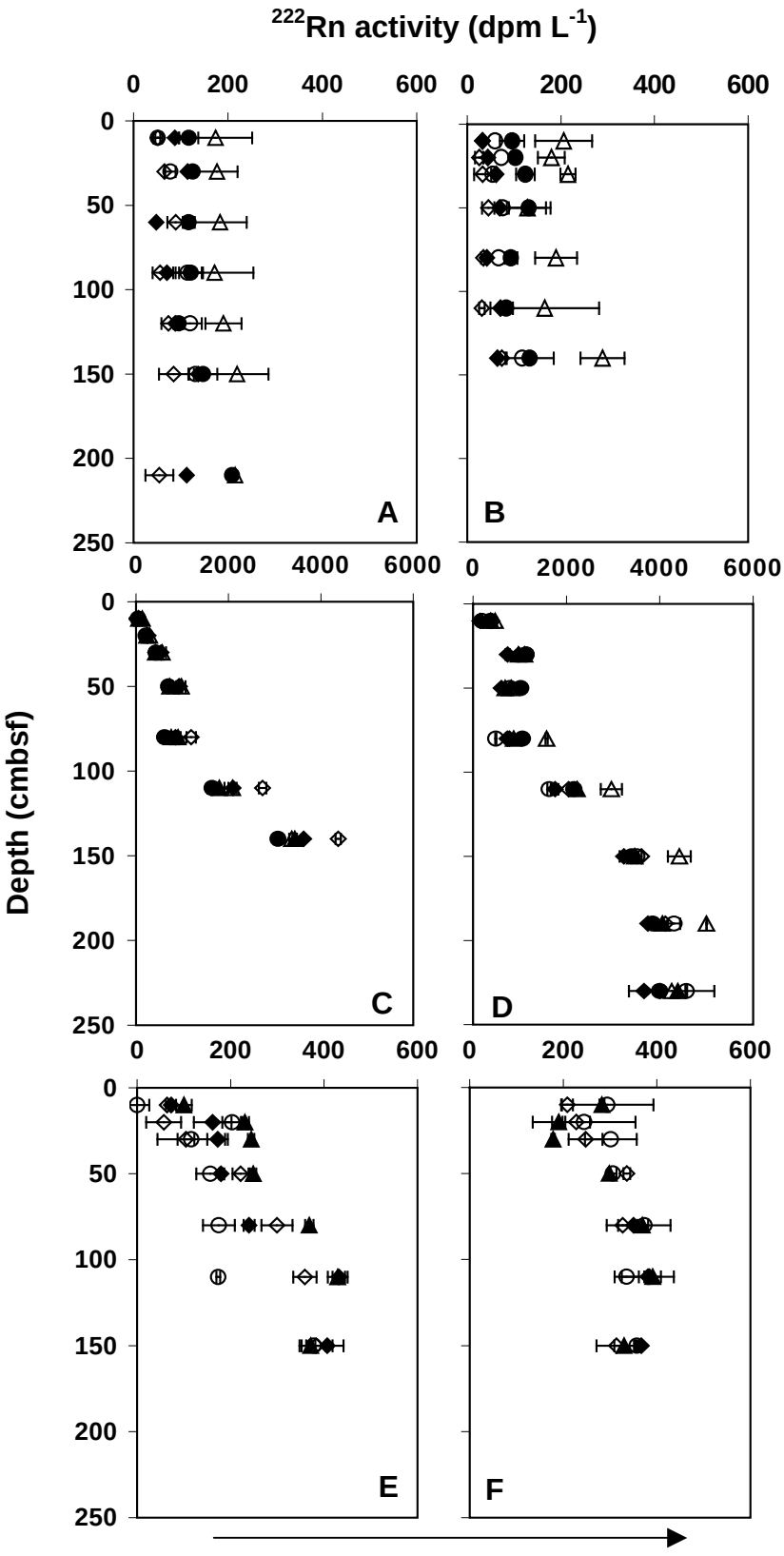

Conductivity (mS cm-1)
Depth (cmbsf)
0
20
40
0
50
100
150
200
250
MB1
A
MB2
B
MB3
C
CP2
D
CP3
E
F
CP4
WP1
G
WP2
H

Figure 2.6. Porewater ^{222}Rn activities (dpm L^{-1}) versus depth at three nearshore sites in the Neuse River Estuary. Mills Branch piezometer MB1(A) 3 m from shoreline and MB3(B) 9 m from shore. Cherry Point piezometer CP2(C) 10 m from shoreline and CP4(D) 20 m from shore. Wilkinson Point piezometer WP1(E) 7 m from shoreline and WP2(F) 10 m from shore. Note scale difference at Cherry Point. Arrow indicates transect direction from shoreline. Data are given as means ± 1 σ (n = 2 for each depth and each month).
Each symbol represents different sampling dates: June 2007 ◆ August 2007 ◇ October 2007 ▲ January 2008 △ April 2008 ● September 2008 ○
.


222Rn activity (dpm L-1)
Depth (cmbsf)
A
B
C
D
E
F

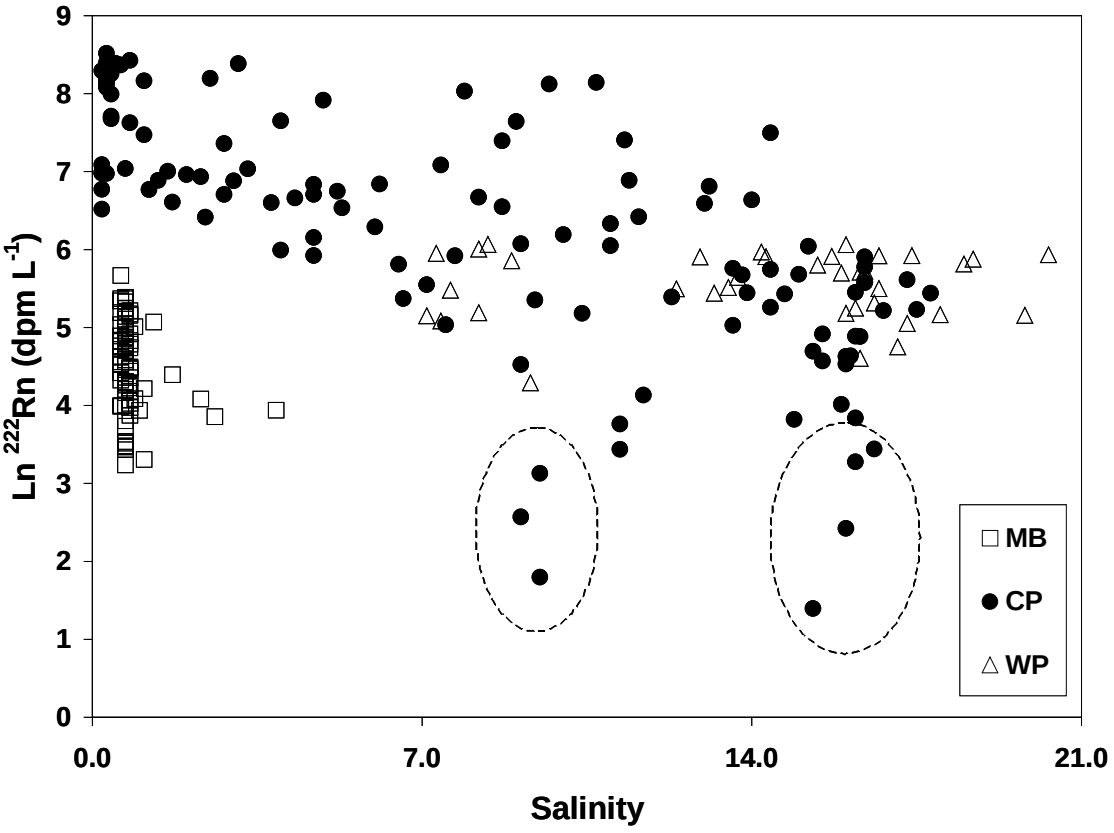
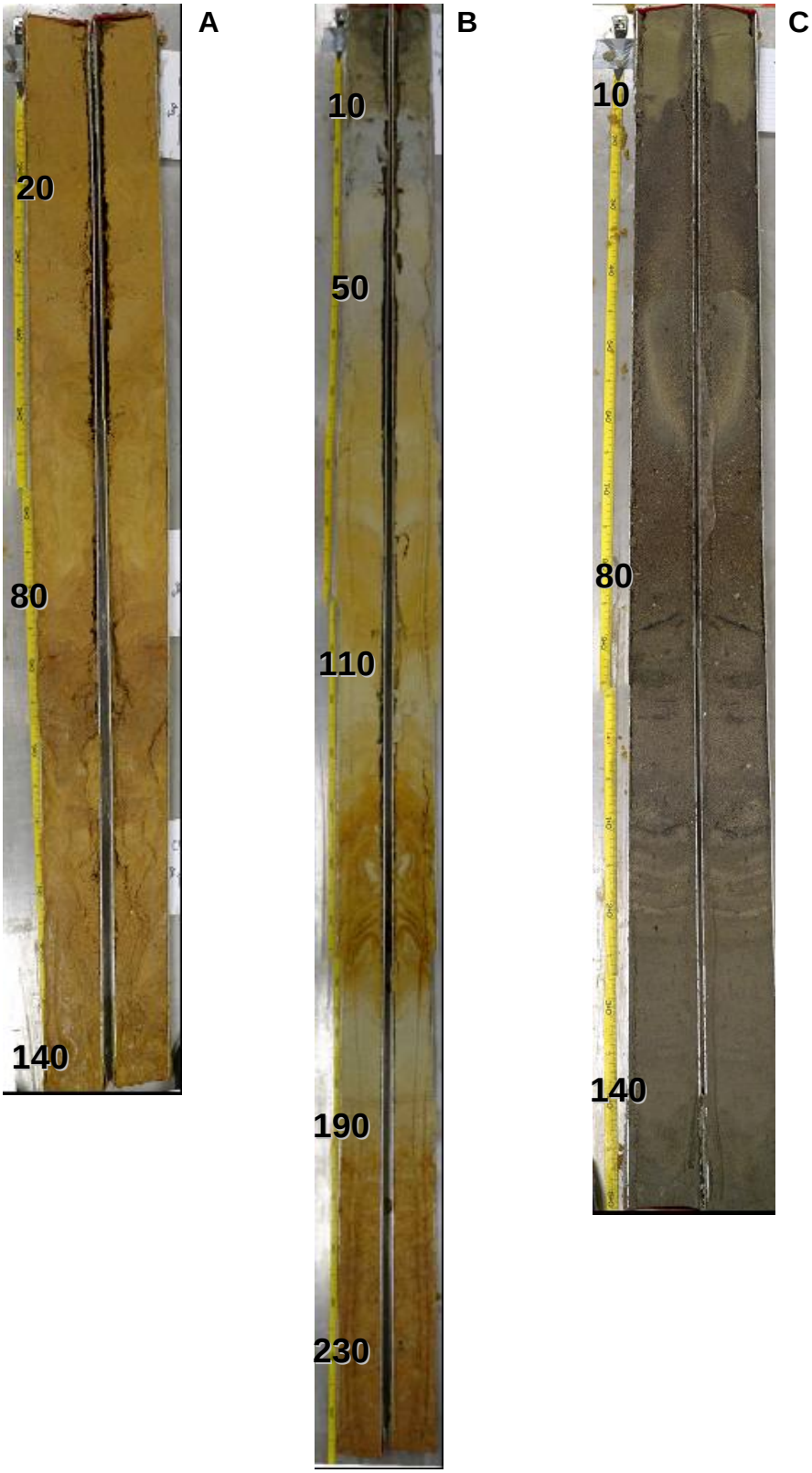


Figure 2.7. Natural log ^{222}Rn versus salinity at all sites during all seasons. Circled symbols represent porewater samples from shallow depths (10 cmbsf).

Figure 2.8. Sediment cores collected for sediment slurry test using a vibracore. (A) Core was taken near piezometer CP2 at Cherry Point. (B) Core representative of sediment near piezometer CP4. (C) Care was taken near piezometer WP2 at Wilkinson Point. Photographs are not to scale. Numbers indicate depth sampled in cm beneath seafloor.


A
20
80
140
B
10
50
110
190
230
C
10
80
140

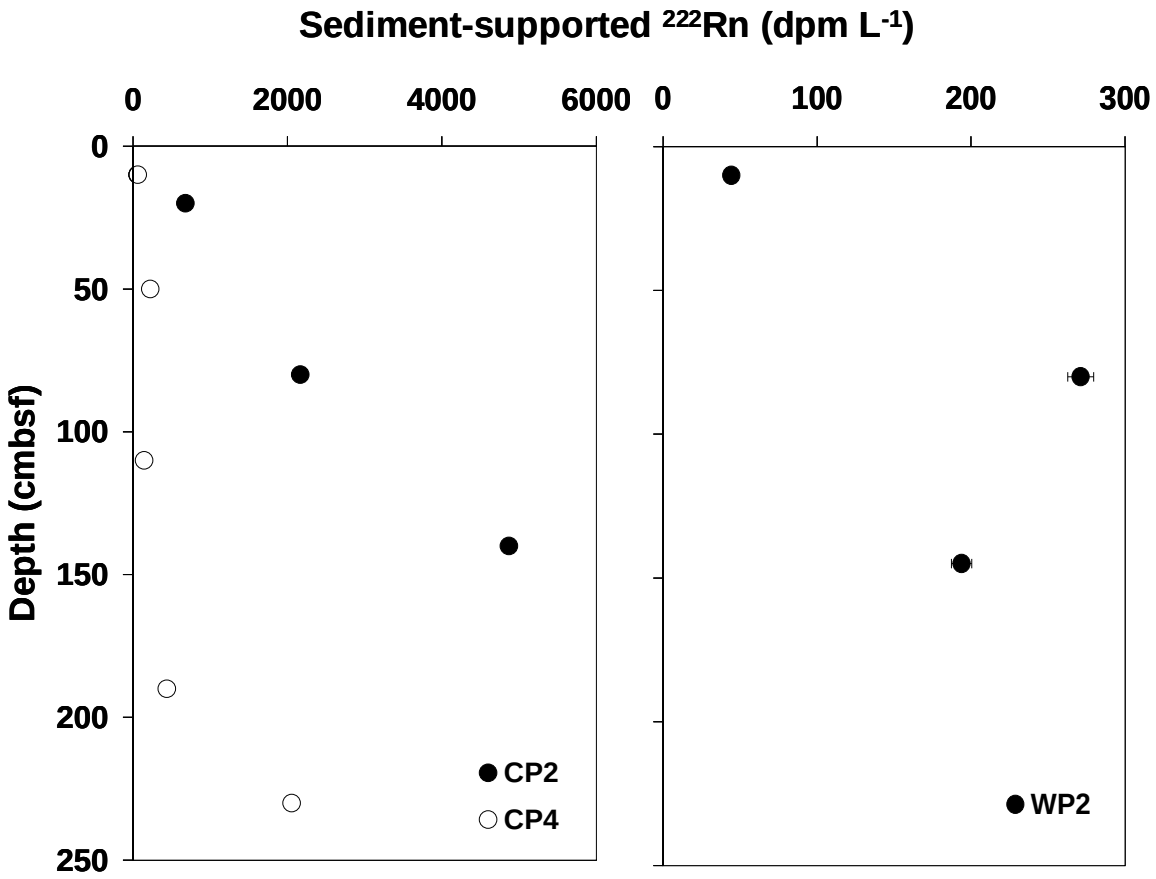


Figure 2.9. Sediment-supported ^{222}Rn versus sediment depth at the two downstream sites, Cherry Point (CP) and Wilkinson Point (WP). CP: CP2 core was taken near the piezometer 15 m offshore and CP4 core was taken near the piezometer located 20 m offshore for sediment slurry experiments of sediments at Cherry Point; and WP: WP2 was collected near the piezometer located 10 m offshore at Wilkinson Point. Note difference in scale for ^{222}Rn.

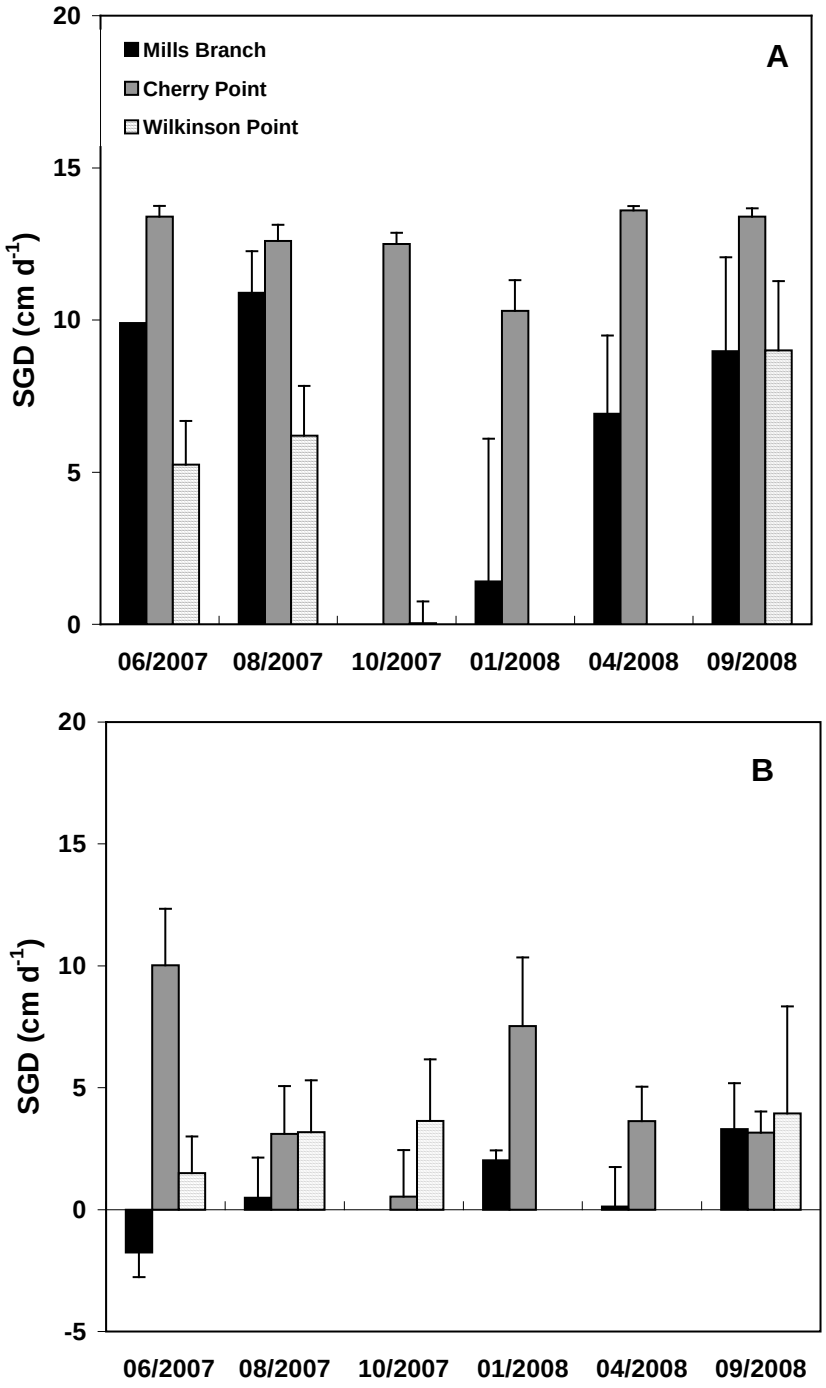


Figure 2.10. Seasonal SGD estimated for each sampling site using (A) ^{222}Rn and (B) seepage meters. Data are given as means +/- 1 σ (^{222}Rn: n = 2; seepage meters: n = 6).

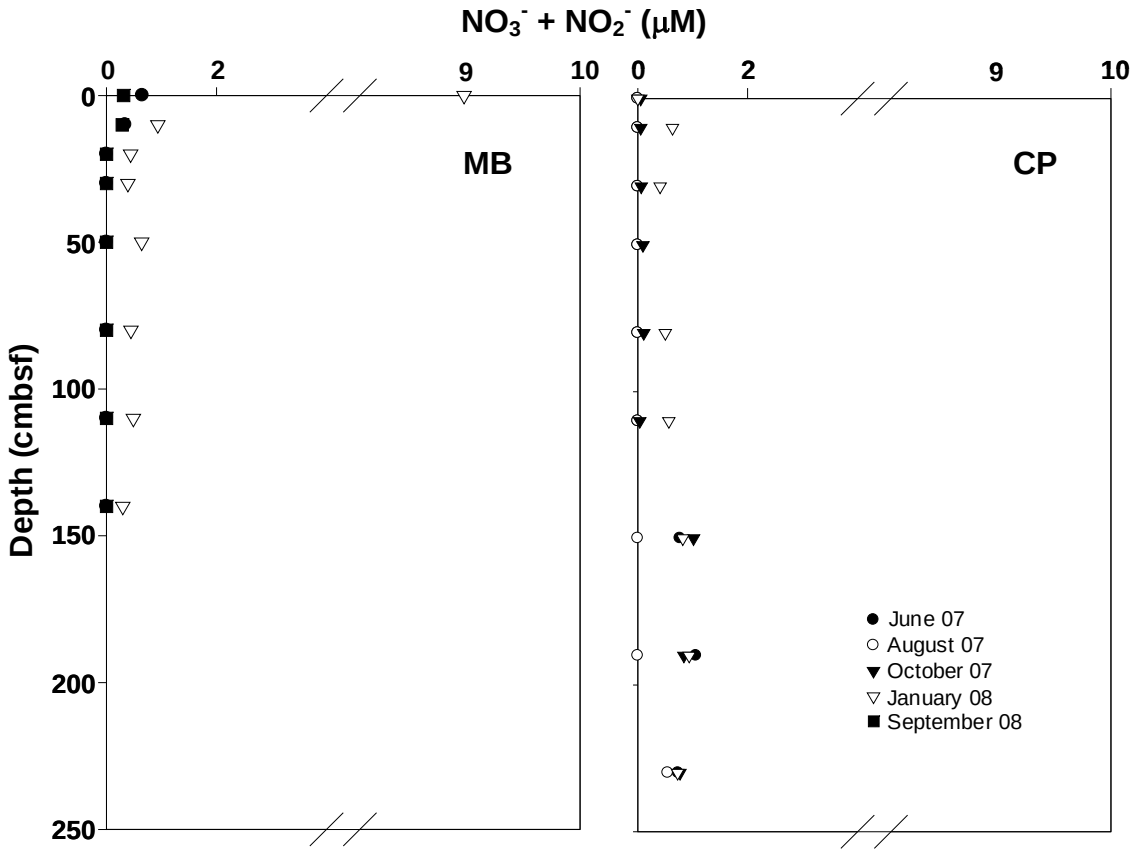


Figure 2.11. Porewater NO_3^-+NO_2^- concentrations at upstream site Mills Branch (MB) and downstream site Cherry Point (CP). Surface water concentrations were graphed as 0 depth at MB; NO_3^-+NO_2^- was not detected in surface waters at CP.

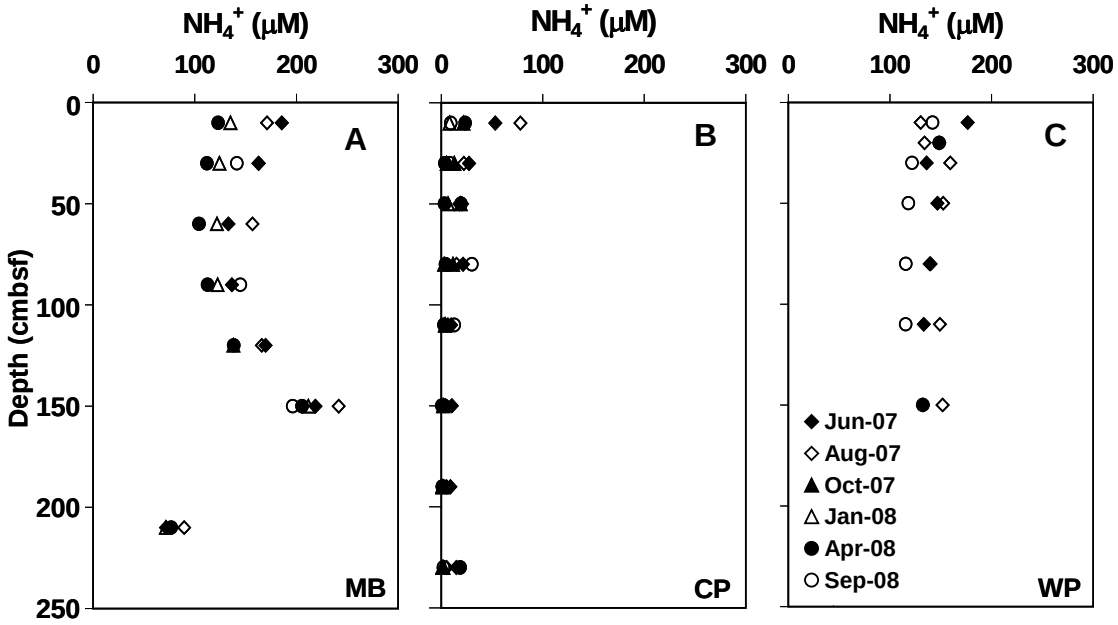


Figure 2.12. Ammonium (NH_4^+) porewater concentrations versus depth at (A) Mills Branch (MB), (B) Cherry Point (CP), and (C) Wilkinson Point (WP).

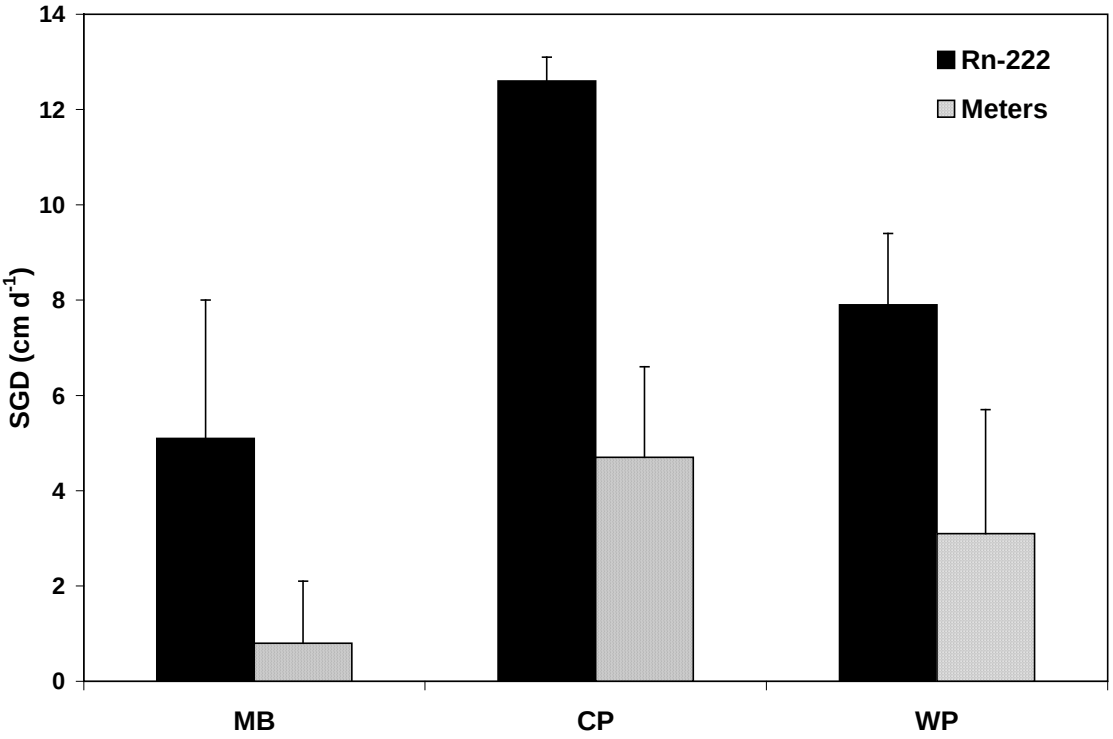


Figure 2.13. Average SGD from ^{222}Rn calculations and seepage meter measurements over all sampling months at Mills Branch (MB, upstream), Wilkinson Point (WP, downstream), and Cherry point (CP, most downstream site). Data are given as means +/- 1 σ (one-way ANOVA; p = 0.0004).

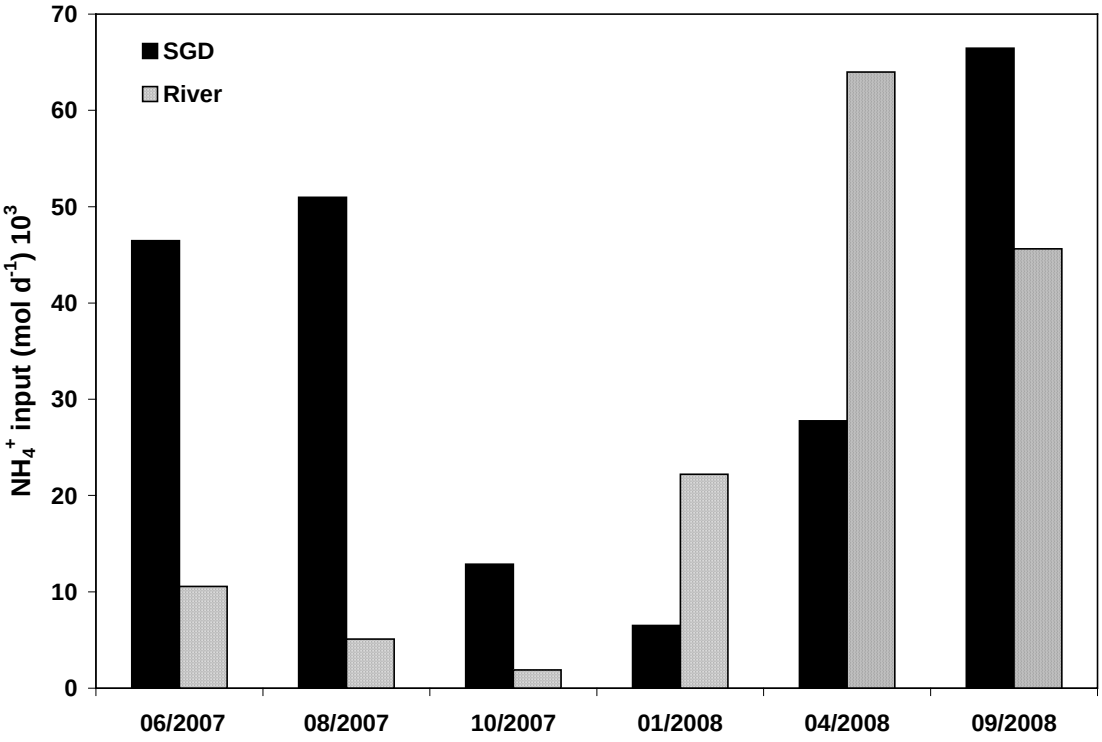


Figure 2.14. Comparison of mean NH_4^+ flux from the upstream Neuse River based on discharge rates at Fort Barnwell, NC (USGS) (http://waterdata.usgs.gov/nwis/monthly?) and NH_4^+ water-column concentrations at Mills Branch (NCSU Center for Applied Aquatic Ecology, unpublished data), versus SGD NH_4^+ flux over the entire estuary. SGD NH_4^+ flux was calculated from the mean advective NH_4^+ flux (this study) as applied to the entire discharge area of the mesohaline portion of the estuary (3.67×10^6 m^2, calculated from Spruill and Bratton 2008).

3. AMMONIUM PRODUCTION AND BENTHIC INORGANIC NITROGEN FLUXES IN THE NEUSE RIVER ESTUARY, NORTH CAROLINA, USA

3.1 Abstract

Ammonium (NH_4^+), nitrate (NO_3^-), and dissolved oxygen (DO) fluxes across the sediment-water interface were measured at three sites in the Neuse River Estuary (NRE), North Carolina, USA. Cores were collected from two shallow nearshore environments (mean water depth < 1 ± 0.2 m) with sandy sediments and one mid-channel site (mean water depth 3 ± 0.1 m) with organic-rich, fine-grained sediments. NH_4^+ was the major form of inorganic N in sediment porewaters and flux to the overlying water; NO_3^- fluxes were small or not detected. NH_4^+ and DO fluxes showed significant seasonal variations at all sites. Diffusive NH_4^+ flux was highly variable and ranged from –29.1 to 811 μmol m^{-2} hr^{-1} among the three sites, with the negative values indicating flux into the sediments from the water column. The highest net diffusive NH_4^+ flux was measured during October at both nearshore and mid-channel sites, whereas the lowest flux occurred in January. Sediment experiments were also conducted at a nearshore and a mid-channel site to measure the NH_4^+ production rates. The nearshore site demonstrated increasing NH_4^+ production with depth, down to 35 cm (0.004 μmol NH_4^+ cm^{-3} wet sediment d^{-1}), whereas the highest NH_4^+ production rate at the mid-channel site (0.001 μmol NH_4^+ cm^{-3} wet sediment d^{-1}) occurred in the 0-10 cm interval. Submarine groundwater discharge contributed significantly more NH_4^+ to the overlying water in the nearshore environment than from the organic-rich, mid-channel sediments based on areal basis. Nearshore sediments of the NRE are sites with significant NH_4^+ production that can be a potentially important N source for benthic and water column primary production. This study quantified NH_4^+ production and flux, which has been

poorly understood in NRE nearshore environments, and may help to explain an overall increase in water-column NH_4^+ concentrations that has been documented in this system and certain other shallow, eutrophic estuaries.

3.2 Introduction

Much of the nitrogen (N) that supports productivity in estuaries is derived from remineralization and recycling from sediments and commonly is not "new" N, such as the N supplied by rivers and atmospheric deposition (Dugdale and Goerring 1967). Once nitrate (NO_3^-) and ammonium (NH_4^+) enter a coastal ecosystem, these inorganic nitrogen (N_i) forms can undergo many processes and transformations depending on environmental conditions. Nitrification, the oxidation of NH_4^+ to NO_2^- or NO_3^-, can strongly influence N availability, and can rapidly occur in surface sediments where dissolved oxygen (DO) levels are high (Codispoti and Christensen 1985, Caffrey et al. 1993). Denitrification, the reduction of NO_3^- or NO_2^- to N_2 or N_2O, can occur just below the oxic zone in anaerobic sediments (Kemp et al. 1990). Nitrification can be coupled with denitrification in areas with strong oxygen gradients, resulting in the removal of bioavailable N. Molecular nitrogen gas (N_2) is not taken up by most microalgae, except for cyanobacteria which are capable of carrying out N_2 fixation (Howarth et al. 1988).

In many coastal systems, the dominant form of biological N_i uptake is NH_4^+, and it can account for the majority of phytoplankton production (Nixon 1995). At concentrations in excess of 2 μM NH_4^+ in the water column, NH_4^+ is the preferred form of N over NO_3^- for assimilation by many phytoplankton (McCarthy et al. 1977, Glibert et al. 1988). Benthic recycling from sediments has been estimated to provide 20-80% of N requirements in shallow estuarine water columns (depth < 50 m; Nixon 1995, Boynton and Kemp 1985). Thus, regeneration from sediments to the overlying water is a significant source of N in

shallow estuaries (Harrison and Platt 1980). In comparison to continental shelves, estuaries typically have a long water-column residence time and substantial algal blooms, in addition to high particulate organic loads from riverine input that may contribute to increased nutrient regeneration from sediments if organic matter is buried. Remineralization of organic matter in sediments forms NH_4^+ that may be released to the overlying water column and stimulate productivity where N commonly limits primary production (Blackburn 1979). Thus, remineralization in sediments has been given considerable attention as a significant source of N for phytoplankton in the pelagic environment (Blackburn and Henriksen 1983). Many factors can affect NH_4^+ flux from the sediment, including porosity/grain size, organic carbon content, dissolved oxygen content, salinity, water-column N concentration and speciation, and various microbial processes such as nitrification that influence N speciation and bioavailability (Henriksen and Kemp 1988, Kemp et al. 1990).

The Neuse River Estuary (NRE) has sustained accelerated eutrophication from increased nutrient loading over the past decade, and NH_4^+ concentrations have increased about 500% in the water column of the mesohaline estuary during the past decade (Burkholder et al. 2006). Previously in the NRE and other estuarine environments, most research concerning sediment nutrient supply has focused on the organic-rich muddy sediments, which have been considered the major source of benthic nutrients to the overlying water. The permeable, sandy nearshore environments were thought to have low organic content, therefore contributing only a small portion of the nutrients to the overlying water. Moreover, previous studies on benthic nutrient flux in the NRE were conducted prior to the documented NH_4^+ concentration increase in the water column. The focus of this study was NH_4^+ production and regeneration in the poorly

characterized sandy nearshore environments of the mesohaline NRE, also including a mid-channel site for comparison. NH_4^+ production, as well as N_i diffusive and advective fluxes were determined for the NRE over a one year period. Nearshore environments were expected to contribute NH_4^+ to the overlying water via diffusional processes and advection. Furthermore, advection (submarine groundwater discharge, SGD) was expected to produce higher NH_4^+ flux than molecular diffusion. Spatially over the extent of the estuary, it was anticipated that nearshore environments would contribute comparable NH_4^+ flux to the overlying water as the organic-rich, mid-channel sediments.

3.3 Study Area

The Neuse River Estuary is a drowned river valley that receives drainage from its watershed, ~16,000 km^2, and flows from the Piedmont of North Carolina to the coast (Matson and Brinson 1990). Over the past few decades, the upper Neuse River basin has experienced substantial urbanization. Wastewater treatment plants and package plants have increased, 30 % and 324 %, respectively, and the wetland and forested areas have decreased, 3 % and 9 %, respectively (Rothenberger et al. 2009). In the lower basin, industrialized swine production has been identified as one of the highest contributor of nutrients to the Neuse surface waters (Rothenberger et al. 2009). The eutrophic estuary is known for major fish kills, harmful algal blooms, and oxygen deficits (Burkholder et al. 2006).

The NRE is ~ 4.55×10^8 m^2 in area and drains into the Pamlico Sound, the second largest estuarine system in the United States (Steel 1991), along the eastern seaboard of North Carolina (Figure 3.1). The average discharge of the Neuse River is approximately 113 $m^3\ s^{-1}$ and ranges from 55 to 173 $m^3\ s^{-1}$, based on the United States Geological Survey mean monthly discharge measurements near Fort Barnwell, NC since 1996, ~30 km upstream from the oligahaline estuary (Figure 3.2) (USGS Surface-Water Monthly Statistics: http://waterdata.usgs.gov/nwis/monthly?). The NRE is a shallow estuary with mean water depth of 4.5 m (Roelofs and Bumpus 1953) and limited direct inputs from the ocean. The tidal influence in the NRE is minimal (Luettich et al. 2000), and winds are the predominant mixing force in this shallow system (Reed et al. 2004). The mixing between river waters and Pamlico Sound waters generates water residence times on the order of 50-100 days, which contributes to extensive recycling of nutrients (Christian et al. 1991; Steel 1991). The flow

regime of the mesohaline estuary is surface-water outflow and bottom-water inflow (Reed et al. 2004). Stratification frequently occurs during late summer months when winds are reduced, but sometimes persists from April through October (Burkholder et al. 2006). Stratification and strong winds influence the oxygenation and the nature of nutrient availability within the estuary. Winds play a significant role in sediment resuspension and nutrient release from the mid-channel benthic environment (Giffin and Corbett 2003).

Distinct sediment boundaries are present in the NRE and the sediment regimes can be distinguished based on grain size and porosity, among other characteristics. The sediments of the center channel consist of organic-rich, fine-grained silt and clay with a porosity > 0.8, and comprise approximately half of the estuarine surface area (Alperin et al. 2000). The center of the channel collects fine-grained sediment because it is the deepest area of the channel and wave energy is minimal. Nearshore sediments of the channel are mainly fine- to medium-grained sand with an average porosity of < 0.6 (Alperin et al. 2000).

As part of this study, three sites in the NRE were characterized, including two nearshore sites and one mid-channel site (Figure 3.1). Nearshore site Mills Branch (MB) was farthest upstream in shallow oligohaline waters (mean depth 0.45 ± 0.2 for dates sampled). The second nearshore site, Cherry Point (CP), was 30 km downstream in mesohaline waters. CP is a higher-energy environment than MB and has a shallower mean depth (0.22 ± 0.2 m on the dates sampled). The mid-channel site (MID, mean water depth 3 ± 0.1 m on dates sampled) was ~ 5 km upstream of CP. The two nearshore sandy sites had sediment porosities < 0.7, whereas the sediment porosity of the mid-channel site was >0.8 (data from this study). MB was located near a housing subdivision with a nearby boat ramp and wildlife

area. The vegetation along the shoreline included a few sparse cypress trees and wetland vegetation. CP was also located near a housing subdivision, with the beach area protected by riprap. Very little shoreline vegetation was present at CP.

3.4 Methods

3.4.1 Porewater Nutrients

Three multi-level piezometers (Martin et al. 2003) were installed in transects (up to 20 m offshore) perpendicular to the shoreline at each of the two nearshore study sites, Mills Branch (MB) and Cherry Point (CP), during June 2006. The piezometers were 150 cm or 230 cm in length and had screened ports at 10- to 30-cm intervals. PVC tubing ran from the intake port along the inside of the PVC pipe to the surface so that samples could be collected using a peristaltic pump. Samples were collected into an overflow container to measure temperature (T), salinity (S), conductivity, and dissolved oxygen (DO) once the abundances of these tracers stabilized. Data were collected using a handheld YSI-85 (YSI Incorporated, Yellow Springs, OH). Samples were also collected in acid-stripped polypropylene bottles for analysis of ammonium (NH_4^+) and nitrate+nitrite (NO_3^-+NO_2^-). The piezometers were sampled along with water-column measurements approximately bimonthly from June 2007 to September 2008.

3.4.2 Nutrient Flux Across the Sediment-water Interface

Net sediment nutrient and oxygen flux measurements were conducted using cylindrical flux chambers constructed from plexiglass (length 25 cm, diameter 15 cm). The chambers enabled collection of minimally disturbed sediment cores (Kemp et al. 1990, Blair et al. 1996, Thomas and Blair 2002), which were used to conduct benthic flux measurements of O_2, NH_4^+, and NO_3^-+NO_2^-. The cores, including ~15 cm of overlying bottom water, were sealed gas-tight and served as incubation chambers to measure O_2 consumption rates and NH_4^+ and NO_3^-+NO_2^- fluxes. For all experiments the cores were left open during transport to the lab, and therefore, were oxygenated at the start of the flux experiments. The flux cores were incubated at *in situ* temperatures and under light and dark conditions. Sampling of overlying water in the chambers occurred at 2- to 6-h intervals over a 24 to 48 h period. Chambers were stirred using an external motor and magnet to rotate an internal floating stir bar to prevent stratification. The stirring speed was adjusted so as to not disturb the surface sediment. Samples from the overlying water were pulled from a port for analysis of nutrients and [DO]. [DO] was measured immediately using the micro-Winkler technique (Parsons et al. 1984, Thomas and Blair 2002). Nutrient samples from the chamber experiments were frozen and analyzed within 30 days following accepted procedures (U.S. Environmental Protection Agency [EPA] 1993 - below). Cores were collected approximately bimonthly over an annual cycle, since NH_4^+ inputs and microbial nitrification/denitrification processes show strong seasonality (Kemp et al. 1990). NH_4^+, NO_3^-+NO_2^-, and O_2 fluxes were calculated from the concentration changes over the 1 to 2 day time period. Use of chambers

in short-term incubation experiments such as these were considered to provide a “whole community” approach for determining sedimentary fluxes.

3.4.3 Ammonium Production

On one sampling trip, twelve sediment cores were collected at one nearshore site (CP) in the NRE (Figure 3.1). PVC core liners were used as push corers to collect sediment down to 40-cm depth for NH_4^+ production measurements, following methods modified from Aller and Yingst (1980). Holes had been drilled at 2.5 cm intervals and then sealed with silicone before the core liners were inserted into sediments. Three cores were processed immediately and the remaining cores were transported to the laboratory and incubated for up to eight weeks. Three cores were processed every two weeks by inserting a porewater sipper into each hole. Porewater was extracted by inserting a syringe with a modified tip that had a hollowed out porous stone attached to prevent clogging (Alperin et al. 1999).

Eight sediment cores were also collected from the mid-channel using a Wildco Ogeechee hand corer with liners (Wildlife Supply Company, Yulee, FL). Cores were sliced at three depth intervals (0-10 cm, 10-20 cm, and 20-30 cm). The sediment sections were quickly homogenized and immediately packed with no air bubbles into 60-mL centrifuge tubes. The centrifuge tubes were sealed and placed in mason jars filled with mid-channel sediments to minimize contact with ambient air during incubation. Each mason jar contained triplicate centrifuge tubes for each depth and each incubation time, in order to eliminate exposure to air from opening and reclosing of jars. The effort included a total of 36 centrifuge tubes, with 12 tubes for each of the three depth intervals and each of three incubation times (CP: 0, 17, and 32 d; MID: 0, 7, 32, and 66 d). The rate of NH_4^+ production was measured under anoxic conditions to eliminate nitrification and minimize denitrification and anammox (anaerobic ammonium oxidation) reactions. It should be noted that the role of

oxygen in the decomposition of sedimentary organic matter was eliminated in these laboratory experiments, which may have imposed some artifacts or bias. The NH_4^+ production rate was calculated from the change in porewater NH_4^+ concentration over time for each depth interval.

3.4.4 Submarine Groundwater Discharge

Submarine groundwater discharge (SGD) was measured at the two shallow nearshore sites, MB and CP, using ^{222}Rn as a groundwater tracer, in order to quantify advective flux of NH_4^+ from porewaters to the overlying water. This naturally occurring tracer is elevated in groundwater compared to surface water because it escapes to the atmosphere once it is mixed in the surface water (Cable et al. 1996). ^{222}Rn has been used as a groundwater tracer in many studies (e.g. Cable et al. 1996, 2004; Cable and Martin 2008; Corbett et al. 1999, 2000; Smith et al. 2008). For the purpose of this study, SGD was defined as total advective discharge into a water body across the sediment water interface, including subsurface terrestrial freshwater and recirculated seawater (Taniguchi et al. 2002). Ten milliliters of porewater sampled from the multi-level piezometers were collected for ^{222}Rn analysis from an overflow container using a glass syringe (Chapter 2). The 10-mL sample was transferred to pre-filled vials with 10 mL of high-efficiency mineral oil to eliminate contact with air. Porewater ^{222}Rn was analyzed on a Packard Tri-Carb liquid scintillation counter. The gradient of ^{222}Rn porewater concentrations were used to estimate SGD based on the slope and diffusion of ^{222}Rn (Martin et al. 2007, Cable and Martin 2008, Chapter 2). Details of ^{222}Rn methodology can be found in Chapter 2. The advective flux of NH_4^+ was calculated from the shallowest NH_4^+ concentrations (10 cmbsf) and SGD at each site.

The mid-channel was assumed to have no groundwater flow based on previous studies that measured chloride (Cl^-) (Alperin et al. 2000) and basic hydrogeologic modeling (Spruill and Bratton 2008). The mid-channel may have had significant porewater exchange due to advection

associated with sediment resuspension during storms and wind events (Giffen and Corbett 2003). However, advection in the mid-channel was not measured as part of this study.

3.4.5 Analytical and Statistical Considerations

NH_4^+ and NO_3^-+NO_2^- concentrations were analyzed colorimetrically using an automated Quattro Continuous-Flow Analysis (CFA) system, following EPA method (US EPA 1993 EPA/600/R-93/100). Precision of the Quattro analysis is 0.3 μM for NH_4^+ and 0.1 μM for NO_3^- + NO_2^-. NH_4^+ porewater samples from piezometers and ammonium production experiments were analyzed within 24 h of sampling to eliminate freezing or preservation artifacts. NH_4^+ samples from chamber experiments and all NO_3^- + NO_2^- samples were frozen and analyzed within 30 days following method EPA/600/R-93/100 (US EPA 1993).

Seasonal variation in NH_4^+ porewater concentrations and fluxes was analyzed across all sites and sampling months using one-way analysis of variance (ANOVA) (StatCrunch, Integrated Analytics, LLC). The variance in light and dark incubations was analyzed using ANOVA as well. O_2 consumption and NH_4^+ flux was analyzed by linear regression. All statistical analyses were conducted using StatCrunch (Integrated Analytics, LLC).

3.5 Results

3.5.1 Sediment Nutrient Profiles

NH_4^+ was the primary form of inorganic N in the NRE sediment porewaters, and was elevated in porewaters relative to surface waters at all sites. Surface water NH_4^+ concentrations ranged from 1.2 to10.1 μM at MB and from 0.7 to 3.7 μM at CP. All sites showed significant temporal variability in NH_4^+ porewater concentration between warm (August, September) and cold (January) months (Figure 3.2A, B) ($p = 0.001$, $n = 165$, ANOVA). NH_4^+ porewater concentrations at MB ranged from 71.5 to 345.1 μM (Figure 3.2A). MB NH_4^+ concentrations were almost three-fold higher than the concentrations found at CP. Porewater NH_4^+ concentrations ranged from 0.6 to 88.7 μM at CP, and concentrations decreased with depth (Figure 3.2B).

NO_3^-+NO_2^- was a minor portion of the N measured in porewaters at the three sites. Porewater concentrations ranged from 0.0 to 0.5 μM NO_3^-+NO_2^- at both MB and CP, and were often below analytical detection (0.1 μM) during most sampling months. At the upstream site (MB), NO_3^-+NO_2^- was detected at 10 cmbsf at 0.5 μM during January, when NO_3^-+NO_2^- surface-water concentrations were 9 μM (Figure 3.3A). NO_3^-+NO_2^- was less than 0.4 μM concentrations at depths greater than 150 cmbsf at CP, and was present only during October, January, and April (Figure 3.3B). In shallow porewaters (< 100 cmbsf) at CP, NO_3^-+NO_2^- was not detected except during January.

3.5.2 Nutrient Regeneration and Oxygen Consumption

Seasonal NH_4^+, DO, and NO_3^-+NO_2^- fluxes at the three sites are summarized in Table 3.2. Water-column temperatures ranged from 6.0 ˚C in January to 33.9 ˚C in August. At MB and CP, there was no significant difference in NH_4^+, DO, and NO_3^-+NO_2^- fluxes between light and dark experiments (ANOVA: MB, $p = 0.75$, $n = 18$; CP, $p = 0.89$, $n = 16$). Light experiments were not conducted for MID sediments because the mid-channel benthos is light-limited, receiving less than 50 μE s^{-1} m^{-2} of photosynthetically active radiation (PAR) measured with a Li-Cor Datalogger and 4π sensor (Li-Cor, Lincoln, NE). The NH_4^+ flux ranged from –29.1 to 811 μmol m^{-2} hr^{-1} among the three sites. Negative values indicate flux into the sediment from the overlying water. The highest net NH_4^+ flux occurred in October at all sites, and the lowest flux occurred in January. The upstream MB site released NH_4^+ from the sediments to the overlying water during four of the five months sampled, and showed significant seasonal variation (Figure 3.4A) ($p \leq 0.0001$, $n = 17$). At CP, most of the NH_4^+ flux occurred into the sediment and did not differ significantly among seasons (Figure 3.4B). At MID, NH_4^+ flux ranged from 2 to 203 μmol m^{-2} hr^{-1}, and the flux was significantly higher in October than in January ($p = 0.0097$, $n = 6$) (Figure 3.4C).

Both nearshore sites remained oxygenated (> 60 μM O_2) during all sampling months. In contrast, MID bottom waters frequently sustained anoxia (unpublished data, Center for Applied Aquatic Ecology, NCSU). Overlying water-column O_2 concentrations decreased in every incubation experiment at all sites, indicating benthic consumption of O_2 (Table 3.2) (Figure 3.4D-F). DO showed a significant seasonality, with highest O_2 consumption in

August at all sites ($p = \leq 0.0001$, $n = 34$) (Figure 3.4D-F). The MID site, which was sampled in October, January, and September, had higher sediment O_2 consumption rates in October.

3.5.3 Ammonium Production

NH_4^+ production rates were measured in sediment cores collected from a sandy nearshore site (CP with an incubation period of 32 days) and the organic-rich, mid-channel site (MID with an incubation period of 66 days) at depths down to 35 cmbsf. There was no significant difference in NH_4^+ production from surface sediments at the two sites, but porewater concentrations were higher at MID (Figures 3.5 and 3.6). At the nearshore CP site, porewater NH_4^+ increased substantially from day 17 to day 32 over all depths, and the highest production rate occurred at the 25- to 35-cm depth interval (0.004 μmol NH_4^+ cm^{-3} wet sediment d^{-1}) (Figure 3.6). Porewater NH_4^+ concentrations at MID ranged from 633 μM at 5 cmbsf to 1254 μM at 25 cmbsf. NH_4^+ production experiments showed a smaller increase of NH_4^+ over time from the MID site, and indicated similar production rates with depth as in the nearshore sites. The highest NH_4^+ production rate at MID occurred at the 0- to 10-cm interval (0.001 μmol NH_4^+ wet sediment cm^{-3} d^{-1}) (Figure 3.6).

3.5.4. Submarine Groundwater Discharge

Based on ^{222}Rn measurements, the average SGD at the two nearshore sites over all sampling periods was 5.1 cm d^{-1} for MB and 12.6 cm d^{-1} for CP (Figure 3.7A). CP had higher SGD compared to MB for all sampling months. SGD did not show strong temporal variability, although ^{222}Rn-based SGD estimates were lowest at MB and CP in January (Figure 3.7A).

The advective NH_4^+ flux was calculated by multiplying the SGD estimate and NH_4^+ concentration at 10 cmbsf for each site seasonally. MB had higher mean advective NH_4^+ flux over all sampling months (20 ± 7.2 mmol m^{-2} d^{-1}) compared to 5.4 ± 0.5 mmol m^{-2} d^{-1} at CP (Figure 3.7B). The lowest advective NH_4^+ flux occurred during January at both nearshore sites and the highest flux was observed during September 2008 at MB (39.9 mmol m^{-2} d^{-1}), and August 2007 at CP (12.6 mmol m^{-2} d^{-1}).

3.6 Discussion

3.6.1 Temporal and Spatial Variation of Inorganic N Fluxes

NH_4^+ flux estimates from NRE sediments in this study were comparable to fluxes measured in previous research conducted in the NRE and in similar coastal environments (Table 3.4). Based on fluxes calculated from porewater profiles, Haruthunian (1997) suggested that buried organic matter is being remineralized and more bioavailable N is being recycled back to the water column in summer than in winter (4.5 mmol m^{-2} d^{-1} and 0.69 mmol m^{-2} d^{-1} respectively). In this study, the NH_4^+ flux data from the mid-channel muds as well as upstream sandy nearshore site MB showed seasonal variation ($p = < 0.0001$; $n = 7$ and $n = 18$, respectively - ANOVA). At the downstream nearshore site CP, however, there was no significant seasonal difference in NH_4^+ flux ($p = 0.18$, $n = 16$, ANOVA). These NH_4^+ flux estimates suggest lower diffusive flux than Haruthian (1997) reported, but included consideration of active processes, such as nitrification and benthic algal uptake, that may have influenced the flux across the sediment water interface.

Both nearshore sites showed seasonal differences in benthic oxygen demand, with rates significantly higher during warmer months, especially October (Figure 3.4). These findings may have been attributable to higher organic material inputs from summer blooms and/or associated higher microbial organic matter degradation (as a result of higher temperatures). At the nearshore sites, there was no significant difference between light and dark experiments, indicating that minimal benthic photosynthesis occurred in the light incubation experiments. The CP sediment was qualitatively examined microscopically to determine the presence of benthic algae, which

consisted mostly of diatoms along with sparse dinoflagellates (H. Skelton, personal communication). If benthic algae were low in abundance, any oxygen produced may have been expended in organic matter decomposition, and thus would have resulted in minor differences in light and dark experiments.

O_2 consumption and NH_4^+ flux were not proportional at the two nearshore sites (Figure 3.8). MB had higher fluxes of NH_4^+ and higher oxygen consumption than CP in the chamber experiments, although NH_4^+ fluxes and oxygen consumption were not significantly correlated at either nearshore site (MB: n = 18, $r^2 = 0.16$, p = 0.94; CP: n =16, $r^2 = 0.03$, p = 0.52). If it is assumed that $NH_4^+$and O_2 fluxes result only from aerobic decomposition of organic matter, and that the decomposing matter consisted mostly of phytoplankton, there would have been 1 mole of N (as end product NH_4^+) produced per 6.6 O_2 moles consumed according to Redfield organic matter (Redfield 1934):

$$(CH_20)_{106}(NH_3)_{16}H_3PO_4 + 106O_2 + 16H^+ \Rightarrow 106CO_2 + 16NH_4^+ + H_3PO_4 + 106H_20$$

Redfield stoichiometry, developed for marine phytoplankton, was considered here because phytoplankton are the predominant form of organic matter in the downstream NRE sediments and can contribute up to ten-fold more particulate organic carbon than river runoff (Matson and Brinson 1990). The sediments at MB may have included more terrestrial organic matter. Nevertheless, based on the available literature, it was assumed that the majority of the NH_4^+ produced was from phytoplankton degradation due to the higher

degradation rate of organic matter derived from phytoplankton (Henrichs and Reeburgh 1987).

Considering the ratio of O_2 consumption to NH_4^+ production and flux to the overlying water ($O_2 : NH_4^+$), MB had an $O_2 : NH_4^+$ ratio similar to that of phytoplankton stoichiometry. The $O_2 : NH_4^+$ ratio at MB ranged from 0.41 in October to 23 in August, with many values close to the Redfield ratio, perhaps indicating phytoplankton decomposition during summer. The $O_2 : NH_4^+$ ratio ranged from 30 to 370 over all sampling months for CP, indicating a higher O_2 demand than an equivalent NH_4^+ flux based on values predicted from the aerobic organic matter oxidation equation (Figure 3.8B).

At the mid-channel site, surprisingly there also was no significant correlation between NH_4^+ regeneration and O_2 consumption ($r^2 = 0.02$, $p = 0.95$). The mid-channel site had an $O_2 : NH_4^+$ value of 10.2 in October, similar to that of marine phytoplankton stoichiometry. During January, NH_4^+ flux was low compared to O_2 consumption and in excess during September (Figure 3.8C).

As mentioned, the expected $O_2 : NH_4^+$ values were based on marine phytoplankton stoichiometry and aerobic degradation of organic matter. Therefore, these values represent idealized endmembers, with the following caveats. First, recent findings show that N:P elemental composition of algae can vary depending on alga taxa and environmental conditions (Geider and La Roche 2002). Geider and La Roche (2002) synthesized literature and found that nutrient-replete algae typically have lower N:P (15-30) compared to nutrient-deficient algae, but can encompass a larger range dependent on local variables. Therefore, in order to obtain an accurate value and assessment of the role of aerobic organic matter degradation in nutrient

fluxes, ideally the organic matter type and C:N:P would need to be established. Second, there can be chemical as well as biological consumption of O_2. Although it was assumed that O_2 penetrated 8-10 cm depth in nearshore sediments based on previous literature for permeable sediments (Cook et al. 2007) and physical characteristics (wave action, and presence of ripples) of the sampling sites, O_2 can be consumed chemically, by oxidation of iron and manganese. Furthermore, anaerobic oxidation of organic material is not considered in these calculations but it may alter the $O_2 : NH_4^+$ ratio. Utilization of O_2 and suboxic processes, such as sulfate reduction and methanogenesis, occurring in the sediments would make the $O_2 : NH_4^+$ ratio smaller than the Redfield stoichiometry based on aerobic degradation and can explain many of the values below the expected O:N ratio (Figures 3.8A-C). Sulfate reduction is an important process that occurs in organic-rich estuarine sediments once oxygen is depleted by aerobic respiration (Thamdrup et al.1994). In other research, organic carbon reaching the seafloor in coastal environments, such as Cape Lookout Bight (NC) was found to be reduced by aerobic respiration (27%), sulfate reduction (57%) and methanogenesis (16%) (Martens and Klump 1984). Although anaerobic processes may have been occurring, the magnitude and depth of these processes has not been established, especially in the permeable nearshore environments of the NRE.

Other processes that may influence the $O_2 : NH_4^+$ ratio include adsorption, benthic algal uptake of NH_4^+, nitrification, and denitrification in the sediments. Adsorption of NH_4^+ was not considered in this study but may also have prevented flux of NH_4^+ to the overlying water, especially with the mixing of freshwater and seawater (Gardner et al. 1991). In addition, benthic algae in the nearshore environment may have consumed NH_4^+, and therefore, decreased the flux to the overlying water (Tyler et al. 2003). DIN uptake by benthic algae at the sediment-water

interface can significantly affect DIN fluxes from sediments, particularly in sandy sediments (Reay et al. 1995; Janhke et al. 2000, 2005; Tyler et al. 2003). For example, Henriksen and Kemp (1988) reported that benthic diatom mats caused NH_4^+ and NO_3^- to flux from the water column into sandy sediments. However, in the mid-channel water column of the turbid Neuse system with limited PAR (< 50 $\mu E\ s^{-1}\ m^{-2}$) and reduced light attenuation (mean 1.11 m^{-1}; Mallin and Paerl 1992), benthic algae would not be expected to be as important as in nearshore environments.

Nitrification can be another important influence on the amount of NH_4^+ fluxing from sediments to the overlying water (Focht and Verstraete 1977, Blackburn and Henriksen 1983). Some NH_4^+ from decomposition and deamination of organic N may have been re-oxidized to NO_3^- via nitrification before it moved to the overlying water (Christensen and Rowe 1984). Nitrification can also influence oxygen availability in sediments by altering aerobic conditions and heterotrophy. Two moles of molecular oxygen are consumed for one mole of NH_4^+ oxidized in the nitrification process (Christensen and Rowe 1984). Nitrification would increase O_2 consumption and oxidize NH_4^+ at a ratio of 2:1 in the nearshore environments. Therefore, if decomposition had been occurring but part of the NH_4^+ being produced was being oxidized, the O_2:N ratios would have increased, as was observed at CP. If it is assumed that some of the NH_4^+ was fluxing from the sediment and oxidized to NO_3^-, then the NO_3^-+NO_2^- flux can be added to the NH_4^+ flux to calculate the O_2 : N value, although NO_3^-+NO_2^- was not detected during 14 of 36 flux chamber experiments. A NO_3^-+NO_2^- flux was detected at all sites in October, and at MB during August and January, but NO_3^-+NO_2^- fluxes were low compared to NH_4^+ fluxes (Table 3.1). The O_2 :

$NH_4^+ + NO_3^- + NO_2^-$ ratio from each core indicated that the $NO_3^- + NO_2^-$ concentration was insignificant to the ratio and did not change the O_2 : N values.

Recycling and the regenerative internal flux from the sediments can play a significant role in NH_4^+ availability for estuarine productivity (Glibert 1988). With increased eutrophication of Chesapeake Bay, for example, it was suggested that nitrification and denitrification rates may be reduced, and therefore NH_4^+ would be recycled back to the water-column to further stimulate phytoplankton productivity (Kemp et al. 1990). Thus, recycling and the regenerative internal flux from the sediments can play a significant role in NH_4^+ availability for estuarine productivity (Glibert 1988). Denitrification rates can affect overall water column N_i. In Chesapeake Bay, Boynton and Kemp (1985) found that O_2:N values were more consistent with Redfield organic matter values in summer than in spring, and suggested that the proportionally low release of N from sediments resulting in high O_2:N ratios could be attributed to high denitrification rates. In Narragansett Bay, Berounsky and Nixon (1990) also found high O_2: N values and suggested denitrification as the primary process affecting the O_2:N ratio. In this study, the sediments became more anoxic during the incubation experiments, resulting in final O_2 concentrations less than 300 μM in the overlying water. Increased denitrification resulting in decreased NH_4^+ flux may have occurred as the sediments became more anoxic.

In the NRE, Fear et al. (2005) assessed denitrification from three mid-channel sites along a salinity gradient, and estimated that denitrification removed ~12% of the total annual N load and ~26% of the annual DIN load. From seasonal data, Fear et al. (2005) also estimated that denitrification rates ranged from 0-275 μmol N m^{-2} h^{-1}. Earlier researchers estimated denitrification rates of 0-104 μmol N m^{-2} h^{-1} in the mesohaline NRE (Piehler et al.

2002). Other factors, such as NO_3^- and DO concentration and sediment organic matter content, can also influence denitrification rates. Both Piehler et al. (2002) and Fear et al. (2005) unexpectedly found higher denitrification rates in winter concomitant with increased NO_3^- concentrations, as has been reported for Chesapeake Bay (Kemp et al. 1990). High denitrification rates in winter do not support the low O_2: NH_4^+ ratio found during January incubations, suggesting that other factors contributed to the low NH_4^+ fluxes.

3.6.2 Ammonium Production and Sedimentary Processes

Phytoplankton blooms can be a major source of organic material to sediments, especially in shallow estuaries and coastal waters (Jensen 1990). Organic matter degradation in sediments forms NH_4^+ by deamination in sediments producing high NH_4^+ porewater concentrations. Caffrey (1995) measured NH_4^+ production in shallow sediments (up to 8 cm depth) at five sites in South Bay, San Francisco Bay and reported that NH_4^+ production was highest in spring and fall, but production was not driven by temperature. It was therefore suggested that NH_4^+ production was more closely related to the timing of organic matter inputs.

In this study, NH_4^+ production experiments from cores taken at a nearshore site (CP) and a mid-channel site revealed similar NH_4^+ production rates in the surface sediments, although the sandy nearshore site had higher production in deeper sediments (25-35 cmbsf). In other systems, organic-rich sediments have been described as having lower NH_4^+ production with depth, probably due to decreasing labile organic matter and/or oxidizing agents with sediment depth, for example, coastal waters along Denmark (Blackburn and Henriksen 1983), Long Island Sound (Aller and Yingst 1980), San Francisco Bay (Caffrey 1995).

Moreover, similar rates of NH_4^+ production occurred in the nearshore sediments of the NRE compared to the mid-channel site, despite the higher organic content in the mid-channel and large NH_4^+ pools. Several possible errors may have resulted from the NH_4^+ production methods that were used: First, extractable NH_4^+ was not measured and it may have been a considerable fraction of the NH_4^+ in porewaters of the fine-grained sediments in the mid-channel. Second, different methods were used to analyze NH_4^+ production in the cores. The nearshore cores were large push cores dug out from sediments and left to incubate undisturbed. In contrast,

the mid-channel cores were sliced and packed into centrifuge tubes. During the slicing process, O_2 was introduced and may have stimulated nitrification utilizing a portion of NH_4^+. Because O_2 was introduced, time zero data were not included in calculating production rates for MID. However, the data indicated lower production rates in the organic-rich mid-channel compared to the sandy nearshore environment, and overall lower production (1 mmol NH_4^+ m^{-2} d^{-1}) than previously reported in other studies (e.g. 3.2 - 7.6 mmol m^{-2} d^{-1}) (Aller and Yingst 1980). An explanation that may validate our findings is that the MID site may have older soils with less reactive organic matter accumulating compared to fresh algal organic material in the nearshore sites. This hypothesis was not tested in this study but could be investigated using $\delta^{13}C$ to determine type of organic matter content and ^{14}C to age date organic material. Another possible explanation for lower production at the MID site is that MID was not as advective as the nearshore site, thus allowing porewater NH_4^+ to accumulate although it was not necessarily being produced at a rapid rate.

3.6.3 Advective Porewater Exchange

Although our data indicate that NH_4^+ was being produced in the sandy nearshore sediments, there was a relatively low diffusive flux from the sediments to the overlying water. As mentioned previously, many factors may have influenced these findings, including chemical reactions within the oxic/anoxic boundaries, biological processes such as loss of NH_4^+ through uptake by benthic algae, and advection. Advective transport may be a primary control on NH_4^+ production and diffusion across the sediment-water interface in nearshore NRE environments. Factors regulating the fluxes of nutrients from sediments to the water column include the rates and types of organic matter supplied to the sediments, decomposition rates, biological activity, and exchange rates between porewaters and overlying water. The rate of remineralization ultimately controls the flux of dissolved nutrients from sediments to the overlying water (Klump and Martens 1981), but other factors, such as advective porewater exchange, may play an important role in permeable nearshore environments (Janke et al. 2005). Tidal pumping, wave interaction, and/or groundwater discharge may alter oxygen concentrations, redox potential, and residence time of porewater and influence the remineralization rates of organic matter and NH_4^+ production and flux across the sediment-water interface. Continuous exchange of porewater, also called "flushing", can occur as a result of pressure gradients from wave action and tidal pumping (Burnett et al. 2003). Advective porewater exchange and chemical zones are highly variable spatially and temporally due to the continually changing boundary layer in high-energy environments (i.e ripples) (Burnett et al 2003). Waves can perturb porewaters of high

permeability sediments (Harrison et al.1983) and increase nutrient fluxes and oxygen penetration.

In energetic environments such as the nearshore NRE, fluxes of nutrients and NH_4^+ production may be influenced by advection of porewaters. Physical parameters that may influence nutrient fluxes include tides, water level, and waves. The effect of tides is minimal in the NRE, but water level can fluctuate significantly (Reed et al. 2008), affecting pressure gradients and salinity, which can impact nutrient flux. Significant wave action can occur in portions of the mesohaline NRE, especially when nor'easters occur. CP was often subjected to wave action, and winds often increased during the afternoon, producing white cap conditions. Ripples on the sediment surface were often present as well, indicating the effects of local waves on the sediment-water interface.

Marinelli et al. (1998) investigated NH_4^+ production and nutrient flux on the continental shelf on the South Atlantic Bight (SAB). This system has permeable sandy sediments that showed substantial variation among cores, often with low or undetectable flux of nutrients across the sediment-water interface. Our results are similar to Marinelli et al. 1998, in that there was no significant difference between light and dark experiments for nutrient exchange from sediments to the overlying water in NRE nearshore sites. NH_4^+ production rates were also similar, 0.001-0.002 in the NRE compared to 0.001-0.006 μmol NH_4^+ cm^{-3} d^{-1} in the SAB. Benthic primary production may contribute significantly to nutrient fluxes, but in the light and dark flux incubations of our study, fluxes did not follow a regular pattern. SGD, an advective process, may play a more important role than other processes, such as differential burial of N relative to C and differential diagenetic processes,

in influencing NH_4^+ flux from sediments to the overlying water. With greater SGD, more permeable sediments, and lower organic material, NH_4^+ would not be expected to accumulate in porewaters.

Nearshore environments with advective porewater exchange can have a strong influence on local nutrient budgets (Cook et al. 2007, Spiteri et al 2008). SAB has been hypothesized to have non-local exchange that deplete nutrients down to sediment depths of 10 cm, which would make advection of fluids in this energetic environment more important than molecular diffusion (Marinelli et al. 1998). Using flume experiments, Huettel et al. (1996) similarly found a depth of solute advection to ~ 8 cm below the sediment surface in permeable sediments. Fluxes of nutrients and NH_4^+ production can be influenced by advection of porewaters in energetic environments (Marinelli et al 1998). Advective flows generated by pressure gradients may enhance solute and particle exchange and tend to decrease with depth as resistance increases in the sediment with longer solute flow paths. Advective porewater exchange can be 2.5-fold greater than diffusive exchange of oxygen under conditions of flushing rates ranging from 100-300 L m^{-2} d^{-1} in permeable sediments of the North Sea and Baltic Sea (Cook et al. 2007).

Thus, advective transport may be an important influence on NH_4^+ production and diffusion across the sediment-water interface at energetic nearshore environments in the NRE. In shallow nearshore environments, SGD, including both freshwater and infiltrated seawater, was measured as an advective component that may have affected nutrient production and flux to the overlying water column. NH_4^+ fluxes in the nearshore environments were temporally and spatially variable. CP had significantly higher SGD than

MB during June, April, and September (Figure 3.9). The SGD NH_4^+ flux in the two nearshore sites ranged from 1.1 - 39 mmol m^{-2} d^{-1} with a mean of 12 ± 3.7 (Figure 3.7B). The SGD NH_4^+ flux was seasonally variable and apparently was affected by the temporal variability in NH_4^+ porewater concentrations. Since NH_4^+ porewater concentration is a function of organic matter degradation, changes in organic matter rates and or concentration may be the driving factor in NH_4^+ fluxes, as opposed to changes in advective porewater transport. The NH_4^+ flux was lowest in January at both sites, whereas the highest flux occurred in August or September at MB and CP. The high NH_4^+ flux at MB in September was driven by high porewater concentration (445 μM), especially at 10 cmbsf. MB exhibited higher NH_4^+ flux (average 20 ± 7.2 mmol m^{-2} d^{-1} versus CP, 5.4 ± 0.5 mmol m^{-2} d^{-1}), possibly due to higher organic degradation and lower flow rate (Spiteri et al. 2008).

At MB, the mean advective NH_4^+ flux for each sampling month in this study was greater than the mean diffusive flux during warmer months (Figure 3.9A), while at CP the mean advective NH_4^+ flux was greater than the mean diffusive flux during all sampling months (Figure 3.9B). These data support the hypothesis that advection plays an important role in the flux of NH_4^+ in nearshore NRE environments. Previous research in the NRE mostly has focused on the nutrient fluxes from the organic-rich, mid-channel deposits, and these muds have been estimated to contribute almost half of the phytoplankton N demand (Haruthian 1997). In this study, the nearshore environment contributed similar NH_4^+ loads to the mesohaline NRE as the diffusive flux of the mid-channel (Table 3.4). Advection in the mid-channel was not considered, but wind-related resuspension events may have been a significant source of NH_4^+ to the water column as well (Giffin and Corbett 2003, Morin et al.

1999). This previously unquantified NH_4^+ source in nearshore environments potentially could substantially affect overall NH_4^+ dynamics in the mesohaline estuary, and may be a major contributor to the documented increase in water-column NH_4^+ concentration (Burkholder et al. 2006).

3.7 Conclusions

This study demonstrated that nearshore sediments of the NRE can play an important role in nutrient cycling to the overlying water column. Nearshore environments are extremely heterogeneous, making measurements and quantification difficult, but nearshore sediments are significant to nutrient cycling in the mesohaline estuary. NH_4^+, the predominant form of DIN in porewaters, was produced at rates comparable to rates in the organic-rich mid-channel. However, NH_4^+ did not accumulate in porewaters at nearshore sites, therefore resulting in lower diffusive flux from sediments to the overlying water column. Other processes, such as biological uptake and N transformations, may be influencing the NH_4^+ flux from sandy sediments, but advection also affects nearshore nutrient dynamics. The data suggest that SGD advection generated NH_4^+ fluxes as high as, or higher than, fluxes from the organic-rich mid-channel sediments. The data also suggest that sandy nearshore environments are an important, previously overlooked source of NH_4^+ that likely has contributed to the significant increase in water-column NH_4^+ that has been documented in the NRE over the past decade.

N_i supplied to the water column of the NRE has been assessed as an important nutrient source for phytoplankton. Haruthunian (1997), for example, focused on NH_4^+ flux across the sediment-water interface at three sites from the central part of the NRE channel and estimated that benthic N regeneration supplied 41% of the total N demand by phytoplankton in the mesohaline estuary annually. NH_4^+ is efficiently recycled and is the preferred form of N over NO_3^- by many phytoplankton species (Middelburg and Nieuwenhuize 2000). Over recent years, the Neuse River basin has experienced significant

urbanization and natural habitats have decreased. Wastewater discharges and swine agriculture have been identified as the highest contributors of N to surface waters, respectively, in the upper and lower Neuse River (Rothenberger et al. 2009). These sources are contributing to the sustained eutrophication that the Neuse has sustained over the past few decades, which has led to major fish kills, harmful algal blooms, and oxygen deficits (Burkholder et al. 2006).

The importance of understanding NH_4^+ dynamics is also supported by the striking NH_4^+ increases that have begun to be documented in other eutrophic estuaries (e.g. Cloern 2001, Dugdale et al. 2007). Human disturbances, for example agriculture, manufacturing, and the burning of fossil fuels, are increasing nutrient fluxes to surface waters of rivers and estuaries (Nixon 1995). Mobilization of nutrients to coastal systems is a phenomenon that is escalating worldwide, and many questions remain to be answered about associated synergistic and long-term effects (Cloern 2001, Burkholder et al. 2006).

3.8 References

Aller, R.C., Blair, N.E., Xia, Q., Rude, P.D., 1996. Remineralization rates, recycling, and storage of carbon in Amazon shelf sediments. Cont. Shelf Res. 16, 753-786.

Aller, R.C., Yingst, J.Y., 1980. Relationships between microbial distributions and the anaerobic decomposition of organic matter in surface sediments of long Island Sound, USA. Mar. Biol. 56, 29-42.

Alperin, M.J., Martens, C.S., Albert, D.B., Suayah, I.B., Benninger, L.K., Blair, N.E., Jahnke, R.A., 1999. Benthic fluxes and porewater concentration profiles of dissolved organic carbon in sediments from the North Carolina continental slope. Geochim. et Cosmochim. Acta 63, 427-448.

Alperin, M.J., Clesceri, E.J., Wells, J.T., Albert, D.B., McNinch, J.E., Martens, C.S., 2000. Sedimentary processes and benthic-pelagic coupling, pp. 63-105. In: R. A. Leuttich (ed.), Neuse River Estuary Modeling and Monitoring Project: Final Report – Monitoring Phase. Report. UNC Water Resources Research Institute, Raleigh.

Berounsky, V.M., Nixon, S.W., 1990. Temperature and the annual cycle of nitrification in waters of Narragansett Bay. Limnol. Oceanogr. 35, 1610-1617.

Blackburn, T.H., 1979. N/C ratios and rates of ammonia turnover in anoxic sediments, pp. 148-153. In: Bourquin, A.W., and Pritchard, H. (eds.), Microbial Degradation of Pollutants in Marine Environments. Office of Research and Development, U.S. EPA, Washington, DC.

Blackburn, T.H., Henriksen, K., 1983. Nitrogen cycling in different types of sediments from Danish Waters. Limnol. Oceanogr. 28, 477-493.

Blair, N.E., Levin, L.A., DeMaster, D.J., Plaia, G., 1996. The short-term fate of fresh algal carbon in continental slope sediments. Limnol. Oceangr. 41, 1208-1219.

Boynton, W., Kemp, W., 1985. Nutrient regeneration and oxygen consumption by sediments along an estuarine salinity gradient. Mar. Ecol. Prog. Ser. 23, 45-55.

Burkholder, J.M., Dickey, D.A., Kinder, C., Reed, R.E., Mallin, M.A., Melia, G., McIver, M.R., Cahoon, L.B., Brownie, C., Deamer, N., Springer, J., Glasgow, H., Toms, D., Smith, J., 2006. Comprehensive trend analysis of nutrients and related variables in a large eutrophic estuary: A decadal study of anthropogenic and climatic influences. Limnol. Oceanogr. 51, 463-487.

Burnett, W.C., Bokuniewicz, H., Huettel, M., Moore, W.S., Taniguchi, M., 2003. Groundwater and porewater inputs to the coastal zone. Biogeochemistry 66, 3-33.

Cable, J.E., Martin, J.B., 2008. *In situ* evaluation of nearshore marine and fresh porewater transport into Flamengo Bay, Brazil. Estuar. Coast. Shelf Sci. 76, 473-483.

Cable, J.E., Martin, J.B., Swarzenski, P.W., Lindenberg, M.K., Steward, J., 2004. Advection Within Shallow Porewaters of a Coastal Lagoon, Florida. Ground Water 42, 1011-1020.

Cable, J.E., Bugna, G.C., Burnett, W.C., Chanton, J.P., 1996. Application of 222Rn and CH4 for assessment of groundwater discharge to the coastal ocean. Limnol. Oceanogr. 41, 1347-1353.

Caffrey, J.M., Sloth, N.P., Kaspar, H.F., Blackburn, T.H., 1993. Effect of organic loading on nitrification and denitrification in a marine sediment microcosm. FEMS Microbiol. Ecol. 12, 159-167.

Caffrey, J., 1995. Spatial and seasonal patterns in sediment nitrogen remineralization and ammonium concentrations in San Francisco Bay, California. Estuaries and Coasts 18, 219-233.

Capone, D.G., Bautista, M.F., 1985. A groundwater source of nitrate in nearshore marine sediments. Nature 313, 214-216.

Charette, M.A., Buesseler, K.O., 2004. Submarine groundwater discharge of nutrients and copper to an urban subestuary of Chesapeake Bay (Elizabeth River). Limnol. Oceanogr. 49, 376-385.

Charette, M.A., Buesseler, K.O., Andrews, J.E., 2001. Utility of Radium Isotopes for Evaluating the input and transport of groundwater-derived nitrogen to a Cape Cod estuary. Limnol. Oceanogr. 46, 465-470.

Christian, R.R., Boyer, J.N., Stanley, D.W., 1991. Multi-year distribution patterns of nutrients within the Neuse River Estuary, North Carolina. Mar. Ecol. Prog. Ser. 71, 259-274.

Christensen, J.P., and Rowe, G.T., 1984. Nitrification and oxygen consumption in northwest Atlantic deep-sea sediments. J. Mar. Res. 42, 1099-1116.

Cloern, J.E. 2001. Our evolving conceptual model of the coastal eutrophication problem. Mar. Ecol. Prog. Ser. 210, 223-253.

Codispoti, L.A., Christensen, J.P., 1985. Nitrification, denitrification and nitrous oxide cycling in the eastern tropical South Pacific ocean. Mar. Chem. 16, 277-300.

Cook, P., Wenzhofer, F., Glud, R., Janssen, F., Huettel, M., 2007. Benthic solute exchange and carbon mineralization in two shallow subtidal sandy sediments: Effect of advective porewater exchange. Limnol. Oceanogr. 52, 1943-1963.

Corbett, D.R., Dillon, K., Burnett, W., Chanton, J., 2000. Estimating the groundwater contribution into Florida Bay via natural tracers, 222Rn and CH4. Limnol. Oceanogr. 45, 1546-1557.

Corbett, D.R., Chanton, J., Burnett, W., Dillon, K., Rutkowski, C., Fourqurean, J.W., 1999. Patterns of groundwater discharge into Florida Bay. Limnol. Oceanogr. 44, 1045-1055.

Dugdale, R.C., Goering, J.J., 1967. Uptake of new and regenerated forms of nitrogen in primary productivity. Limnol. Oceanogr. 12, 196-206.

Dugdale, R.C., Wilkerson, F.P., Hogue, V.E., Marchi, A., 2007. The role of ammonium and nitrate in spring bloom development in San Francisco Bay. Estuar. Coast. Shelf Sci. 73, 17-29.

Fear, J., Gallo, T., Hall, N., Loftin, J., Paerl, H., 2004. Predicting benthic microalgal oxygen and nutrient flux responses to a nutrient reduction management strategy for the eutrophic Neuse River Estuary, North Carolina, USA. Estuar. Coast. Shelf Sci. 61, 491-506.

Fear, J., Thompson, S., Gallo, T., Paerl, H., 2005. Denitrification rates measured along a salinity gradient in the eutrophic Neuse River Estuary, North Carolina, USA. Estuar. Coasts 28, 608-619.

Focht, D. D., and Verstraete, W., 1977. Biochemical ecology of nitrification and denitrification. Adv. Microbiol. Ecol. 1, 135-214.

Gardner, W.S., Seitzinger, S.P., Malczyk, J.M., 1991. The effects of sea salts on the forms of nitrogen released from estuarine and freshwater sediments: Does ion pairing affect ammonium flux? Estuaries 14, 157-166.

Geider, R., La Roche, J., 2002. Redfield revisited: variability of C:N:P in marine microalgae and its biochemical basis. Europ. J. Phycol. 37, 1-17.

Giffin, D., Corbett, D.R., 2003. Evaluation of sediment dynamics in coastal systems via short-lived radioisotopes. J. Mar. Syst. 42, 83-96.

Glibert, P. M., 1988. Primary productivity and pelagic nitrogen cycling, pp. 3-31. In T. H. Blackburn and J. Sørensen [eds.], Nitrogen Cycling in Coastal Marine Environments. Scientific Committee on Problems of the Environment, of the International Council of Scientific Unions. SCOPE 33, John Wiley and Sons, New York.

Glibert, P.M., Burkholder, J.M., Parrow, M.W., Lewitus, A.J., Gustafson, D.E., 2006. Direct uptake of nitrogen by *Pfiesteria piscicida* and *Pfiesteria shumwayae*, and nitrogen nutritional preferences. Harmful Algae 5, 380-394.

Harrison, W.D., Musgrave, D., Reeburgh, W.S., 1983. Wave-induced transport process in marine sediments. J. of Geophys. Res. 88, 7617-7622.

Haruthunian, 1997. Seasonal and Spatial Variations in Benthic Organic Nitrogen Remineralization in the Neuse River Estuary, North Carolina. M.S. Thesis, UNC Chapel Hill, 70 pp.

Harrison, W.G., Platt, T., 1980. Variations in assimilation number of coastal marine phyto-phytoplankton: Effects of environmental co-variates. J. Plankton Res. 2, 249-260.

Henrichs, S.M., Reeburgh, W.S., 1987. Anaerobic mineralization of marine sediment organic matter: Rates and the role of anaerobic processes in the oceanic carbon economy. Geomicrobiology Journal 5, 191-237.

Henriksen, K, Kemp, W.M., 1988. Nitrification in estuarine and coastal marine sediments, pp. 207-249. In: Blackburn, H., Sorensen, J. (eds.) Nitrogen Cycling in Coastal Marine Environments. Wiley and Sons, New York.

Howarth, R.W., 1988. Nutrient limitation of net primary production in marine ecosystems. Annu. Rev. Ecol. Syst. 19, 89-110.

Howarth, R.W., Marino, R., Lane, J., Cole, J.J., 1988. Nitrogen fixation in freshwater, estuarine, and marine ecosystems. 1. Rates and importance. Limnol. Oceanogr. 33, 669-687.

Huettel, M., Ziebis, W., Forster, S., 1996. Flow-Induced Uptake of Particulate Matter in Permeable Sediments. Limnol. Oceanogr. 41, 309-322.

Jahnke, R.A., Nelson, J.R., Marinelli, R.L., Eckman, J.E., 2000. Benthic flux of biogenic elements on the Southeastern US continental shelf: influence of pore water advective transport and benthic microalgae. Cont. Shelf Res. 20, 109-127.

Jahnke, R., Richards, M., Nelson, J., Robertson, C., Rao, A., Jahnke, D., 2005. Organic matter remineralization and porewater exchange rates in permeable South Atlantic Bight continental shelf sediments. Cont. Shelf Res. 25, 1433-1452.

Joye, S.B., Hollibaugh, J.T., 1995. Influence of sulfide inhibition of nitrification on nitrogen regeneration in sediments. Science 270, 623-625.

Kemp, W.M., Boynton, W.R., Adolf, J.E., Boesch, D.F., Boicourt, W.C., Brush, G., Cornwell, J.C., Fisher, T.R., Glibert, P.M., Hagy, J.D., Harding, L.W., Houde, E.D.,

Kimmel, D.G., Miller, W.D., Newell, R.I.E., Roman, M.R., Smith, E.M., Stevenson, J.C., 2005. Eutrophication of Chesapeake Bay: historical trends and ecological interactions. Mar. Ecol. Prog. Ser. 303, 1-29.

Kemp, W.M., Sampou, P., Caffrey, J., Mayer, M., Henriksen, K., Boynton, W.R., 1990. Ammonium recycling versus denitrification in Chesapeake Bay sediments. Limnol. Oceanogr. 35, 1545-1563.

Kimmel, D.G., Miller, W.D., Newell, R.I.E., Roman, M.R., Smith, E.M., Stevenson, J.C., 2005. Eutrophication of Chesapeake Bay: historical trends and ecological interactions. Mar. Ecol. Prog. Ser. 303, 1-29.

Klump, J.V., and Martens, C.S., 1981. Biogeochemical cycling in an organic rich coastal marine basin – II. Nutrient sediment-water exchange processes. Geochim. Cosmochim. Acta 45, 101-121.

Lapointe, B., O'Connell, J., Garrett, G., 1999. Nutrient couplings between on-site sewage disposal systems, groundwaters, and nearshore surface waters of the Florida Keys. Biodegradation 10, 289-307.

Lapointe, B., Clark, M., 1992. Nutrient inputs from the watershed and coastal eutrophication in the Florida keys. Estuaries and Coasts 15, 465-476.

LaRoche, J., Nuzzi, R., Waters, R., Wyman, K., Falkowski, P., Wallace, D., 1997. Brown Tide blooms in Long Island's coastal waters linked to interannual variability in groundwater flow. Global Change Biol. 3, 397-410.

Luettich, R.A., Carr, S.D., Reynolds-Fleming, J.V., Fulcher, C.W., McNinch, J.E., 2002. Semi-diurnal seiching in a shallow, micro-tidal lagoonal estuary. Cont. Shelf Res. 22, 1669-1681.

Luettich 2000 Leuttich, R., McNinch, J., Paerl, H., Peterson, C., Wells, J., Alperin, M., Martens, C., Pinckney, J., 2000. Neuse River Estuary Modeling and Monitoring Project Stage 1: Hydrography and Circulation, Water Column Nutrients and Productivity, Sedimentary Processes and Benthic-Pelagic Coupling, and Benthic Ecology. Report No. 325-B. UNC Water Resources Research Institute, Raleigh.

Mallin, M.A., Paerl, H.W., 1992. Effects of variable irradiance on phytoplankton productivity in shallow estuaries. Limnol. Oceanogr. 37, 54-62.

Marinelli, R.L., Jahnke, R.A., Craven, D.B., Nelson, J.R., Eckman, J.E., 1998. Sediment nutrient dynamics on the South Atlantic Bight Continental Shelf. Limnol. Oceanogr. 43, 1305-1320.

Martens, C., Klump, J., 1984. Biogeochemical cycling in an organic-rich coastal marine basin. 4. An organic carbon budget for sediments dominated by sulfate reduction and methanogenesis. Geochim. Cosmochim. Acta 48, 1987-2004.

Martin, J.B., Hartl, K.M., Corbett, D.R., Swarzenski, P.W., Cable, J.E., 2003. A multi-level pore-water sampler for permeable sediments. J. of Sed. Res. 73, 128-132.

Martin, J., Cable, J., Smith, C., Roy, M., Cherrier, J., 2007. Magnitudes of submarine groundwater discharge from marine and terrestrial sources: Indian River Lagoon, Florida. Water Resour. Res. 43, W05440, 1-15.

Matson, E.A., Brinson, M.M., 1990. Stable carbon isotopes and the C: N ratio in the estuaries of the Pamlico and Neuse Rivers, North Carolina. Limnol. Oceanogr. 35, 1290-1300.

McCarthy, J.J., W. Rowland Taylor, Taft, J.L., 1977. Nitrogenous nutrition of the plankton in the Chesapeake Bay. 1. Nutrient availability and phytoplankton preferences. Limnol. Oceanogr. 22, 996-1011.

McCaffrey, R.J., Myers, A.C., Davey, E., Morrison, G., Bender, M., Luedtke, N., Cullen, D., Froelich, P., Klinkhammer, G., 1980. The relation between porewater chemistry and benthic fluxes of nutrients and manganese in Narragansett Bay, Rhode Island. Limnol. Oceanogr. 25, 31-44.

Middelburg, J.J. and Nieuwenhuize, J., 2000. Uptake of dissolved inorganic nitrogen in turbid, tidal estuaries. Mar. Ecol. Prog. Ser. 192, 79-88.

Middelburg, J.J., Nieuwenhuize, J., 2001. Nitrogen isotope tracing of dissolved inorganic nitrogen behaviour in tidal estuaries. Estuar. Coast. Shelf. Sci. 53, 385-391.

Moore, W.S., 2003. Sources and fluxes of submarine groundwater discharge delineated by radium isotopes. Biogeochemistry 66, 75-93.

Moore, W.S., 1999. The subterranean estuary: a reaction zone of ground water and sea water. Mar. Chem. 65, 111-125.

Morin, J., Morse, J.W., 1999. Ammonium release from resuspended sediments in the Laguna Madre estuary. Mar. Chem. 65, 97-110.

Nixon, S.W., 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia 41, 199-219.

Parsons, T., Takahashi, M., Hargrave, B., 1984. Biological Oceanographic Proceses. Pergamon Press, New York.

Piehler, M., Thompson, S., Dyble, J., Moisander, P., Fear, J., Paerl, H., 2002. Biologically Mediated Nitrogen Dynamics in Eutrophying Estuaries - Assessing Denitrification, N_2 Fixation and Primary Productivity Responses to Proposed N Loading Reductions in the Neuse River Estuary. Report No. 339. UNC Water Resources Research Institute, Raleigh.

Peters, K.E., Sweeney, R.E., Kaplan, I.R., 1978. Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. Limnol. Oceanogr. 23, 598-604.

Peterson, B.J., 1999. Stable isotopes as tracers of organic matter input and transfer in benthic food webs: A review. Acta Oecol. 20, 479-487.

Reay, W.G., Gallagher, D.L., Simmons, G.M., 1995. Sediment-water column oxygen and nutrient fluxes in nearshore environments of the lower Delmarva Peninsula, USA. Mar. Ecol. Prog. Ser. 118, 215-227.

Redfield, A.C., 1934. On the proportions of organic derivatives in seawater and their relation to the composition of plankton, pp. 177-192. In: Daniel, R.J., Ed., 1934. James Johnson Memorial Volume, Liverpool Univ. Press, Liverpool.

Reed, R.E., Dickey, D.A., Burkholder, J.M., Kinder, C.A., Brownie, C., 2008. Water level variations in the Neuse and Pamlico Estuaries, North Carolina due to local and remote forcing. Estuar. Coast. Shelf Sci. 76, 431-446.

Reed, R.E., Glasgow, H.B., Burkholder, J.M., Brownie, C., 2004. Seasonal physical–chemical structure and acoustic Doppler current profiler flow patterns over multiple years in a shallow, stratified estuary, with implications for lateral variability. Estuar. Coast. Shelf Sci. 60, 549-566.

Roche, J., 1983. Ammonium regeneration: its contribution to phytoplankton nitrogen requirements in a eutrophic environment. Mar. Biol. 75, 231-240.

Roelofs, E.W., Bumpus, D.F., 1953. The hydrography of Pamlico Sound. Bulletin Marine Science of the Gulf and the Caribbean 3, 181–205.

Rothenberger, M., Burkholder, J.M., Brownie, C., 2009. Long-term effects of changing land use practices on surface water quality in a major lagoonal estuary. Environmental Management 44, 505-523.

Slomp, C.P., Van Cappellen, P., 2004. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. Journal of Hydrology 295, 64-86.

Smith, C.G., Cable, J.E., Martin, J.B., Roy, M., 2008. Evaluating the source and seasonality of submarine groundwater discharge using a radon-222 porewater transport model. Earth Planet. Sci. Lett. 273, 312-322.

Smith, V.H., Tilman, G.D., Nekola, J.C., 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. Environmental Pollution 100, 179-196.

Spiteri, C., Slomp, C.P., Tuncay, K., Meile, C., 2008. Modeling biogeochemical processes in subterranean estuaries: Effect of flow dynamics and redox conditions on submarine groundwater discharge of nutrients. Water Resour. Res. 44, W02430, doi:10.1029/2007WR006071, 1-18.

Spruill, T., Bratton, J., 2008. Estimation of Groundwater and Nutrient Fluxes to the Neuse River Estuary, North Carolina. Estuaries and Coasts 31, 501-520.

Steel, J. (Ed.), 1991. Albemarle-Pamlico estuarine system, technical analysis of status and trends. A/P Estuarine Study Report 90-01, 80 pp.

Taniguchi, M., Burnett, W.C., Cable, J.E., Turner, J.V., 2002. Investigation of submarine groundwater discharge. Hydrological Processes 16, 2115-2129.

Thamdrup, B., Fossing, H., Jørgensen, B., 1994. Manganese, iron, and sulfur cycling in a coastal marine sediment, Aarhus Bay, Denmark. Geochim. Cosmochim. Acta 58, 5115-5129.

Thomas, C.J., Blair, N.E., 2002. Transport and digestive alteration of uniformly ^{13}C-labeled diatoms in mudflat sediments. J. Mar. Res. 60, 517-535.

Twomey, L., Piehler, M., Paerl, H., 2005. Phytoplankton uptake of ammonium, nitrate and urea in the Neuse River Estuary, NC, USA. Hydrobiologia 533, 123-134.

Tyler, A.C., McGlathery, K.J., Anderson, I.C., 2003. Benthic algae control sediment: Water column fluxes of organic and inorganic nitrogen compounds in a temperate lagoon. Limnol. Oceanogr. 48, 2125-2137.

United States Environmental Protection Agency (U.S. EPA). 1992. Methods for the determination of chemical substances in marine and estuarine samples. Report #EPA/600/R-92/121. U.S. EPA Office of Research and Development EPA/600/R-92/121.

Valiela, I., Costa, J., Foreman, K., Teal, J., Howes, B., Aubrey, D., 1999. Transport of groundwater-borne nutrients from watersheds and their effects on coastal waters. Biodegradation 10, 177-197.

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.G., 1997. Human alteration of the global nitrogen cycle: Sources and consequences. Ecol. Appl. 7, 737-750.

Walker, J.T., Aneja, V.P., Dickey, D.A., 2000. Atmospheric transport and wet deposition of ammonium in North Carolina. Atmos. Environ. 34, 3407-3418.

Whitall, D., Hendrickson, B., Paerl, H., 2003. Importance of atmospherically deposited nitrogen to the annual nitrogen budget of the Neuse River estuary, North Carolina. Environ. Int. 29, 393-399.

Wilkerson, F., Dugdale, R., Hogue, V., Marchi, A., 2006. Phytoplankton blooms and nitrogen productivity in San Francisco Bay. Estuaries and Coasts 29, 401-416.

Table 3.1. Parameters collected and sampling dates.

Samples	Site		
	MB	CP	MID
Porewater (nutrients, physical)	6/2007 – 9/2008	6/2007 - 9/2008	
Flux chambers	6/2007 – 9/2008	6/2007 - 4/2008	6/2007 -9/2008
NH_4^+ production		9/2008	9/2008
SGD (^{222}Rn)	6/2007 – 9/2008	6/2007 - 9/2008	

Table 3.2. NH_4^+, NO_3^-+NO_2^-, and DO fluxes (µmol m^{-2} hr^{-1}) at the two nearshore sites (Mills Branch and Cherry Point) and the mid-channel site. Negative values indicate flux from the overlying water into the sediment (L = light, D = dark; ND = not detected).

Site	Date	Chamber	Replicates	NH_4^+ Flux µmol m^{-2} hr^{-1}			O_2 Flux µmol m^{-2} hr^{-1}			NO_3- + NO_2^- Flux µmol m^{-2} hr^{-1}			Temperature °C	Salinity
Mills Branch	Aug 07	L	N=2	183.8	+/-	107.8	-1587	+/-	249	21.2	+/-	15.3	30.2	2.9
		D	N=3	110.1	+/-	32.1	-1653	+/-	25.9	10.2	+/-	8.8		
	Oct 07	D	N=2	811.3	+/-	23.8	-413	+/-	142	0.5	+/-	10.3	No Data	
	Jan 08	L	N=2	9.9	+/-	68.2	-468	+/-	352	-34.6	+/-	36.9	10.9	0.9
		D	N=2	55.7	+/-	10.1	-219	+/-	62.8	-14.7	+/-	11.8		
	April 08	L	N=2	-280.2	+/-	91.5	-498	+/-	18.5	ND	+/-		16.8	0.2
		D	N=1	28.5			-657			ND				
	Sept 08	L	No Data										28.8	11.0
		D												
Cherry Point	Aug 07	L	N=2	-29.1	+/-	27.9	-257.1	+/-	10.7	ND	+/-		33.9	16.6
		D	N=2	-13.4	+/-	17.6	-255.5	+/-	5.8	ND	+/-			
	Oct 07	L	N=3	-3.4	+/-	38.9	-421.1	+/-	51.9	18.2	+/-	68.8	20.4	16.0
		D	N=2	104.5	+/-	10.7	-544.2	+/-	7	-7.2	+/-	0.12		
	Jan 08	L	N=1	-5.1			-68			ND	+/-		6.0	15.0
		D	N=2	-1.2	+/-	1.9	-155.1	+/-	51.7	ND	+/-			
	April 08	L	N=2	5.3	+/-	13.4	-257.1	+/-		ND	+/-		21.4	11.5
		D	N=2	-6.3	+/-	5.6	-254.5	+/-		ND	+/-			
Mid channel	Oct 07	D	N=2	203.2	+/-	140.9	-1569	+/-	21.2	132	+/-	165	20.5	12.4
	Jan 08	D	N=3	2.8	+/-	20.1	-75.4	+/-	121		+/-			
	Sept 08	D	N=3										26.1	19.1

Table 3.3. Average nearshore advective NH_4^+ flux calculated from Mills Branch and Cherry Point and diffusive NH_4^+ flux from the mid-channel site in the Neuse River Estuary. NA indicates data not available.

Sampling Month	Nearshore Advective NH_4^+ Flux mmol m^{-2} d^{-1}	Mid-channel Diffusive NH_4^+ Flux mmol m^{-2} d^{-1}
06/2007	16.4	NA
08/2007	18.3	NA
10/2007	3.5	4.9
01/2008	1.8	0.1
04/2008	7.6	NA
09/2008	20.8	15.9

Table 3.4. Comparison of NH_4^+ and NO_3^++NO_2^+ (stated as NO_3^+) fluxes from studies in the Neuse River Estuary and other locations.

NH_4^+ Flux (μmol m^{-2} hr^{-1}) mean	range	NO_3^- Flux(μmol m^{-2} hr^{-1}) range	Method	Location	Sediment	Reference
95.4	(-177) - 173	-34.6 - 68.7	Chambers	Neuse (nearshore)	sand	This study
88.7	2 - 203	15.1 - 248	Chambers	Neuse (mid)	mud	This study
167	15 - 475		Porewater gradient	Neuse (mid)	mud	Haruthian (1997)
224	70 - 454	0-6.4	Chambers	Neuse	mud/sand	Fisher et al. (1982)
100	-45 - 500	-100 - 100	Cores	Neuse	sand and mud	Rizzo and Christian (1996)
	25-350		Chambers	Chesapeake Bay	muddy sand - mud	Kemp et al. 1990
6.6	-13.9 - 39.2		Cores	SAB	sand	Marinelli et al. 1989
	91.3 - 821	-125 - 288	*In situ* chambers	Chesapeake Bay	mud	Boynton and Kemp 1985

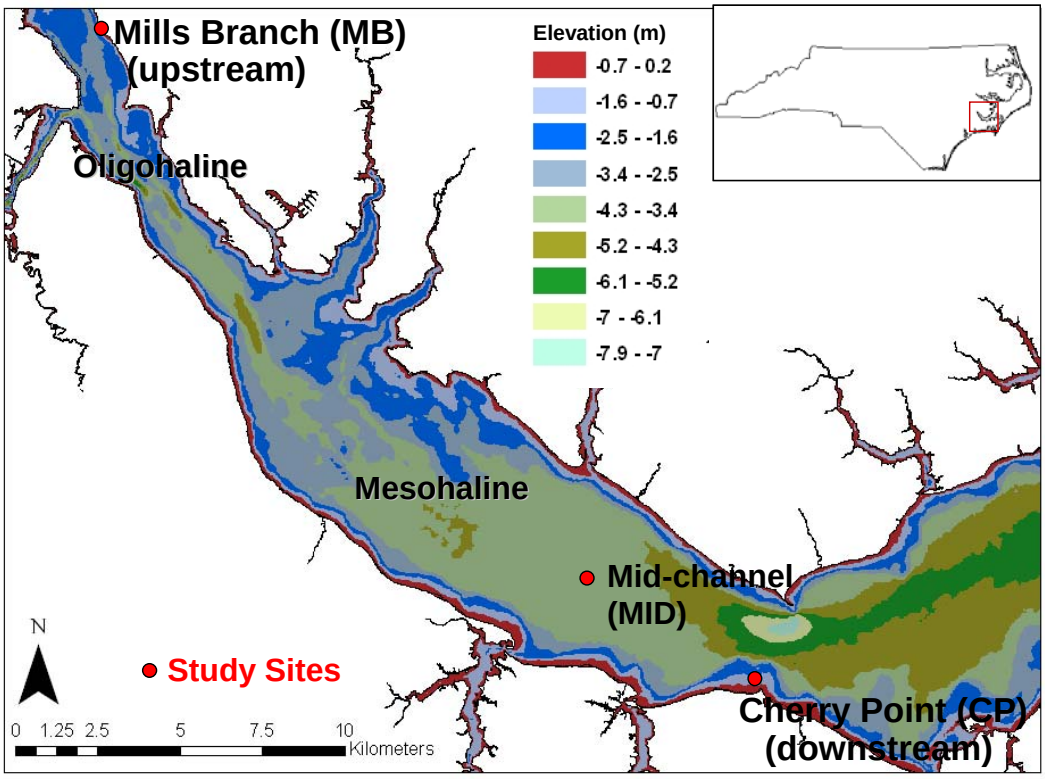


Figure 3.1. Bathymetric map of the Neuse River Estuary, North Carolina and location of sampling sites. Sampling sites include two nearshore sites, Mills Branch (MB) and Cherry Point (CP), and one mid-channel site (MID).

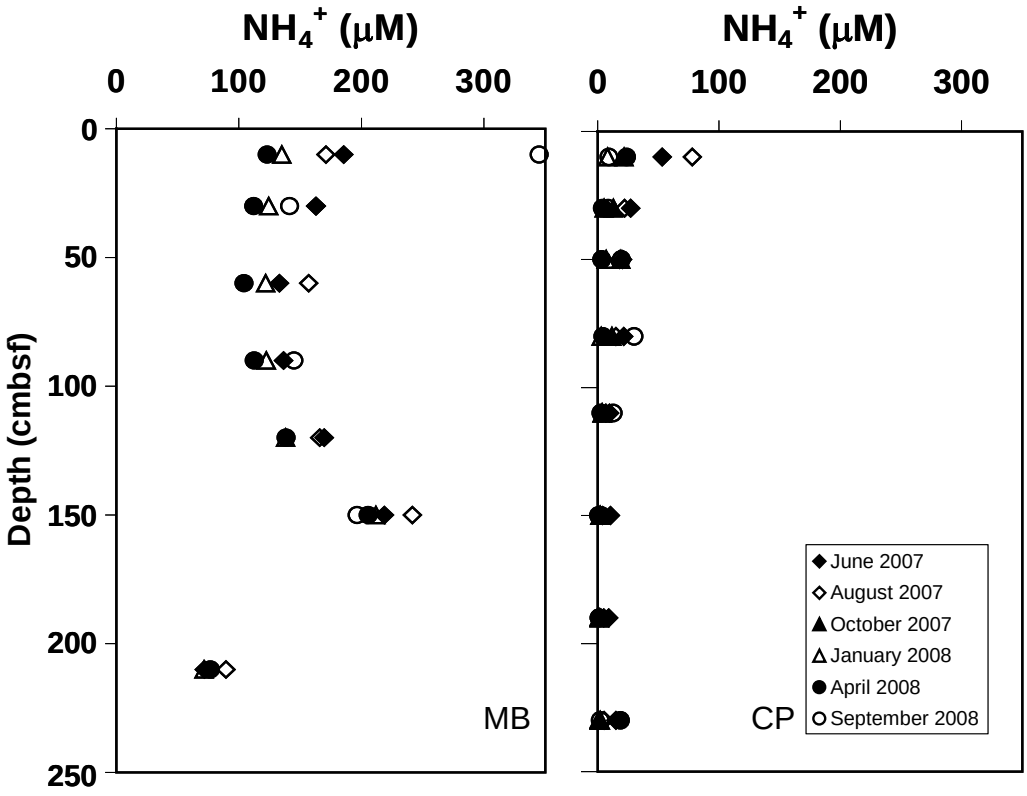


Figure 3.2. Porewater NH_4^+ concentrations versus depth at Mills Branch (MB) and Cherry Point (CP) in the Neuse River Estuary.

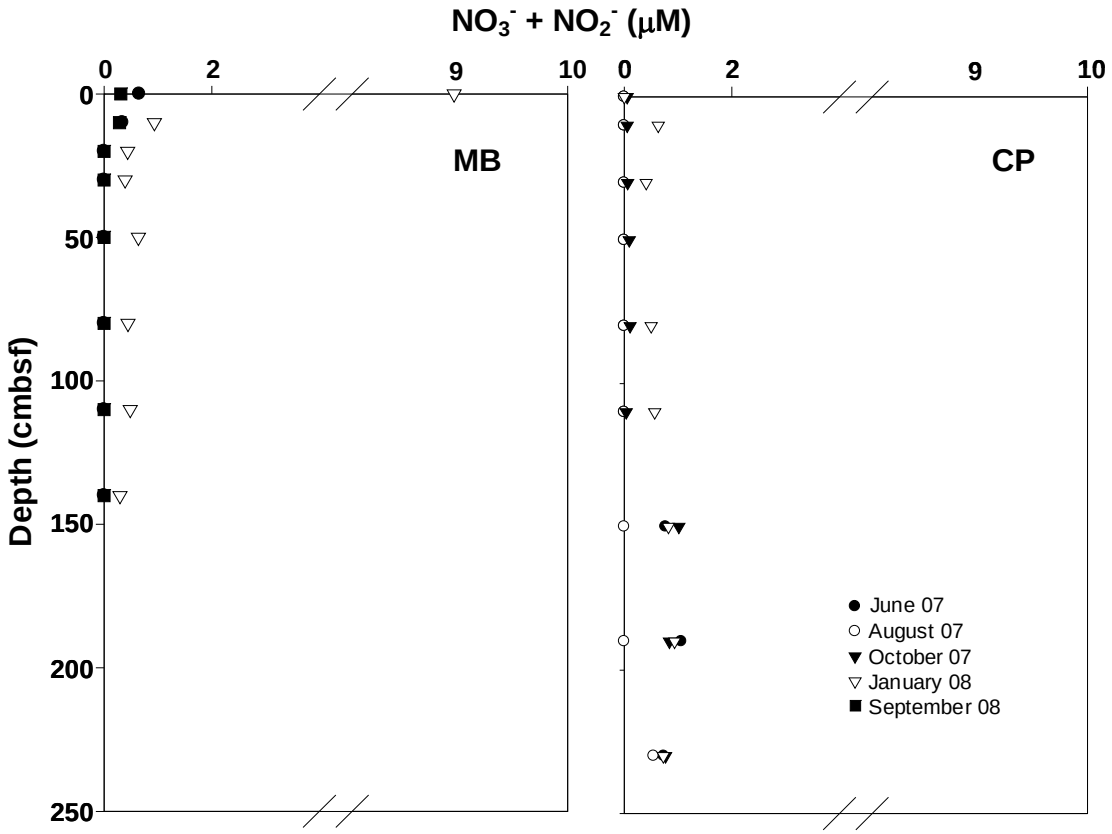
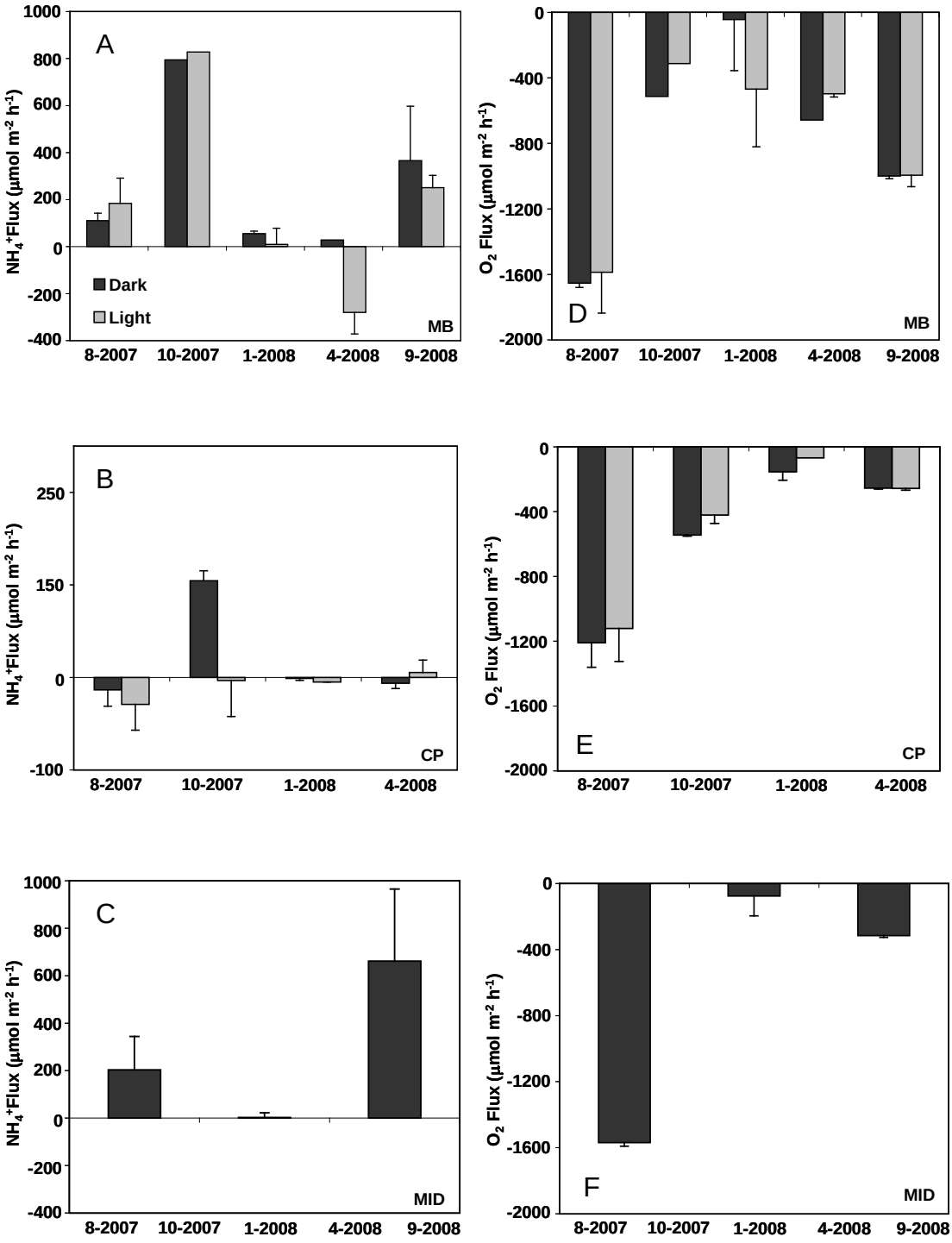


Figure 3.3. Porewater NO_3^-+NO_2^- concentrations at nearshore sites Mills Branch (MB, upstream) and Cherry Point (CP, downstream). Surface-water concentrations were graphed as 0 depth at MB; NO_3^-+NO_2^- was not detected in surface waters at CP.

Figure 3.4. Seasonal sediment NH_4^+ and O_2 fluxes at the two nearshore sites (Mills Branch, MB; Cherry Point, CP) and the mid-channel site (MID). Dark bars represent dark experiments and light bars represent experiments conducted at in situ light conditions. Flux chamber cores were not collected for CP during September 2008. Note scale difference for NH_4^+ flux for CP.


A
B
C
D
E
F
MB
CP
MID
Dark
Light
NH_4^+Flux (µmol m^{-2} h^{-1})
O_2 Flux (µmol m^{-2} h^{-1})
8-2007
10-2007
1-2008
4-2008
9-2008

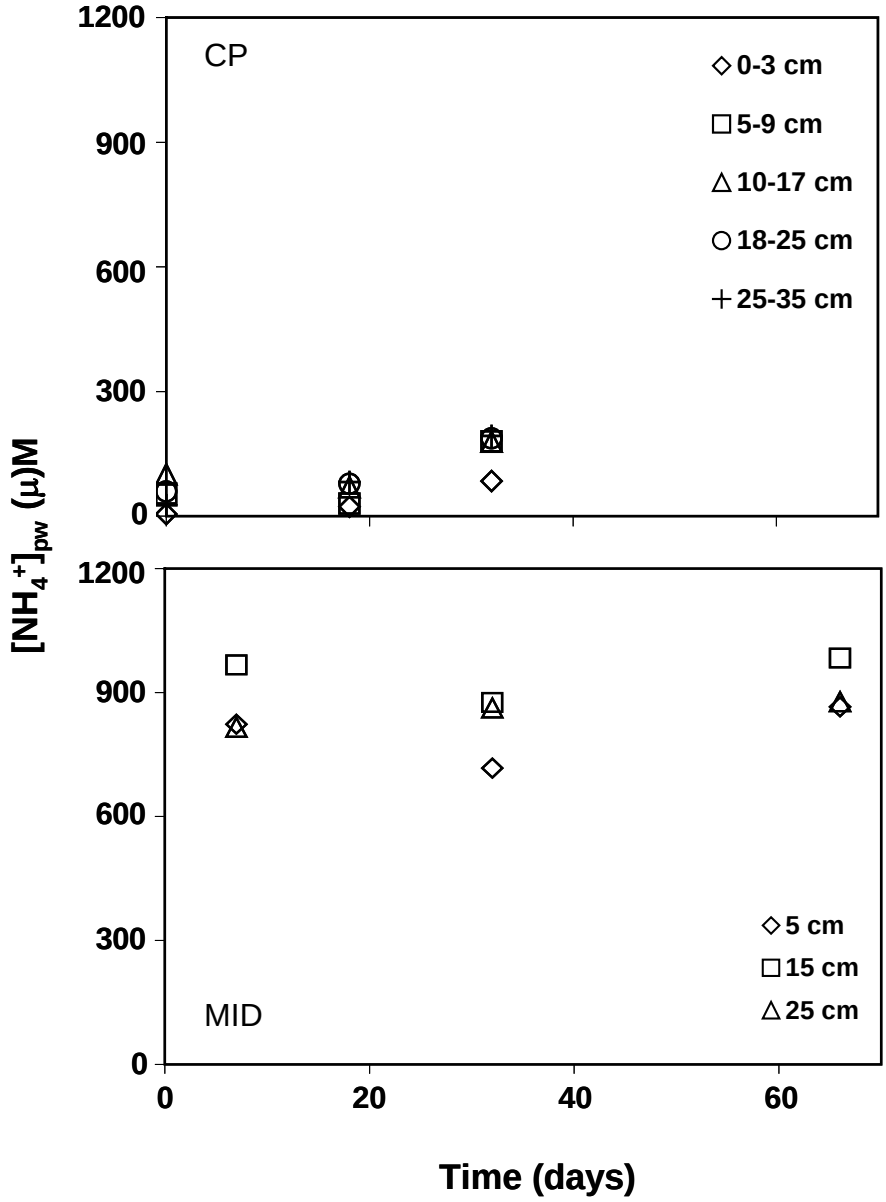


Figure 3.5. NH_4^+ porewater concentrations in sediment incubation experiments from cores taken at the Cherry Point (CP) and mid-channel (MID) sites. Incubations were maintained at ~ 21 °C.

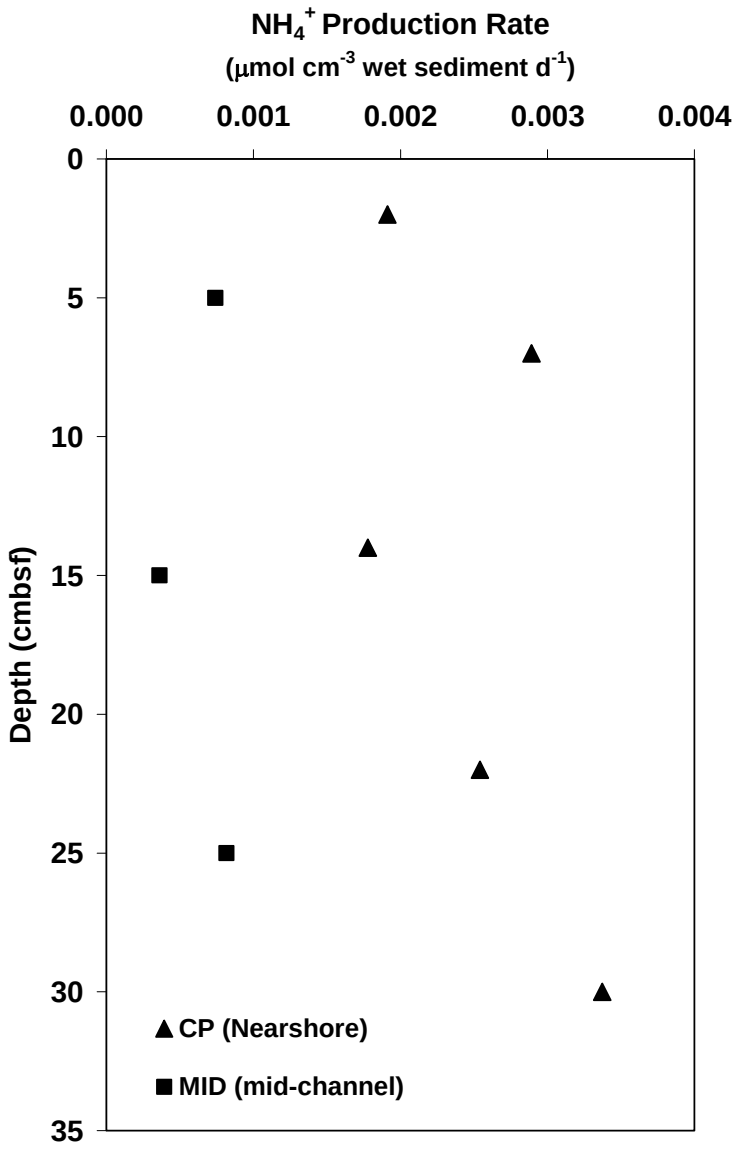


Figure 3.6. NH_4^+ production rate (change in porewater concentration over time for each depth interval) in μmol cm^{-3} wet sediment d^{-1} from the Cherry Point (CP, diamond) and mid-channel (MID, squares) sites.

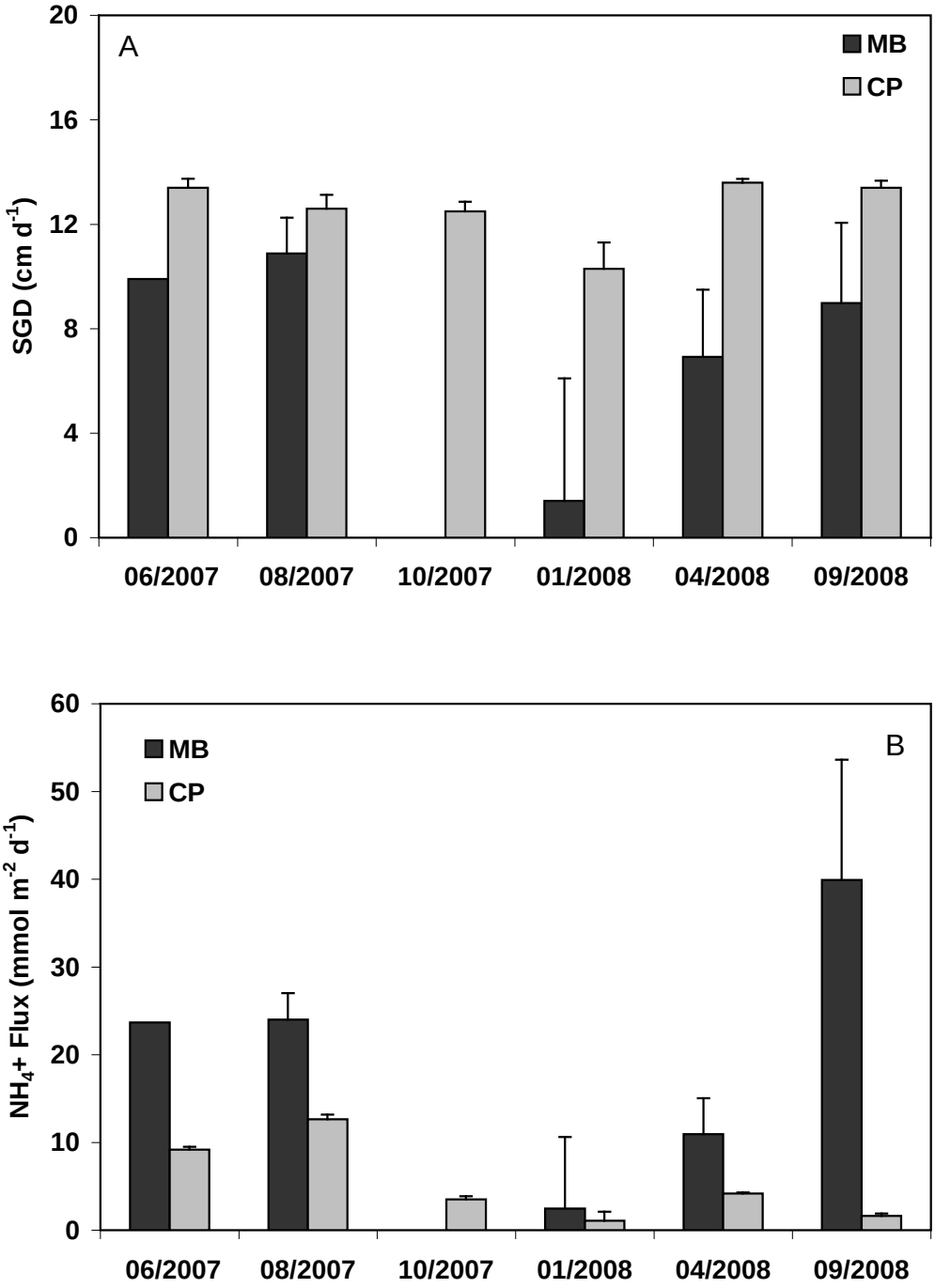
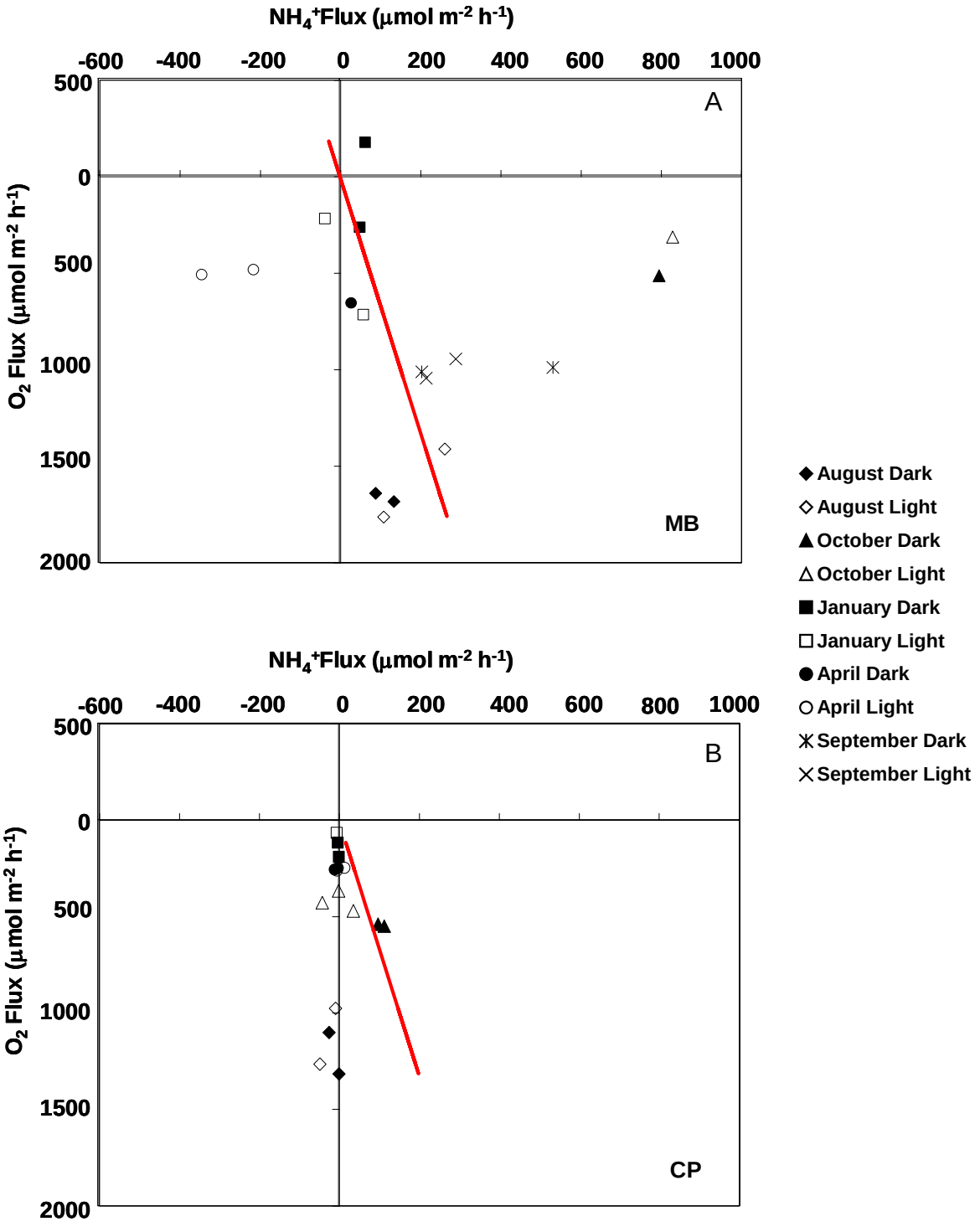
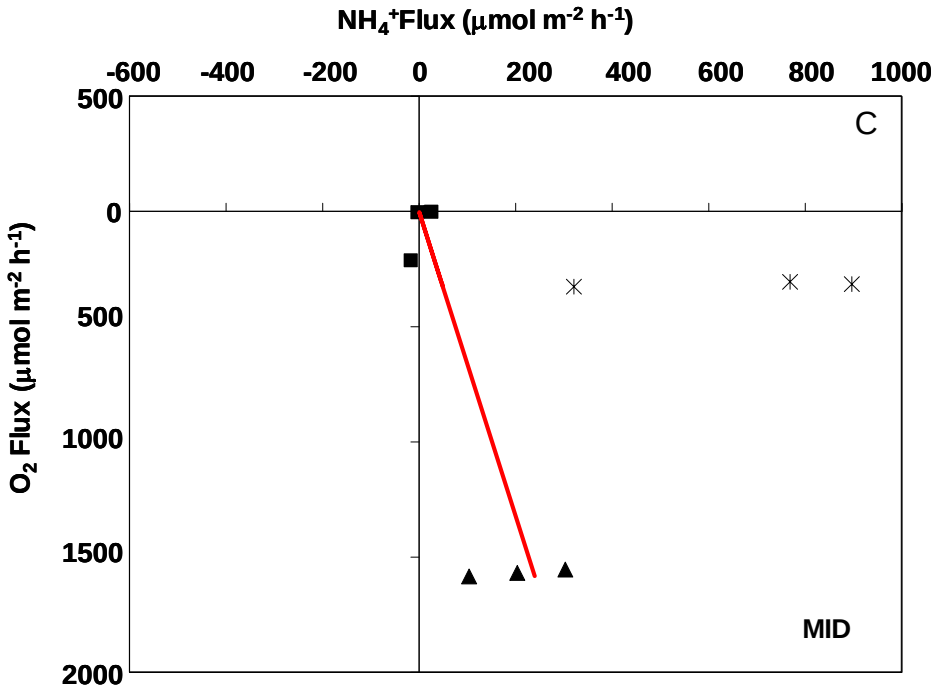


Figure 3.7. (A) Submarine groundwater discharge (SGD) in cm d^{-1} at Mills Branch (MB) and Cherry Point (CP). (B) NH_4^+ advective flux in mmol m^{-2} d^{-1} at MB and CP.

Figure 3.8. NH_4^+ flux versus oxygen consumption (μmol m^{-2} y^{-1}) at (A) nearshore site Mills Branch (MB), (B) nearshore site Cherry Point (CP), and (C) the mid-channel site (MID). Filled symbols represent dark experiments and open symbols represent light experiments for each month sampled. Red lines represent expected Redfield O_2:N ratios.


NH4+Flux (µmol m-2 h-1)
-600
-400
-200
0
200
400
600
800
1000
500
0
500
1000
1500
2000
O2 Flux (µmol m-2 h-1)
A
MB
NH4+Flux (µmol m-2 h-1)
B
CP
August Dark
August Light
October Dark
October Light
January Dark
January Light
April Dark
April Light
September Dark
September Light


NH4+Flux (µmol m-2 h-1)
-600
-400
-200
0
200
400
600
800
1000
500
0
500
1000
1500
2000
O2 Flux (µmol m-2 h-1)
C
MID

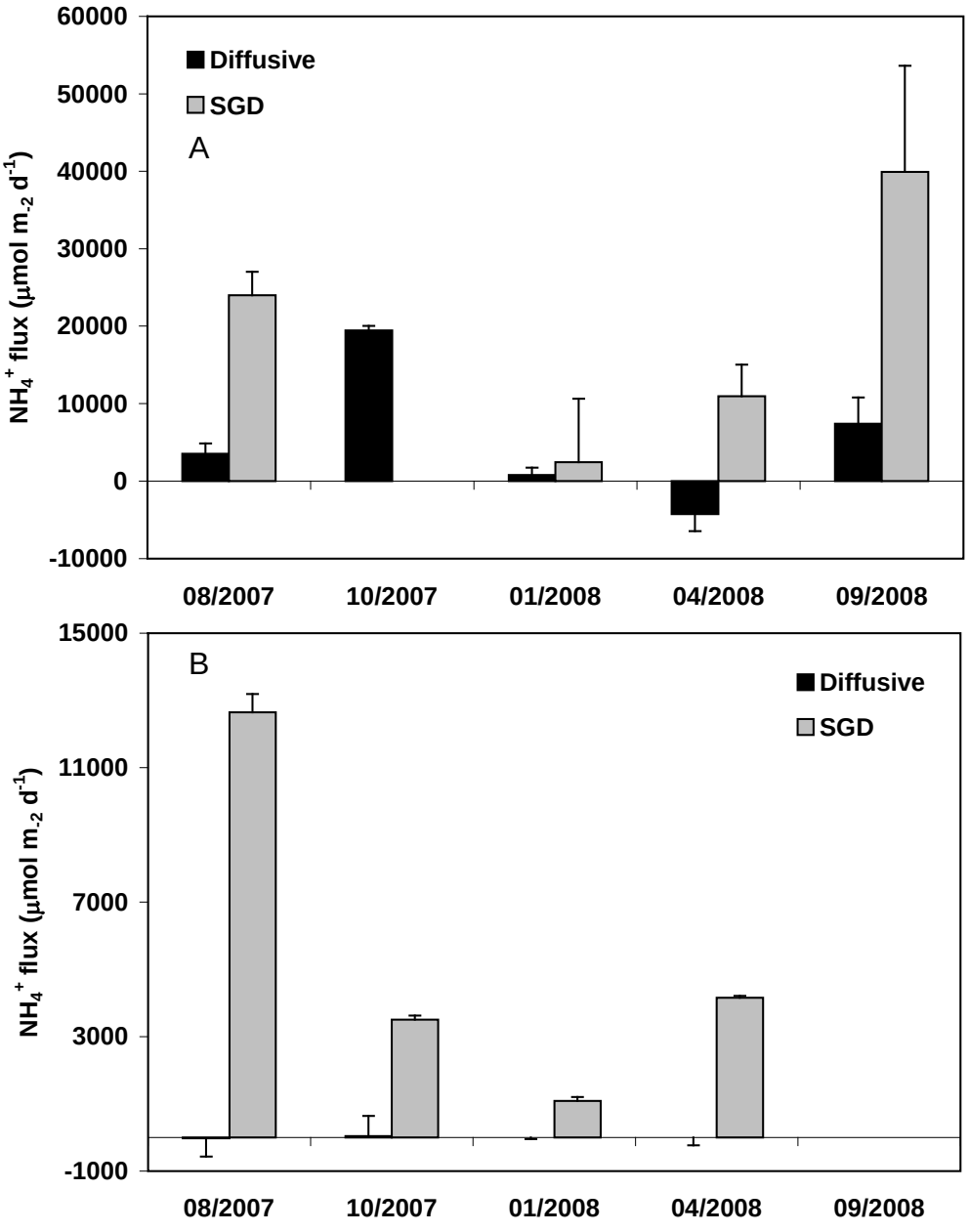


Figure 3.9. Average NH_4^+ flux calculated from both nearshore environments Mills Branch (A) and Cherry Point (B) for each sampling month. NH_4^+ flux is graphed as diffusive flux and advective flux from submarine groundwater discharge (SGD).

4. MODELING AMMONIUM SOURCES AND CYCLING IN THE NEUSE RIVER ESTUARY: A MASS BALANCE APPROACH

4.1 Abstract

A mass balance of ammonium (NH_4^+) in the mesohaline Neuse River Estuary (NRE) was developed to investigate a documented 5-fold increase of NH_4^+ in the water column over the past decade. Data from this work and other studies conducted in the NRE were applied to a simple box model to assess seasonal variation in NH_4^+ sources. Many factors influencing NH_4^+ dynamics in the NRE are driven by temperature and climate, and therefore exhibited seasonal variability. In the "winter" period, designated as November through April, the dominant NH_4^+ source (> 40%) was estimated to be *in situ* regeneration in the water column. Flux from the organic-rich mid-channel contributed the a major portion (> 40%) of the NH_4^+ to the water column during the "summer" period, designated as May through October. Advection terms and other climate-related parameters, including submarine groundwater discharge (SGD), advective porewater exchange, and resuspension events, were of greater importance during winter. The advection term represented ~23% of the NH_4^+ inputs in winter and ~21% in summer. Advective porewater exchange was the dominant advection term during both seasons. The nearshore environment was relatively consistent between summer (~22%) and winter (~21%) with regard to diffusive and advective fluxes from SGD. This study provides insights about NH_4^+ fluxes in shallow estuaries such as the NRE, and indicates the importance of nearshore environments and advection in affecting NH_4^+ fluxes. More generally, the findings can assist resource managers in efforts to mitigate chronic effects of eutrophication in shallow lagoonal estuaries.

4.2 Introduction

Cultural eutrophication in estuarine and coastal environments is a widely recognized problem that has been documented over the past several decades (e.g. Richardson and Jørgensen 1996, Nixon 1995, Cloern 2001), but continues to require investigation to further understand it as an environmental threat. Nitrogen (N) loading to many coastal systems has rapidly increased as a result of rising human populations and development in coastal watersheds (National Research Council 2000). Jaworski et al. (1997) estimated, based on ten watersheds in the northeastern U.S., that N inputs to coastal environments have increased 5- to 14-fold from anthropogenic activities. An increase in N has also been documented in many other aquatic environments such as the Danube River, Baltic Sea, and Black Sea (Cloern 2001, Boesch 2002). Increased N availability profoundly alters estuarine ecosystems by stimulating phytoplankton production including harmful algal blooms, and also by decreasing dissolved oxygen, reducing water clarity, and enhancing nutrient cycling (Burkholder 1998, Smith 1999, 2003, Glibert et al. 2005).

Most of the N that supports productivity in estuaries historically has been considered to be derived from remineralization in the water column and sediments, rather than being "new" N from external sources such as supplied by rivers and atmospheric deposition (Dugdale and Goerring 1967, Paerl 1997). Historically, NO_3^- has been considered the dominant form of new N introduced to a system, whereas NH_4^+ has been regarded as the recycled form from organic matter regeneration. More recently, however, some shallow estuaries have also sustained high inputs of watershed NH_4^+ as a "new" source (e.g. Whitall et al. 2003, Aneja et al. 2003, Burkholder et al. 2006, Dugdale et al. 2007). Investigation of

N loading to coastal systems involves different forms of N, but the data are often grouped into one value as total nitrogen (TN) or dissolved inorganic nitrogen (DIN) (EPA 2008). Recent studies, however, have highlighted the importance of investigating the different forms of bioavailable N (Dugdale et al. 2007, Rothenberger et al. 2009a). NH_4^+ is generally the preferred form of N for phytoplankton uptake, and it can inhibit NO_3^- uptake at elevated concentrations (Dugdale et al. 2007) or influence phytoplankton assemblages by altering the dominant species (Smith et al. 1999, Rothenberger et al. 2009a).

Once NO_3^- and NH_4^+ enter a coastal ecosystem, these N forms can undergo many processes depending on environmental conditions. Nitrification (oxidation of NH_4^+ to NO_2^- or NO_3^-) can occur rapidly via microbial processes in estuarine waters or surface sediments where dissolved oxygen levels are high (Henriksen and Kemp 1988). Denitrification (reduction of NO_3^- or NO_2^- to N_2) may occur in deeper anaerobic sediments by nitrate diffusing down through the overlying sediments (Kemp et al. 1990), or regenerated nitrate near the sediment-water interface can diffuse back into the water column (Koike and Sorensen 1988). Nitrification can be coupled with denitrification in areas with strong dissolved oxygen gradients, resulting in the removal of bioavailable nitrogen (Henriksen and Kemp 1988). Molecular nitrogen (N_2) is not taken up by most microalgae (pelagic and benthic), except for cyanobacteria that are able to carry out N_2 fixation (Capone 1988). If nitrification rates are low, denitrification may be limited by available nitrate, causing NH_4^+ to accumulate in the porewater (Kemp et al. 1990). The NH_4^+ may also flux from the sediment into the water column and be assimilated by benthic microalgae and phytoplankton. In shallow systems, strong winds and storms can cause resuspension of sediment and release

large amounts of NH_4^+ to the water column after it has accumulated in porewaters (Giffin and Corbett 2003).

In addition to resuspension, submarine groundwater discharge (SGD) has been documented as an important advective force driving nutrients and other constituents to the overlying water (e.g. Moore 1996, 2006, Charette and Buesseler 2004, Slomp and Van Cappellen 2004). In many nearshore environments, SGD and porewater flushing of permeable sediments is a driving mechanism that contributes to the enhanced aerobic degradation and release of nutrients and other constituents to surface waters (Huettel et al. 1996, Billenbeck et al. 2006). SGD has been documented to contribute a significant flux of nutrients to the water column and stimulate phytoplankton production (e.g. LaPointe et al. 1992, LaRoche et al. 1997). Many systems show a tight coupling between the benthic and pelagic environments (Marinelli and Williams, 2003). Therefore, responses to water-column nutrient enrichment, such as increased algal biomass, are reflected in the associated flux from the sediments.

Over the past decade the eutrophic Neuse River Estuary (NRE), North Carolina, USA, has sustained a ~500% increase in water-column NH_4^+ concentrations despite resource managers' efforts to reduce N loading (Figure 4.1) (Burkholder et al. 2006). Previous research in the Neuse system has begun to contribute estimates of N sources including atmospheric deposition (Walker et al. 2000a, Aneja et al. 2003, Whitall et al. 2003), sedimentary processes (Haruthunian 1997, Alperin et al. 2000, Piehler et al. 2002, Giffin and Corbett 2003, Fear et al. 2004, 2005), and groundwater (Bratton 2004, Fear et al. 2007, Spruill and Bratton 2008), but further research is needed to understand N dynamics and the

striking increase of NH_4^+ over the past decade in this system. This increase has occurred in other river systems in the Southeast U.S. such as the Cape Fear (Burkholder et al. 2006), and in eutrophic estuaries in other regions (e.g. Cloern 2001, Dugdale et al. 2007). The objectives of this study were to 1) identify and quantify direct NH_4^+ sources to the NRE in a simple box model of NH_4^+ inputs and outputs; 2) quantify the role of SGD compared to other NH_4^+ sources to the estuary; and 3) resolve seasonal variations in NH_4^+ supply to NRE waters.

4.3 Methods

4.3.1 Site Description

The Neuse River flows ~200 km from the Piedmont of North Carolina to the coast, draining a watershed ~16,000 km^2 in area (Matson and Brinson 1990) (Figure 4.2). The average discharge is ~113 $m^3 s^{-1}$ with mean monthly discharge ranging from 55 to 173 $m^3 s^{-1}$, based on United States Geological Survey (USGS) mean monthly discharge measurements near Fort Barnwell, NC since 1996 (approximately 30 km upstream from the oligohaline estuary; USGS Surface-Water Monthly Statistics: http://waterdata.usgs.gov/nwis/monthly?).

The NRE is ~ 455 km^2 in area and drains into the Pamlico Sound along the eastern seaboard of North Carolina (Figure 4.2). This study was conducted at one upstream oligohaline site, Mills Branch (MB), and two downstream mesohaline sites, Cherry Point (CP) and Wilkinson Point (WP) (Figure 4.2). This shallow estuarine system has a mean water depth of 4.5 m and is characterized by limited inputs from the Atlantic Ocean. Winds are the predominant mixing force, and are much more important than astronomical tidal mixing (Reed et al. 2004). The limited oceanic exchange generates flushing times on the order of three months, which contributes to the extensive recycling of nutrients (Christian et al. 1991). The mesohaline estuarine flow regime is surface downstream and bottom water upstream (Reed et al. 2004). Stratification can often occur during late summer months when winds are reduced. Stratification and strong winds influence the oxygenation and nutrient availability in the estuary (Luettich et al. 2002). Winds also play a significant role in sediment resuspension and nutrient release from the benthic environment (Giffin and Corbett 2003).

Several types of sediment occur in the NRE and the distinct sediment regimes can be distinguished based on porosity (among other characteristics). The central portion of the main channel is comprised of organic-rich, fine-grained silt and clay with porosity > 0.8 (Alperin et al. 2000). The center of the channel collects the fine-grained sediment because it is the deepest portion of the channel and wave energy is minimal. The flanks of the channel are mainly fine- to medium-grained sand with porosity < 0.6 (Alperin et al. 2000).

4.3.2 Major Nutrient Sources

Significant nutrient loads from wastewater effluent, agricultural runoff, fertilizers, animal waste, atmospheric deposition, and urban runoff delivered to coastal environments such as the NRE can cause overgrowth of algae and create oxygen deficits leading to habitat degradation, as well as stimulation of noxious or toxic algal species (Bricker et al. 1999, Anderson et al. 2002). The entire Neuse system has been formally classified by state resource managers as "Nutrient-Sensitive Waters" during the late 1980s because of excessive algal blooms, oxygen deficits, and fish kills (NC DENR 1997). Among several major tributaries, the Neuse is the largest contributor of nutrients to Pamlico Sound (McMahon and Woodside 1997, Qian 2000).

Among various sources of N to the NRE, a major and relatively new non-point source is from confined animal feed operations, which first appeared in the Neuse watershed during the late 1980s (Burkholder et al. 2006, and references therein). Swine populations have increased by ~285% over the past decade in this watershed (Rothenberger et al. 2009b). Most swine operations in the Coastal Plain of North Carolina are sited on drained or ditched wetlands (water table ~1 m below the soil surface; Burkholder et al. 1997). The untreated, anaerobic animal wastes are held in large cess pits referred to by the industry as lagoons (Burkholder et al. 1997), and NH_4^+ concentrations in the waste lagoons range from 180 to 2,070 mg/L (10-115 mmol/L) (Ham and DeSutter 2000). Research has documented substantial lagoon seepage into subsurface waters (Westerman et al. 1985), which can comprise about half of the Neuse River discharge under low-flow conditions (Spruill et al. 1996). NH_4^+ is also contributed to surface waters in the watershed via aerosols from

spraying the swine lagoon effluent onto nearby fields in land application practices (Mallin 2000, Aneja et al. 2003). NH_4^+ in precipitation within the Neuse watershed has significantly increased over the past decade (Walker et al. 2000b). Atmospheric NH_4^+ settles out as dry particulates or falls into receiving waters as precipitation within a ~60- to 80-km radius of the spray origin (Walker et al. 2000a). High NH_4^+ loading has been documented to occur during times of low discharge (i.e., periods with long water retention times) in the NRE (Christian et al. 1991). Enhanced NH_4^+ loading can also occur during the summer season as a result of the flux of NH_4^+ from estuarine sediments (Rizzo et al. 1992). Several studies suggest that sediment regeneration may be a significant NH_4^+ source to the estuary (Fisher et al. 1982, Christian et al. 1991, Rizzo and Christian 1996, Haruthian 1997).

In addition to confined swine feed operations, over recent years wastewater treatment plants and package plants have also increased by 30% and 324%, respectively, especially in the upper watershed, whereas wetland and forested areas have decreased by 3% and 9%, respectively (Rothenberger et al. 2009b). Human wastewater discharges (in the upper watershed) and industrialized swine agriculture (in the mid- to lower watershed) have been identified as the highest contributors of N to the Neuse surface waters (Rothenberger et al. 2009b).

4.3.3 Model Construction

The box model was constructed by compiling NH_4^+ sources and fluxes from this study as well as other research conducted over the past two decades. Detailed methodology of NH_4^+ flux from SGD and chamber experiments are described in Chapters 2 and 3. Years were split into two periods referred to as "summer" and "winter", defined as May through October and November through April, respectively. The two seasonal periods were selected for comparison of climatic extremes in temperature, river discharge, and NH_4^+ water-column and sediment turnover. It was assumed that NH_4^+ fluxes were constant over each of the two six-month periods. All data and references used in the model are shown in Table 4.1 and 4.2.

4.3.4 Calculated Fluxes and Assumptions

Atmospheric deposition was calculated by multiplying the total weight deposition of NH_4^+ converted to moles of NH_4^+ by the surface area of the NRE. The seasonal deposition data from the National Atmospheric Deposition Program (NADP) site NC06 (Beaufort, NC) were used and combined to fit the two seasonal periods. Riverine flux of NH_4^+ was calculated using average Neuse River discharge data from Fort Barnwell since 2000 (USGS Surface-Water Monthly Statistics: http://waterdata.usgs.gov/nwis/monthly?). Monthly discharge data were averaged over each summer and winter and multiplied by the average NH_4^+ concentration of surface waters at the upstream site (MB). Surface water NH_4^+ concentrations were averaged over the duration of the study (2007-2008) for each seasonal period from monitoring data collected by the North Carolina State University Center for Applied Aquatic Ecology (NCSU CAAE). Water-column regeneration values were estimated from water-column organic carbon (OC) production data (21 mol OC m^{-2} yr^{-1}) (Matson et al. 1983) and the flux of OC to the seabed (9 mol OC m^{-1} yr^{-1}; Matson et al. 1983, Clesceri 1997). Therefore, it was assumed that ~50 % of the NH_4^+ taken up by phytoplankton was regenerated in the water column, similar to organic carbon. For this study the NRE was partitioned into two zones, a mid-channel zone and a nearshore zone base on sediment type. The mid-channel deposits are organic-rich, fine-grained sediments and the nearshore deposits are sandy, permeable sediments. A diffusive and advective term was calculated for each zone. Mid-channel and nearshore diffusive fluxes were estimated from average seasonal fluxes measured in this study (Chapter 3) and multiplied by their respective sediment surface area for each environment (mid-channel or nearshore). Approximately half of the estuarine

area (1.22×10^8 m^2) was estimated to consist of organic-rich, mid-channel sediments and the other half was sandy, nearshore sediments (Alperin et al. 2000). Fluxes into the sediment (negative values) were averaged as zero values because negative values indicated biological uptake (a completely different process or sink) rather than a source. SGD NH_4^+ flux was estimated from SGD calculated from ^{222}Rn as a tracer and NH_4^+ concentration at 10 centimeters beneath seafloor (cmbsf) (Chapter 2). The discharge area did not encompass the entire nearshore environment but, rather, was based on the estimate from Spruill and Bratton (2008) for groundwater discharge area, taken as 9.66×10^6 m^2 which is ~3% of the total NRE area. Thus, the discharge area of the mesohaline estuary was estimated to be ~3% of the total surface area of the mesohaline section, or 1.22×10^8 m^2. This groundwater discharge area was considered as the zone of freshwater and infiltrated seawater (SGD). The permeable porewater exchange is the advective flux of porewaters and NH_4^+ in the permeable sediments between the fresh groundwater discharge area and the fine-grained, mid-channel deposits. This area for the permeable porewater exchange was calculated by subtracting the freshwater discharge zone (SGD) from the total area of permeable sediments, 6.12×10^7 m^2. Unfortunately, flux measurements of advective porewater exchange and associated NH_4^+ flux were not available, so these parameters were estimated from recent data taken in other estuaries. The flux of NH_4^+ from porewater exchange in permeable sediments was estimated by multiplying the diffusive NH_4^+ flux in sandy sediments (this study; Chapter 3) by 1.25 and the estimated permeable-porewater exchange area (5.75×10^7 m^2). The 1.25 value is a conservative estimate based on a recent study by Cook et al. (2007), who found that advective porewater exchange in permeable sediments can increase the flux up to 2.5 times

the diffusive flux. The advective flux in this zone was calculated separately from the flux in the SGD zone because it was assumed that freshwater discharge did not occur past the SGD zone; thus, a smaller advective term is needed to be imposed based on a per unit area. The net exchange with the lower NRE and Pamlico Sound was estimated from Reed et al.'s (2004) acoustic Doppler current profiler (ADCP) data. Exchange in the summer and winter periods was estimated at 75 $m^3 s^{-1}$ and 150 $m^3 s^{-1}$, respectively. These values were multiplied by the average water-column NH_4^+ concentration at Cherry Point (unpublished data from the NCSU CAAE). Resuspension inputs were estimated using an average NH_4^+ concentration (250 μM) at a mid-channel sediment depth of 1 cm (Haruthian 1997), presuming that 2 cm of sediment are resuspended during strong wind events that occurred over 4% of the year (approximately 15 days total with more events occurring in winter than summer; Dillard 2008). Assimilation was calculated from Twomey et al.'s (2005) NH_4^+ uptake values and applied to 25% of the volume of the mesohaline NRE. Because of the typically turbid conditions (Mallin and Paerl 1992), limited assimilation was assumed at depths greater than 1.5 m. Nitrification output flux of NH_4^+ was based on values from experiments by Berousky and Nixon (1990) that were conducted in Narragansett Bay, Rhode Island, and were applied to 25% of the volume of the mesohaline estuary. Nitrification data from Narragansett Bay were chosen for the model in consideration of the limited nitrification data available in the NRE and similarities between the two systems. Narragansett Bay is well-mixed with similar freshwater inputs as the NRE, influenced by sewage and fertilization sources of N, and the suspended organic matter is dominated by phytoplankton origin (Nixon 1995).

4.4 Results and Discussion

4.4.1 Seasonal Differences

In this box model, many parameters characterizing NH_4^+ dynamics were driven by temperature, emphasizing the importance of assessing the system during the summer/winter differing temperature regimes rather than considering only annual averages (Figure 4.5). Overall, there was higher input of NH_4^+ to the mesohaline NRE in summer (2.9×10^8 mol NH_4^+ season^{-1}) compared to winter (0.4×10^8 mol NH_4^+ season^{-1}) (Figure 4.5). Analysis on a seasonal rather than annual basis also showed that the dominant NH_4^+ inputs to the NRE changed from water-column regeneration during winter to diffusive flux of NH_4^+ from mid-channel sediments in summer. Consistent with this observation, Burkholder et al. (2006) noted an increase in bottom-water NH_4^+ concentration during warmer months. Higher NH_4^+ fluxes from sediments during the summer period coincided with increased primary production (Mallin et al. 1991) and remineralization rates (Alperin et al. 2000). Overall, TN increased during high-precipitation events from increased riverine N discharge to the mesohaline estuary (as in Burkholder et al. 2006). River discharge was more important in winter when discharge was highest, contributing ~13% of the NH_4^+ input to the NRE (Figure 4.5). In contrast, during the summer period when river discharge was significantly less, riverine flux was less than 2% of the NH_4^+ input. Mid-channel diffusive flux showed the most seasonal variation. Most of the flux occurred in the summer period, contributing more than 40% of NH_4^+ inputs. Majority of the increase in the diffusive flux during summer was

probably associated with an increase of productivity in surface sediments due to warmer temperatures.

Uncertainty in the model can arise in computing fluxes necessary for the overall NH_4^+ budget, based on some of the assumptions. Depending on the season, the uncertainty in total NH_4^+ inputs ranged from 0.4 % to 2.7 %, based on the error calculated from the mid-channel and nearshore diffusive flux and from the nearshore advective flux. Higher uncertainty was associated with data for the winter period. Nitrification rates imposed a 5.4% to 28% error associated with NH_4^+ outputs (but also note that the nitrification rate values were taken from a different system, Narragansett Bay)

In the summer period, values for NH_4^+ inputs were greater than outputs (Tables 4.1), whereas in the winter period, NH_4^+ sources were 1 % lower than NH_4^+ consumption rates, but within the same magnitude (Table 4.2; and see below). This imbalance in winter may be a natural phenomenon or may have been due, in part, to error or underestimates of other parameters in the model that are not well quantified, such as atmospheric NH_4^+ deposition, water-column regeneration, or lack of tributary inputs. The nearest sample collection site of the National Atmospheric Deposition Program is ~ 30 km southeast of the mesohaline NRE. Moreover, the data used in this model were measured over the past decade, and nutrient cycling and fluxes may have changed during that period, suggested, for example by the documented increase in water-column NH_4^+ concentrations (Burkholder et al. 2006). Water-column regeneration rates are not well quantified in the NRE, and may have been overestimated here because the values used in the model were based on organic matter burial and assimilation rates. Furthermore, water-column regeneration rates during winter would be

expected to be even lower than the assimilation-based estimates, because assimilation can occur in the water-column concomitant with slower regeneration of organic material at lower temperatures. For example, based on sediment regeneration and diffusive flux data, the diffusive flux of NH_4^+ from the mid-channel sediments, it is 50-fold lower during winter than in summer, presumably due to enhanced regeneration rates during summer as a result of warmer temperatures. However, based on assimilation and burial, water-column regeneration was only 3-fold lower in winter than in summer. Other input parameters that have not been well quantified include release of NH_4^+ during resuspension events, and exchange with the lower NRE and Pamlico Sound. Parameters not considered in this study due to limited data included NH_4^+ inputs from tributaries of the NRE and desorption of NH_4^+ from sediments during mixing of fresh and saline waters (Seitzinger et al. 1991). NH_4^+ inputs from tributaries could be possibly a significant source of NH_4^+, especially during high discharge periods during winter.

Many factors can affect NH_4^+ flux from the sediment to the overlying water, including porosity/grain size, organic carbon content, dissolved oxygen content, salinity, water-column N concentration and speciation, temperature, and various microbial processes. Numerous studies have shown that nitrification and other microbial processes strongly influence the speciation and availability of bio-available N in estuaries (Blackburn and Henriksen 1983, Henriksen and Kemp 1988, Berounsky and Nixon, 1990). In this study during the summer period, NH_4^+ fluxes influenced by biological activity (regeneration in sediments and water column, assimilation, and nitrification) were elevated due to the warmer temperatures. Temperature influenced microbial metabolic activities and phytoplankton

assimilation and therefore, NH_4^+ availability. NH_4^+ concentration was elevated in porewaters relative to surface water at all three sites (MB, CP, WP) (Chapter 2), and the sites showed significant temporal variability in NH_4^+ porewater concentration between warm (August, September) and cold (January) months. At CP, but not at WP, NH_4^+ porewater concentrations decreased with depth. MB had the highest concentrations among the three sites, with maximum porewater NH_4^+ at 150 cmbsf (> 200 μM), consistent across seasons.

Water-column temperatures ranged from 6.0 ˚C in January to 33.9 ˚C in August. Seasonal NH_4^+, DO, and NO_3^-+NO_2^- fluxes at the three sites are summarized in Chapter 3. Briefly, NH_4^+ flux ranged from –29.1 to 811 μmol m^{-2} hr^{-1} among the three sites. Negative values indicated flux into the sediment from the overlying water, which, as mentioned, were averaged as zero input for the model. The highest net diffusive NH_4^+ flux occurred in October at all sites, and the lowest flux occurred in January. The upstream MB site released NH_4^+ from the sediments to the overlying water during four of the five months sampled, and showed significant seasonal variation (Chapter 3, Figure 3.4A; $p \leq 0.0001$, $n = 17$). At CP, most of the NH_4^+ flux occurred into the sediment and did not differ significantly among seasons (Chapter 3, Figure 3.4B). At MID, NH_4^+ flux ranged from 2 to 203 μmol m^{-2} hr^{-1}, and the flux was significantly higher in October than in January ($p = 0.0097$, $n = 6$) (Chapter 3, Figure 3.4C).

Temperate estuarine systems typically demonstrate seasonal variability in nutrient cycling (e.g. Klump and Martens 1989). For example, organic matter oxidation in sediments of Cape Lookout Bight, NC showed seasonality due to the temperature dependence of microbial activity (Klump and Martens 1989). Nitrification rates were strongly correlated

with temperature in Narragansett Bay, Rhode Island, with higher rates during summer months (Berounsky and Nixon 1990). NH_4^+ regeneration from sediments in Chesapeake Bay was higher during summer, and of greater importance for sustaining primary productivity (Boynton and Kemp 1985).

In contrast, other fluxes influenced by climate, such as river discharge, atmospheric deposition, and exchange with Pamlico Sound, were higher during winter (Figure 4.5). SGD generally is driven by precipitation and climate (Freeze 1969). The NH_4^+ flux resulting from SGD is affected by the flow of SGD as well as the NH_4^+ porewater concentration, which in turn, is strongly affected by the temperature and organic matter degradation rate. The NH_4^+ flux associated with SGD was higher during summer (9.2×10^6 mol season^{-1}) than winter (3.1×10^6 mol season^{-1}) (Table 4.1 and 4.2, and see Chapter 2), but this finding was attributed to higher NH_4^+ porewater concentrations during summer because SGD was actually lower during this seasonal period. Thus, the flux of NH_4^+ from SGD, although climatically driven, appears to have been heavily influenced by temperature and rates of microbial activity.

4.4.2 Advection and Nearshore Environments

Advection, including SGD, porewater exchange, and resuspension events, was of slightly greater importance during the winter period. The advection terms (SGD, porewater exchange, and resuspension) represented ~23% of the NH_4^+ inputs during the winter period and ~21% during the summer. The small difference between the seasons was driven by the porewater exchange estimate in permeable sediments, which was calculated from the diffusive flux. Permeable porewater exchange was the dominant advection term during both seasonal periods. However, on an areal basis, SGD was the predominant driver in NH_4^+ contribution. SGD was found to be an important factor influencing the amount of NH_4^+ flux from nearshore sediments to the overlying water column (Chapters 2 and 3). Although the percentage of NH_4^+ flux from SGD was lower during the summer period, the actual moles of NH_4^+ flux during summer (9.25×10^6 mol NH_4^+ $season^{-1}$) were significantly higher than the winter flux (3.1×10^6 mol NH_4^+ $season^{-1}$). When considering the flux on an areal basis, the NH_4^+ contribution from SGD was significantly higher than from diffusive flux (Chapter 3). The area of nearshore diffusive flux was larger than the SGD zone, therefore creating an overall higher diffusive NH_4^+ flux in the model. Combining advection and diffusion in both NRE sedimentary environments, sediments contribute more than 70% of the NH_4^+ to the NRE water-column during summer and more than 30% during winter.

Sandy nearshore environments historically have been considered to have minimal microbial activity and provide only small nutrient fluxes to the overlying water (D'Andrea et al. 2002, Charette and Buesseler 2004). In this study, the nearshore environment was relatively consistent between summer and winter with regard to diffusive and advective flux

from SGD, ~18% and ~15% of the total NH_4^+ flux, respectively. On an annual basis, if the NH_4^+ flux from nearshore environments are combined with the advective porewater exchange flux, the coarser sediments nearer shore are estimated to contribute 34% of the total NH_4^+ inputs (Figure 4.5). SGD had a higher percentage of the seasonal NH_4^+ flux to the overlying water in winter when discharge rates were greatest. Compared to advection, the diffusive flux was of greater importance in nearshore and mid-channel environments during summer, probably due to increased rates of microbial regeneration. Increased diffusive fluxes during summer months have been demonstrated in other estuaries (Boynton and Kemp 1985, Jensen et al. 1990). Although sandy sediments are typically lower in organic matter, they support substantial mineralization (D'Andrea et al. 2002, Huettel et al. 2003, Billerbeck et al. 2006). Permeable nearshore sediments facilitate porewater transport and fluxes of constituents that often exceed the transport from diffusional processes (Huettel and Webster 2001). In this study, the magnitude of the NH_4^+ flux from the coarser sedimentary environment supports the premise that permeable sediments and SGD significantly contribute to nutrient cycling in the NRE.

4.4.3 Excess NH_4^+

Although the mass balance estimates produced a deficit of inputs compared to outputs during winter, the surplus of NH_4^+ during summer created an annual excess of NH_4^+ (4.1 x 10^7 mol) to the mesohaline portion of the NRE (Table 4.5). This excess is high compared to the value expected for a ~500% increase in water-column NH_4^+ concentrations demonstrated over the past decade (Burkholder et al. 2006). If NH_4^+ is increasing at a rate of ~500% per decade, an excess of NH_4^+ of 3.3 x 10^5 mol NH_4^+ would be expected based on the current standing stock of 6.6 x 10^5 mol. Furthermore, if a maximum SGD zone (increase of 30%) is imposed based on Spruill and Bratton (2008) and the maximum porewater exchange rate is applied to the permeable zone (2.5 times the diffusive flux; Cook et al. 2007), the excess NH_4^+ is doubled compared to the previous estimate (Table 4.5).

The mass balance model showed additional NH_4^+ entering the mesohaline NRE during summer periods in which the NH_4^+ deficit during winter periods cannot compensate, creating annual excess. The high estimates of excess NH_4^+ in this study may be due to the fact that the majority of the measurements for SGD and diffusive fluxes were made during a 3-year drought. Based on USGS Neuse River discharge data at Fort Barnwell, the discharge was approximately 40 m^3 s^{-1} lower (~30% lower) than the 13-year average. Less freshwater input likely decreases flushing rates of the system and enhances nutrient recycling. If drought conditions become more frequent due to warming trends in climate change, NH_4^+ in the NRE may be increase more rapidly than previously estimated. These findings can have a significant impact on future studies and management practices in the NRE.

4.4.4 Management Implications

Often, nutrient contributions to estuarine environments are estimated simply from measurements of riverine discharge and riverine NH_4^+ concentration, and the resulting riverine NH_4^+ flux is used as the standard for nutrient management strategies. Riverine discharge frequently is the dominant source of NO_3^- in estuaries, and consequently, NH_4^+ can be obscured in the DIN measurement. In addition, resource managers often consider the total bioavailable DIN rather than assessing each nutrient form separately (e.g. US EPA 2008).

Riverine input is an important source of NH_4^+ to the NRE, but in this study, water-column regeneration and flux from the sediments were the predominant sources. TN (NH_4^+ + organic N + NO_3^-) decreased in the mesohaline estuary during 1994-2003, but this decrease was driven by drought conditions over three years at the end of the period analyzed (Burkholder et al. 2006). While NO_3^- concentrations were static, NH_4^+ increased significantly. Other estuarine systems in the Southeast region, such as some areas of the Cape Fear, have also sustained up to a 315% increase in NH_4^+ over the past ~decade (Burkholder et al. 2006). Estuarine water bodies such as the Chesapeake Bay in the eastern United States and the Peel-Harvey estuary in western Australia have sustained cultureal eutrophication and increased NH_4^+ and NO_3^- concentrations (Kemp et al. 2005, McComb and Humphries 1992). Resource managers of both systems have taken actions to reduce nutrient loads because of harmful algal blooms and overall declines in water quality.

Resource managers generally emphasize nutrient loads (National Research Council 2000), but the ambient concentration of the water column and different forms of N need to be addressed as well, including consideration of sources such as SGD and advection. Upstream

NO_3^- + NO_2^- concentrations near MB averaged 21 μM and ranged from 2 to 50 μM, depending on river discharge (NCSU CAAE, unpubl. data). NO_3^- + NO_2^- were lower downstream at CP, averaging 4 μM and ranging from 0 to 35 μM. In contrast, water-column NH_4^+ concentrations at MB and CP averaged 4 μM and 2 μM, respectively. Water-column N_i forms are important to the ecology of the estuary. Previous research has indicated that NH_4^+ is the dominant N form taken up by phytoplankton in the NRE, in comparison to urea and NO_3^-; NH_4^+ represented about half of the N uptake in the mesohaline estuary, followed by urea and then NO_3^- (Twomey et al. 2005). These findings emphasize the importance of NH_4^+ to the estuarine phytoplankton assemblages, and the need to further understand the documented increase in water-column NH_4^+ concentrations.

The consequences of this NH_4^+ increase are poorly understood, but in other systems, increased NH_4^+ has significantly affected trophic dynamics. For example, in San Francisco Bay (SFB), Dugdale et al. (2007) reported that NO_3^- uptake by the diatom flora was limited by excessive NH_4^+, leading to an overall decline in chlorophyll concentrations. The ecological response to increasing nutrient concentrations may vary among estuarine systems because of differences in tidal influence, mean water depth, freshwater input, nutrient form, and other factors (Cloern 2001). In this shallow estuary, temperature and TN:TP ratios were found to be the most important factors influencing phytoplankton assemblages, and increasing NH_4^+ concentrations were linked to stimulation of certain harmful algal species (Rothenberger et al. 2009a). Chlorophyll *a* concentrations, used as an indicator of algal biomass, also have increased over the past 15 years, especially during drought conditions

(NCSU CAAE, unpubl. data). These findings support the need to assess both forms of bioavailable inorganic N, rather than combining them as DIN.

Other studies have also demonstrated the importance of assessing NH_4^+ in estuarine environments (e.g. Rocha 1998, Middleburg and Nieuwenhuize 2000). In the Sado Estuary, intertidal sediment demonstrated significant NH_4^+ fluxes between times of atmospheric exposure and tidal flooding (Rocha 1998). Significant NH_4^+ was flushed from sediments by advective porewater exchange (44 mmol m^{-2}), indicating rapid remineralization of organic matter and high turnover rate, 37-43 d (Rocha 1998). Middleburg and Nieuwenhuize (2000) reported more rapid turnover rates (0.1 – 27 d) of NH_4^+ in six European estuaries. NO_3^- had a longer residence time (19 to 216 d) compared to NH_4^+, expected since NH_4^+ is the preferred N form by phytoplankton (Middleburg and Nieuwenhuize 2000). Also, NO_3^- had lower uptake rates, and therefore, most NO_3^- flowed through the estuaries unless it wasdenitrified or buried (Middleburg and Nieuwenhuize 2000). These findings further suggest that while significant NO_3^- loading affects estuaries, but eutrophic estuaries are mostly driven by NH_4^+ and its regenerative nature.

A decrease in bottom-water DO concentrations has also been documented in the NRE over the past ~decade (Burkholder et al. 2006). Depleted oxygen in waters overlying sediments reduces the oxidation-reduction potential and alters sediment biogeochemistry and nutrient cycling (Stumm and Morgan 1970). Low redox conditions in turn promote elevated fluxes of NH_4^+ and PO_4^{-3} from sediments (Stumm and Morgan 1970). When oxygen is present, nitrification oxidizes NH_4^+ to NO_3^-, but nitrifying bacteria are inhibited by the high levels of hydrogen sulfide and low levels of oxygen characteristic of anoxic conditions

(Henriksen and Kemp 1988). For example, Chesapeake Bay, the largest estuary on the U.S. mainland, has been affected by accelerated eutrophication since the 1880s (Cooper et al. 2004, Kemp et al. 2005). In this system high nitrification rates occur during spring and fall, but negligible rates have been measured during anoxic summer periods (Kemp et al. 1990). Increased phytoplankton production from increased nutrient loading has led to a decrease in bottom-water DO concentrations and an increase in NH_4^+ flux from the sediments, providing a feedback loop that has amplified eutrophication (Kemp et al. 2005). N sources to Chesapeake Bay include 60% from the watershed, 12% from atmospheric deposition, and the remainder from point sources (Kemp et al. 2005). Nitrification is an important sink for 26% of the TN inputs and burial accounts for 35% in this system. In this study of the NRE, similar nitrification values were found during the summer period. A difference between the approaches used was that the Chesapeake Bay study compared TN sources as compared to separate N forms, and thus reported a higher contribution from atmospheric deposition. A higher contribution from atmospheric deposition to the NRE would be expected when considering TN (Aneja et al. 2003, Whitall et al. 2003).

This work demonstrates the importance of sediments as a source of nutrients to the overlying water column in the NRE. Advection and diffusion in both sediment environments were estimated to contribute more than 70% of the NH_4^+ to the NRE water-column during the summer period and more than 30% during the winter period. More importantly, the results from this study emphasize the importance of considering advection, especially in permeable nearshore sediments, in overall nutrient budgets. On an annual basis, nearshore environments (including SGD, advective porewater exchange, and diffusive fluxes) were

estimated to contribute almost 30% of the NH_4^+ (Figure 4.5), a source previously not considered in budgets. SGD had higher NH_4^+ flux rates compared to riverine inputs in summer when river discharge was lowest, emphasizing the importance of establishing a better baseline of SGD for management purposes. The estimates in this study can provide a baseline for direction of future research and management practices in terms of establishing and monitoring nutrient budgets. For example, future management practices may consider installing monitoring wells to establish better estimates of SGD along the estuarine shorelines and to monitor for changes in water level and seawater intrusion. Unfortunately, monitoring SGD as a source of nutrients to shallow estuarine systems such as the NRE and quantitatively applying the data to budgets is in the beginning stages. It is often costly and labor intensive to establish an SGD nutrient budget for entire system, even at specific locations, and therefore many assumptions are necessary.

4.4.5 Other Models of N dynamics in the NRE

Two other attempts have been made to assess total N flow for the NRE. First, Christian and Thomas (2003) reported that N recycling in the NRE dominated over N loading in terms of phytoplankton uptake. Christian and Thomas (2003) used a seasonal network of standing stock and flows of N in the NRE to understand the relationship of N loading and recycling. Recycling of N was an important influence on phytoplankton production (Christian and Thomas 2003). This study similarly found that in the mesohaline NRE, fluxing from sediments and internal cycling in the water column were the predominant sources of NH_4^+. As expected, the residence time of N in the estuary was also an important factor influencing N fate (Christian and Thomas 2003). The freshwater residence time in the NRE was estimated to range from 30 to 215 days, with a mean of 51 days (Christian et al. 1991). In marked contrast, NH_4^+ has been estimated to have a residence time of 0.2 to 11 days relative to internal cycling in the NRE (Boyer et al. 1988), depending on freshwater discharge to the estuary.

Second, based on a network analysis, Whipple et al. (2007) attributed most of the variation in N cycling in the NRE to seasonal changes. They used 16 seasonal steady-state networks of N stocks and flow to analyze the system on a macro-level analysis of whole systems and an index of whole environ activity. The findings from Whipple et al. (2007) support the results of this study and those of Christian and Thomas (2003) in that the microbial processes associated with regeneration were influenced by temperature.

4.5 Conclusions

This study applied a simple box model to investigate NH_4^+ fluxes in the mesohaline portion of the NRE and provides insight for further biogeochemical research. Many of the model components for NH_4^+ dynamics demonstrated temporal variability, and the dominant source of NH_4^+ to the mesohaline NRE changed depending on the seasonal period. Advection, including SGD, porewater exchange, and resuspension events, contributed 21-23% of the total NH_4^+ flux throughout the year (summer and winter periods). On an annual basis, diffusive and advective fluxes in nearshore environments were estimated to contribute approximately 30% of the total NH_4^+ supply to the estuary. The magnitude of the NH_4^+ flux in the nearshore environment provides evidence that permeable sediments and SGD significantly contribute to nutrient cycling in the NRE. Initial estimates indicate that SGD NH_4^+ fluxes account for 4-8% of the NH_4^+ supply to the estuary. It should be noted that these values were based on data acquired from only three locations within the estuary, and additional sites would improve flux estimates. Overall, considering advection and diffusion in both sediment environments, sediments contribute more then 70% of the NH_4^+ to the NRE water-column during summer and more than 30% during winter.

This model indicated an apparent surplus of NH_4^+ during the summer period, possibly because the SGD and diffusive flux experiments were taken during a drought. Lower freshwater inputs can decrease flushing rates and enhance nutrient recycling. If drought conditions increase during warming trends in climate change, NH_4^+ in the system may increase more rapidly than previously estimated, adversely affecting management strategies to reduce cultural eutrophication in the NRE.

Beyond the Neuse, the analysis of NH_4^+ sources and sinks contributed by this study provides insights about nutrient dynamics in nitrogen-sensitive estuarine systems. Many estuaries and coastal environments are sustaining increased nutrient loading from watershed urbanization, industrialized agriculture, and other sources. In addition to water-column nutrient cycling, diffusive and advective fluxes in nearshore environments are important N sources that are often poorly quantified, and they should be considered when developing nutrient budgets for shallow eutrophic estuaries.

4.6 References

Alperin, M.J., Clesceri, E.J., Wells, J.T., Albert, D.B., McNinch, J.E., Martens, C.S., 2000. Sedimentary processes and benthic-pelagic coupling, pp. 63-105. In: R. A. Leuttich (ed.), Neuse River Estuary Modeling and Monitoring Project: Final Report – Monitoring Phase. Report. UNC Water Resources Research Institute, Raleigh.

Anderson, D.M., Glibert, P.M., Burkholder, J. M., 2002. Harmful algal blooms and eutrophication: nutrient sources, composition, and consequences. Estuaries, 25, 704-726.

Aneja, V. P., Nelson, D.R., Roelle, P.A., Walker, J.T., 2003. Agricultural ammonia emissions and ammonium concentrations associated with aerosols and precipitation in the southeast United States. J. Geophys. Res. 108(D4), ACH12-1 – 12-11.

Berounsky, V.M., Nixon, S.W., 1990. Temperature and the annual cycle of nitrification in waters of Narragansett Bay. Limnol. Oceanogr. 35, 1610-1617.

Billerbeck, M., Werner, U., Polerecky, L., Walpersdorf, E., deBeer, D., Huettel, M., 2006. Surficial and deep pore water circulation governs spatial and temporal scales of nutrient recycling in intertidal sand flat sediment. Mar. Ecol. Prog. Ser. 326, 61-76.

Blackburn, T.H., Henriksen, K., 1983. Nitrogen cycling in different types of sediment from Danish waters. Limnol. Oceanogr. 28, 477-493.

Boesch, D.F., 2002. Challenges and opportunities for science in reducing nutrient over-enrichment of coastal ecosystems. Estuaries 25: 886-900.

Boyer, J., Stanley, D, Christian, R., Rizzo, W., 1988. Modulation of nitrogen loading impacts within an estuary, pp. 165-176. In: Coastal Water Resources - Proceedings of a symposium. American Water Resources Association, Bethesda (MD).

Boynton, W., Kemp, W., 1985. Nutrient regeneration and oxygen consumption by sediments along an estuarine salinity gradient. Mar. Ecol. Prog. Ser. 23: 45-55.

Bratton, J., 2004. Integrated Science Team Deploys New Tools to Study Submarine Ground Water in North Carolina.USGS, Soundwaves, vol. FY2004, No. 62, 3-4.

Bricker, S., Clement, C., Pirhalla, D., Orlando, S., Farrow, D., 1999. National Estuarine Eutrophication Assessment: Effects of Nutrient Enrichment in the Nation's Estuaries. National Oceanic and Atmospheric Administration, Silver Spring, MD.

Burkholder, J.M., Dickey, D.A., Kinder, C., Reed, R.E., Mallin, M.A., Melia, G., McIver, M.R., Cahoon, L.B., Brownie, C., Deamer, N., Springer, J., Glasgow, H., Toms, D.,

Smith, J., 2006. Comprehensive trend analysis of nutrients and related variables in a large eutrophic estuary: A decadal study of anthropogenic and climatic influences. Limnol. Oceanogr. 51, 463-487.

Burkholder, J. M., Mallin, M.A., Glasgow, H.B., Larsen, L.M., McIver, M.R., Shank, G.C., Deamer-Melia, N., Briley, D.S., Springer, J., Touchette, B.W., Hannon, E.K., 1997. Impacts to a coastal river and estuary from rupture of a large swine waste holding lagoon. J. Environ. Qual. 26, 1451-1466.

Capone, D.G., 1988. Benthic nitrogen fixation, pp. 85-123. In: Blackburn, H., Sorensen, J. (Eds.) Nitrogen Cycling in Coastal Marine Environments. Wiley and Sons, New York.

Charette, M.A., Buesseler, K.O., 2004. Submarine groundwater discharge of nutrients and copper to an urban subestuary of Chesapeake Bay (Elizabeth River). Limnol. Oceanogr. 49, 376-385.

Christian, R.R., Boyer, J.N., Stanley, D.W., 1991. Multi-year distribution patterns of nutrients within the Neuse River Estuary, North Carolina. Mar. Ecol. Prog. Ser. 71, 259-274.

Christian, R.R., Thomas, C.R., 2003. Network analysis of nitrogen inputs and cycling in the Neuse River estuary, North Carolina, USA. Estuaries and Coasts 26, 815-828.

Clesceri, E., 1997. Sources and Reactivity of Natural Organic Matter in Two Sediments from the Neuse River Estuary and Pamlico Sound, North Carolina. M.S. Thesis, UNC Chapel Hill, 90 pp.

Cloern, J.E., 2001. Our evolving conceptual model of the coastal eutrophications problem. Mar. Ecol. Prog. Ser. 210, 223-253.

Cook, P., Wenzhofer, F., Glud, R., Janssen, F., Huettel, M., 2007. Benthic solute exchange and carbon mineralization in two shallow subtidal sandy sediments: Effect of advective porewater exchange. Limnol. Oceanogr. 52, 1943-1963.

Cooper, S.R., McGlothin, S.K., Madritch, M., Jones, D.L., 2004. Paleoecological evidence of human impacts on the Neuse and Pamlico Estuaries of North Carolina, U.S.A. Estuaries 27, 617-633.

D'Andrea, A.F., Aller, R.C., Lopez, G.R., 2002. Organic matter flux and reactivity on a South Carolina sandflat: The impacts of porewater advection and macrobiological structures. Limnol. Ocean. 47, 1056-1070.

Dillard, S. 2008. Resuspension Events and Seabed Dynamics in the Neuse River Estuary, North Carolina. M.S. Thesis, East Carolina University, Greenville, 148 pp.

Dugdale, R.C., Goering, J.J., 1967. Uptake of new and regenerated forms of nitrogen in primary productivity. Limnol. Oceanogr. 12, 196-206.

Dugdale, R.C., Wilkerson, F.P., Hogue, V.E., Marchi, A., 2007. The role of ammonium and nitrate in spring bloom development in San Francisco Bay. Estuar. Coast. Shelf Sci. 73, 17-29.

Fear, J., Gallo, T., Hall, N., Loftin, J., Paerl, H., 2004. Predicting benthic microalgal oxygen and nutrient flux responses to a nutrient reduction management strategy for the eutrophic Neuse River Estuary, North Carolina, USA. Estuar. Coast. Shelf Sci. 61, 491-506.

Fear, J., Thompson, S., Gallo, T., Paerl, H., 2005. Denitrification rates measured along a salinity gradient in the eutrophic Neuse River Estuary, North Carolina, USA. Estuar. Coasts 28, 608-619.

Fisher, T.R., Carlson, P.R., Barber, R.T., 1982. Sediment nutrient regeneration in three North Carolina estuaries. Estuar. Coast. Shelf Sci. 14, 101-116.

Freeze, A., 1969. The mechanism of natural groundwater recharge and discharge-1. One-dimensional, vertical, unsteady, unsaturated flow above a recharging or discharging groundwater flow system. Water Resources Res. 5, 153-171.

Giffin, D., Corbett, D.R., 2003. Evaluation of sediment dynamics in coastal systems via short-lived radioisotopes. J. Mar. Syst. 42, 83-96.

Glibert, P.M., Seitzinger, S., Heil, C.A., Burkholder, J.M., Parrow, M.P., Codispoti, L.A., Kelly, V., 2005. Eutrophication – new perspectives on its role in the global proliferation of harmful algal blooms. Oceanography 18, 198-209.

Ham, J., DeSutter, T., 2000. Toward site-specific design standards for animal-waste lagoons: Protecting ground water quality. Journal of Environmental Quality 29, 1721-1732.

Haruthunian, 1997. Seasonal and Spatial Variations in Benthic Organic Nitrogen Remineralization in the Neuse River Estuary, North Carolina. M.S. Thesis, UNC Chapel Hill, 70 pp.

Henriksen, K, Kemp, W.M., 1988. Nitrification in estuarine and coastal marine sediments, pp. 207-249. In: Blackburn, H., Sorensen, J. (Eds.) Nitrogen Cycling in Coastal Marine Environments. Wiley and Sons, New York.

Huettel, M., Roy, H., Precht, E., Ehrenhauss, S., 2003. Hydrodynamical impact on biogeochemical processes in aquatic sediments. Hydrobiologia 494, 231-236.

Huettel, M., Webster, I.T., 2001. Porewater flow in permeable sediments, pp. 144-170. In: Boudreau, B.P., Jørgensen, B.B. (eds.), The Benthic Boundary Layer-Transport Processes and Biogeochemistry. Oxford University Press, Oxford.

Huettel, M., Ziebis, W., Forster, S., 1996. Flow-Induced Uptake of Particulate Matter in Permeable Sediments. Limnol. Oceanogr. 41, 309-322.

Jahnke, R.A., Nelson, J.R., Marinelli, R.L., Eckman, J.E., 2000. Benthic flux of biogenic elements on the Southeastern US continental shelf: influence of pore water advective transport and benthic microalgae. Cont. Shelf Res. 20, 109-127.

Jaworski, N.A., Howarth, R.W., Hetling, L.J., 1997. Atmospheric deposition of nitrogen oxides onto landscape contributes to coastal eutrophication in northeast United States. Env. Sci. Tech. 31, 1995-2004.

Jensen, M., Lomestein, E., Sorensen, J., 1990. Benthic NH_4^+ and NO_3^- flux following sedimentation of a spring phytoplankton bloom in Aarhus Bight, Denmark. Mar. Ecol. Prog. Ser. 61, 87-96.

Kemp, W.M., Sampou, P., Caffrey, J., Mayer, M., Henriksen, K., Boynton, W.R., 1990. Ammonium recycling versus denitrification in Chesapeake Bay sediments. Limnol. Oceanogr. 35, 1545-1563.

Kemp, W.M., Boynton, W.R., Adolf, J.E., Boesch, D.F., Boicourt, W.C., Brush, G., Cornwell, J.C., Fisher, T.R., Glibert, P.M., Hagy, J.D., Harding, L.W., Houde, E.D., Kimmel, D.G., Miller, W.D., Newell, R.I.E., Roman, M.R., Smith, E.M., Stevenson, J.C., 2005. Eutrophication of Chesapeake Bay: historical trends and ecological interactions. Mar. Ecol. Prog. Ser. 303, 1-29.

Klump, J.V., Martens, C.S., 1989. The seasonality of nutrient regeneration in organic-rich coastal sediments: Kinetic modeling of changing porewater nutrient and sulfate distributions. Limnol. Oceanogr. 34, 559-577.

Koike, I., Sorensen, J., 1988. Nitrate reduction and denitrification in marine sediments, pp. 251-273. In: Blackburn, H., Sorensen, J. (eds.) Nitrogen Cycling in Coastal Marine Environments. Wiley and Sons, New York.

Lapointe, B., Clark, M., 1992. Nutrient inputs from the watershed and coastal eutrophication in the Florida Keys. Estuaries and Coasts 15, 465-476.

LaRoche, J., Nuzzi, R., Waters, R., Wyman, K., Falkowski, P., Wallace, D., 1997. Brown Tide blooms in Long Island's coastal waters linked to interannual variability in groundwater flow. Global Change Biol. 3, 397-410.

Luettich, R.A., Carr, S.D., Reynolds-Fleming, J.V., Fulcher, C.W., McNinch, J.E., 2002. Semi-diurnal seiching in a shallow, micro-tidal lagoonal estuary. Cont. Shelf Res. 22, 1669-1681.

Mallin, M.A., 2000. Impacts of industrial-scale swine and poultry production on rivers and estuaries. Am. Sci. 88, 26-37.

Mallin, M.A., Paerl, H.W., 1992. Effects of Variable Irradiance on Phytoplankton Productivity in Shallow Estuaries. Limnol. Oceanogr. 37, 54-62.

Mallin, M.A., Paerl, H.W., Rudek, J., 1991. Seasonal phytoplankton composition, productivity and biomass in the Neuse River Estuary, North Carolina. Estuar. Coast. Shelf Sci. 32, 609-623.

Marinelli, R., Williams, T., 2003. Evidence for density-dependent effects of infauna on sediment biogeochemistry and benthic-pelagic coupling in nearshore systems. Est. Coast. Shelf Sci. 57, 179-192.

Martens, C.S., Kipphut, G.W., Klump, J.V., 1980. Sediment-water chemical exchange in the coastal zone traced by in situ radon-222 flux measurements. Science 208, 285-288.

Matson, E., Brinson, M., Cahoon, D., Davis, G., 1983. Biogeochemistry of the Sediments of the Pamlico and Neuse River Estuaries, North Carolina. UNC Water Resources Research Institute, Raleigh, 116 pp.

Matson, E.A., Brinson, M.M., 1990. Stable carbon isotopes and the C: N ratio in the estuaries of the Pamlico and Neuse Rivers, North Carolina. Limnol. Oceanogr. 35, 1290-1300.

McComb, A., Humphries, R., 1992. Loss of nutrients from catchments and their ecological impacts in the Peel-Harvey estuarine system, Western Australia. Estuaries and Coasts 15, 529-527.

McMahon, G., Woodside, M.D., 1997. Nutrient mass balance for the Albemarle-Pamlico drainage basin, North Carolina and Virginia. J. Am. Water Resour. Assoc. 33, 573-590.

Middelburg, J.J., Nieuwenhuize, J., 2000. Uptake of dissolved inorganic nitrogen in turbid, tidal estuaries. Mar. Ecol. Prog. Ser. 192, 79-88.

Moore, W., 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. Nature 380, 612-614.

Moore, W., 2006. The role of submarine groundwater discharge in coastal biogeochemistry. J. of Geochem. Explorat. 88, 389-393.

North Carolina Department of Environment and Natural Resources (NC DENR), 1997. Neuse River Nutrient-Sensitive Waters (NSW) Management Strategy. NC DENR, Raleigh.

National Research Council (NRC), 2000. Clean Coastal Waters – Understanding and Reducing the Effects of Nutrient Pollution. National Academy Press, Washington, DC.

Nixon, S.W., 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia 41, 199-219.

Paerl, H., 1997. Coastal eutrophication and harmful algal blooms: Importance of atmospheric deposition and groundwater as "new" nitrogen and other sources. Limnol. Ocean. 42, 1154-1165.

Piehler, M., Thompson, S., Dyble, J., Moisander, P., Fear, J., Paerl, H., 2002. Biologically mediated nitrogen dynamics in eutrophying estuaries. Assessing Denitrification, N_2 Fixation and Primary Productivity Responses to Proposed N Loading Reductions in the Neuse River Estuary. Report No. 339. UNC Water Resources Research Institute, Raleigh.

Qian, S.S., Borsuk, M.E., Stow, C.A., 2000. Seasonal and long-term nutrient trend decomposition along a spatial gradient in the Neuse River watershed. Environ. Sci. Technol. 34, 4474-4482.

Reed, R.E., Glasgow, H.B., Burkholder, J.M., Brownie, C., 2004. Seasonal physical–chemical structure and acoustic Doppler current profiler flow patterns over multiple years in a shallow, stratified estuary, with implications for lateral variability. Estuar. Coast. Shelf Sci. 60, 549-566.

Richardson, K., Jørgensen, B., 1996. Eutrophication: definition, history and effects, pp. 1-20. In: Jørgensen, K., Richardson, B.B. Eutrophication in Coastal Marine Ecosystems. American Geophysical Union, Washington, D.C.

Rizzo, W., Lackey, G., Christian, R., 1992. Significance of euphotic, subtidal sediments to oxygen and nutrient cycling in a temperate estuary. Mar. Ecol. Prog. Ser. 86, 51-61.

Rizzo, W., Christian, R., 1996. Significance of subtidal sediments to heterotrophically-mediated oxygen and nutrient dynamics in a temperate estuary. Estuaries 19, 475-487.

Rocha, C., 1998. Rhythmic ammonium regeneration and flushing in intertidal sediments of the Sado Estuary. Limnol. Oceanogr. 43, 823-831.

Rothenberger, M., Burkholder, J.M., Wentworth, T., 2009a. Multivariate analysis of phytoplankton and environmental factors in a eutrophic estuary. Limnol. Oceanogr. 54, 2107-2127.

Rothenberger, M., Burkholder, J.M., Brownie, C., 2009b. Long-term effects of changing land use practices on surface water quality in a major lagoonal estuary. Environmental Management 44, 505-523.

Seitzinger, S.P., Gardner, W.S., Spratt, A.K., 1991. The effect of salinity on ammonium sorption in aquatic sediments: Implications for benthic nutrient cycling. Estuaries and Coasts 14, 167-174.

Slomp, C.P., Van Cappellen, P., 2004. Nutrient inputs to the coastal ocean through submarine groundwater discharge: controls and potential impact. J. of Hydrology 295, 64-86.

Smith, V.H., Tilman, G.D., Nekola, J.C., 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. Environmental Pollution 100, 179-196.

Spiteri, C., Slomp, C.P., Tuncay, K., Meile, C., 2008. Modeling biogeochemical processes in subterranean estuaries: Effect of flow dynamics and redox conditions on submarine groundwater discharge of nutrients. Water Resour. Res. 44, W02430, doi:10.1029/2007WR006071, 1-18.

Spruill, T., Bratton, J., 2008. Estimation of groundwater and nutrient fluxes to the Neuse River Estuary, North Carolina. Estuaries and Coasts 31, 501-520.

Spruill, T., Eimers, J., Morey, A., 1996. Nitrate-Nitrogen Concentrations in Shallow Ground Water of the Coastal Plain of the Albemarle-Pamlico Drainage Study Unit, North Carolina and Virginia. USGS Fact Sheet 241-96, USGS, Raleigh.

Stumm, W., Morgan, J.J., 1970. Aquatic Chemistry, Wiley, New York, 583 p.

Twomey, L., Piehler, M., Paerl, H., 2005. Phytoplankton uptake of ammonium, nitrate and urea in the Neuse River Estuary, NC, USA. Hydrobiologia 533, 123-134.

United States Environmental Protection Agency (U.S. EPA). 1997. Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices, 2nd ed. Document EPA/600/R-97-072. Office of Research and Development, U.S. EPA, Washington, D.C.

United States Environmental Protection Agency (U.S. EPA). 1993. Methods for Determination of Inorganic Substances in Environmental Samples. Document EPA/600/R-93/100. Office of Research and Development, U.S. EPA, Washington, D.C.

United States Environmental Protection Agency (U.S. EPA), 2008. U.S. EPA's 2008 Report on the Environment (Final Report). Report EPA/600/R-07/045F (NTIS PB2008-112484). U.S. EPA, Washington, D.C.

Valiela, I., Costa, J., Foreman, K., Teal, J., Howes, B., Aubrey, D., 1999. Transport of groundwater-borne nutrients from watersheds and their effects on coastal waters. Biodegradation 10, 177-197.

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.G., 1997. Human alteration of the global nitrogen cycle: Sources and consequences. Ecol. Appl. 7, 737-750.

Walker, J., Aneja, V., Dickey, D., 2000a. Atmospheric transport and wet deposition of ammonium in North Carolina. Atmosphere and Environment 34, 3407-3418.

Walker, J., Nelson, D., Aneja, V., 2000b. Trends in ammonium concentrations in precipitation and atmospheric ammonia emissions at a coastal plain site in North Carolina, U.S.A. Environmental Science and Technology, 34, 3527-3534.

Westerman, P. W., Overcash, M. R., Evans, R. O., King, L. D., Burns, J. C., Cummings, G. A., 1985. Swine lagoon effluent applied to coastal bermudagrass: III. Irrigation and rainfall runoff. J. of Environ. Qual. 14, 22-25.

Whipple, S.J., Borrett, S.R., Patten, B.C., Gattie, D.K., Shramski, J.R., Bata, S.A., 2007. Indirect effects and distributed control in ecosystems: Comparative network environ analysis of a seven-compartment model of nitrogen flow in the Neuse River estuary, USA-Time series analysis. Ecological Modelling 206, 1-17.

Whitall, D., Hendrickson, B., Paerl, H., 2003. Importance of atmospherically deposited nitrogen to the annual nitrogen budget of the Neuse River estuary, North Carolina. Environ. Int. 29, 393-399.

Table 4.1. Summer NH_4^+ sources and sinks to the mesohaline Neuse River Estuary.

NH_4^+ Sources	**original data**	**units**	**Conversion**	**Neuse Estuary volume or area**		**Result**	**Reference**
Atmospheric Deposition	0.98	kg ha^{-1}	0.007	1.22E+08	m^2	8.54E+05	[1]NADP site NC06
River	72.7	$m^3 s^{-1}$	1.13063E+12			3.49E+06	USGS Neuse R. discharge at FortBarwell, NC [2]Ave. NH_4^+ concentration from CAAE
Water-column regeneration						5.45E+07	[3]Clesceri 1997 organic carbon values
Mid-channel Diffusive Flux	478	μmol m^{-2} hr^{-1}	2.06496	6.12E+07	m^2	1.26E+08	This study
Nearshore Diffusive Flux	163	μmol m^{-2} hr^{-1}	0.70416	6.12E+07	m^2	4.31E+07	This study
Nearshore Flux SGD	14	mmol m^{-2} d^{-1}	2.52	3.67E+06	m^2	9.25E+06	This study
Permeable Porewater Exchange	163	μmol m^{-2} hr^{-1}	0.70416	5.75E+07	m^2	5.06E+07	This study; [4]Cook et al. 2007
Exchange with Pamlico Sound	75	$m^3 s^{-1}$	1.1664E+12			2.10E+06	Reed et al. 2007; [2]CAAE NH_4^+ concentration
Resuspension (162 hrs yr^{-1})	250	μmol L^{-1}	0.005	6.12E+07	m^2	2.07E+06	[5]Dillard 2008; Giffin and Corbett 2007
Total Inputs						**2.92E+08**	
NH_4^+ Sinks							
Assimilation	6.79	μg L^{-1} hr^{-1}	0.0016296	6.69E+10	L	1.09E+08	Twomey et al. 2005
Exchange with Pamlico Sound	148	$m^3 s^{-1}$	2.3017E+12			2.30E+06	Reed et al. 2007; [2]CAAE NH_4^+ concentration
Nitrification	11	μmol L^{-1} d^{-1}	0.00198	6.69E+10	L	1.32E+08	Berounsky and Nixon 1990
Total Outputs						**2.44E+08**	

1. NADP (National Atmospheric Deposition Program) site NC06 Beaufort, NC.
2. Average NH_4^+ water-column concentration (data from NCSU Center for Applied Aquatic Ecology).
3. 50% of organic carbon is buried (Clesceri 2003); assume remaining is remineralized in water-column.
4. Advective porewater exchange in permeable sediments in zone between freshwater discharge zone (SGD) and mid-channel; calculated 2.5 times the diffusive flux (Cook et al. 2007).
5. Average NH_4^+ porewater concentration at 2 cm depth is 250 μmol L^{-1}; resuspension events suspend ~2 cm of sediment 4% of year (~15 days) with 5% occurring more in January than July (Dillard 2009).

Table 4.2. Winter NH_4^+ sources and sinks to the mesohaline Neuse River Estuary.

NH_4^+ Sources	original data	units	Conversion	Neuse Estuary volume or area	units	Result	Reference
Atmospheric Deposition	0.73	kg ha^{-1}	0.005214286	1.22E+08	m^2	6.36E+05	[1]NADP site NC06
River	118	$m^3 s^{-1}$	1.83514E+12			5.30E+06	USGS Neuse R. discharge at FortBarwell, NC [2]Ave. NH_4^+ concentration from CAAE
Water-column regeneration						1.60E+07	[3]Clesceri 1997 organic carbon values
Mid-channel Diffusive Flux	8.85	μmol m^{-2} hr^{-1}	0.038232	6.12E+07	m^2	2.34E+06	This study
Nearshore Diffusive Flux	11.5	μmol m^{-2} hr^{-1}	0.04968	6.12E+07	m^2	3.04E+06	This study
Nearshore Flux SGD	4.7	mmol m^{-2} d^{-1}	0.846	3.67E+06	m^2	3.10E+06	This study
Permeable Porewater Exchange	11.5	μmol m^{-2} hr^{-1}	0.04968	5.75E+07	m^2	3.57E+06	This study; [4]Cook et al. 2007
Exchange with Pamlico Sound	150	$m^3 s^{-1}$	2.3328E+12			4.20E+06	Reed et al. 2007; [2]CAAE NH_4^+ concentration
Resuspension (198 hrs yr^{-1})	250	μmol L^{-1}	0.005	6.12E+07	m^2	2.52E+06	[5]Dillard 2008; Giffin and Corbett 2007
Total Inputs						**4.07E+07**	
NH_4^+ Sinks							
Assimilation	1.99	μg L^{-1} hr^{-1}	0.0004776	6.69E+10	L	3.20E+07	Twomey et al. 2005
Exchange with Pamlico Sound	268	$m^3 s^{-1}$	4.16794E+12			4.17E+06	Reed et al. 2007; [2]CAAE NH_4^+ concentration
Nitrification	1	μmol L^{-1} d^{-1}	0.00018	6.69E+10	L	1.20E+07	Berounsky and Nixon 1990
Total Outputs						**4.82E+07**	

1. NADP (National Atmospheric Deposition Program) site NC06 Beaufort, NC.
2. Average NH_4^+ water-column concentration (data from NCSU Center for Applied Aquatic Ecology).
3. 50% of organic carbon is buried (Clesceri 2003); assume remaining is remineralized in water-column.
4. Advective porewater exchange in permeable sediments in zone between freshwater discharge zone (SGD) and mid-channel; calculated 2.5 times the diffusive flux (Cook et al. 2007).
5. Average NH_4^+ porewater concentration at 2 cm depth is 250 μmol L^{-1}; resuspension events suspend ~2 cm of sediment 4% of year (~15 days) with 5% occurring more in January than July (Dillard 2009).

Table 4.3. Calculated percent of total NH_4^+ sources and sinks for the summer season in the Neuse River Estuary.

NH_4^+ Sources	**mol NH_4^+ per season**	**Percent of total**
Direct Atmospheric Deposition	8.5E+05	0.3%
River	3.5E+06	1.2%
Water-column Regeneration	5.5E+07	18.6%
Mid-channel Diffusive Flux	1.3E+08	43.2%
Nearshore Diffusive Flux	4.3E+07	14.7%
Nearshore Flux SGD	9.2E+06	3.2%
Permeable Porewater Exchange	5.1E+07	17.3%
Exchange with Pamlico Sound	2.1E+06	0.7%
Resuspension	2.1E+06	0.7%
Total Inputs	**2.9E+08**	
NH_4^+ Sinks		
Assimilation	1.1E+08	44.7%
Exchange with Pamlico Sound	2.3E+06	0.9%
Nitrification	1.3E+08	54.3%
Total Outputs	**2.4E+08**	

Table 4.4. Calculated percent of total NH_4^+ sources and sinks for the winter season in the Neuse River Estuary.

NH_4^+ Sources	**mol NH_4^+ per season**	**Percent of total**
Direct Atmospheric Deposition	6.4E+05	1.6%
River	5.3E+06	13.0%
Water-column Regeneration	1.6E+07	39.3%
Mid-channel Diffusive Flux	2.3E+06	5.7%
Nearshore Diffusive Flux	3.0E+06	7.5%
Nearshore Flux SGD	3.1E+06	7.6%
Permeable Porewater Exchange	3.6E+06	8.8%
Exchange with Pamlico Sound	4.2E+06	10.3%
Resuspension	2.5E+06	6.2%
Total Inputs	**4.1E+07**	
NH_4^+ Sinks		
Assimilation	3.2E+07	66.3%
Exchange with Pamlico Sound	4.2E+06	8.7%
Nitrification	1.2E+07	25.0%
Total Outputs	**4.8E+07**	

Table 4.5. Summary of NH_4^+ sources and sinks in the Neuse River Estuary, including conservative and upper limit calculations. Annual excess of NH_4^+ is listed as the sum of the differences between sources and sinks for each season.

	moles NH_4^+ season^{-1}	
Summer	Conservative	Upper Limit
Sources	2.9E+08	3.4E+08
Sinks	2.4E+08	2.4E+08
Winter		
Sources	4.1E+07	4.5E+07
Sinks	4.8E+07	4.8E+07
Annual Excess NH_4^+	4.1E+07	9.7E+07

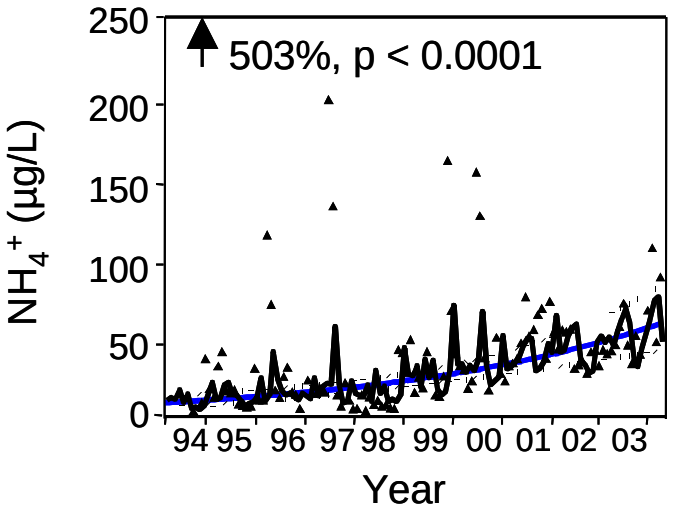


Figure 4.1. Increase of NH_4^+ concentrations at six stations in the Neuse River Estuary over a decadal study, based on weekly to biweekly data in April - October and monthly data in November - March. The solid black line is the predicted model value and the solid blue line is the linear trend (Burkholder et al. 2006).

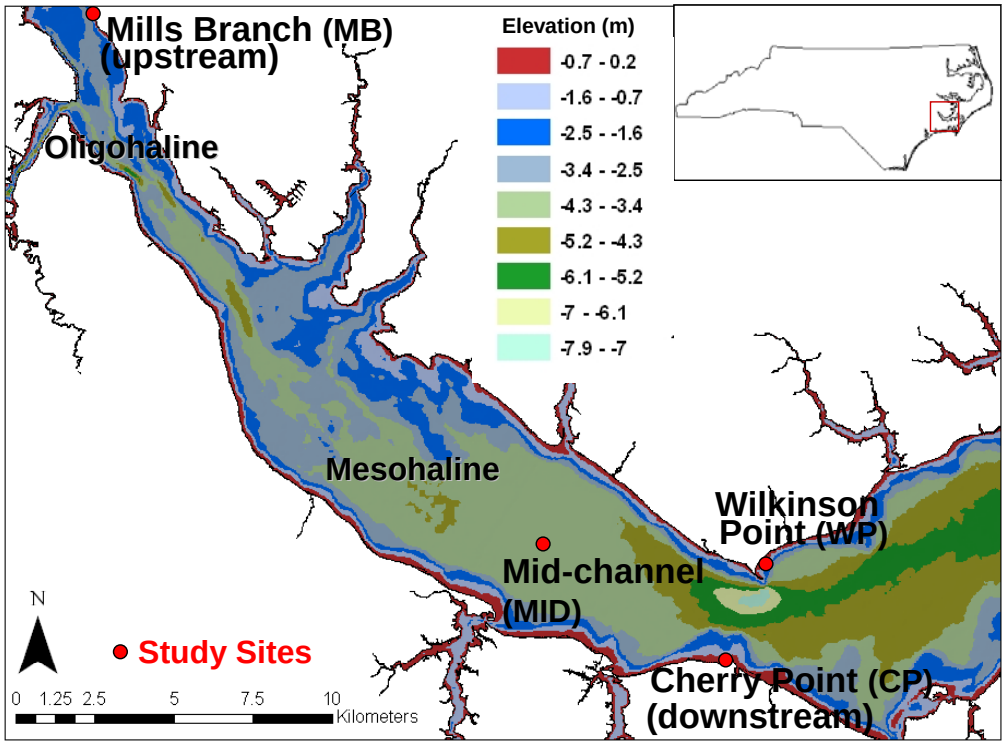


Figure 4.2. Bathymetric map of the Neuse River Estuary and location of sampling sites. during the study. Study sites are one upstream nearshore site, Mills Branch (MB), two downstream nearshore sites, Cherry Point (CP) and Wilkinson Point (WP), and one mid-channel site (MID).

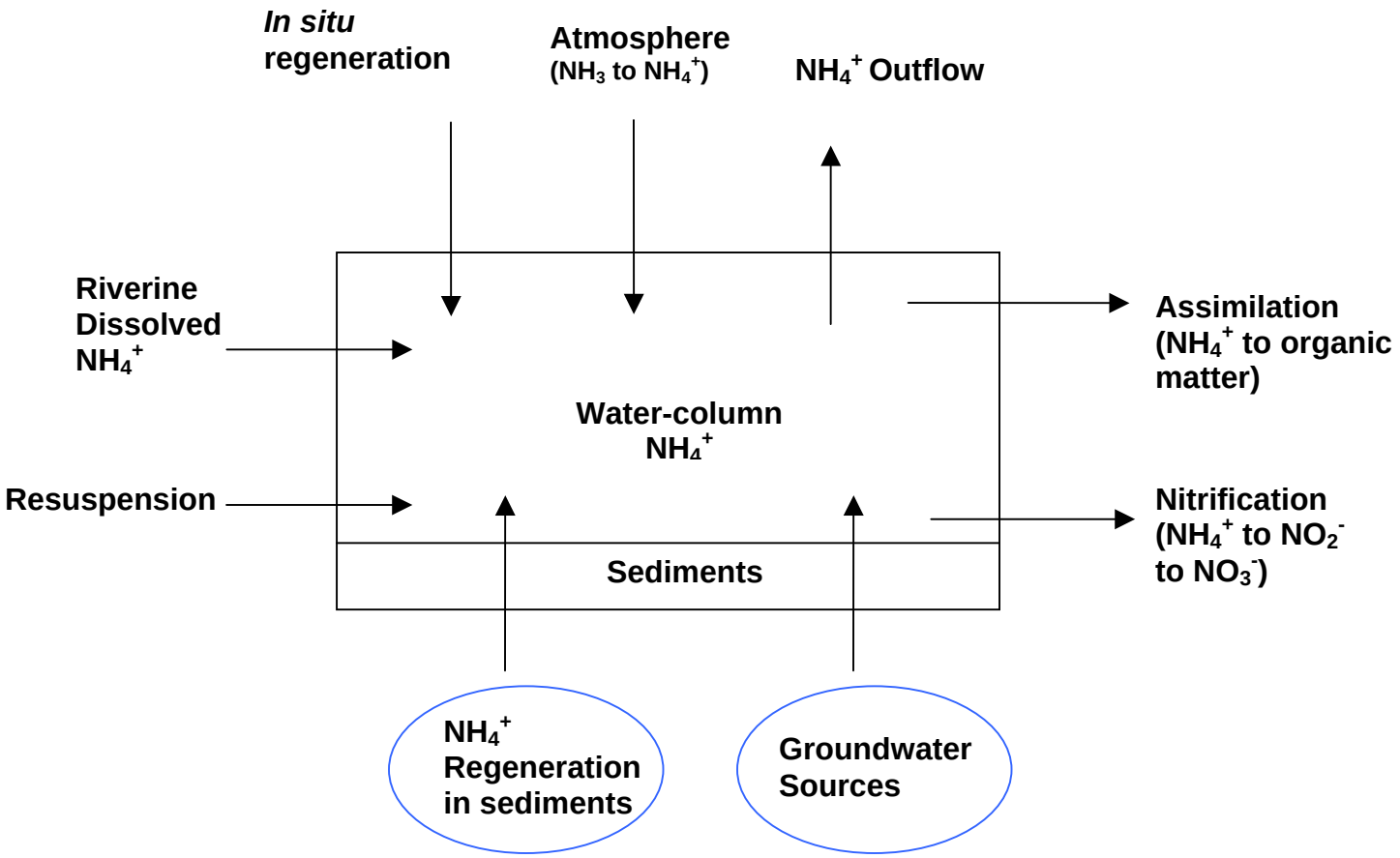


Figure 4.3. NH_4^+ sinks and sources in the Neuse River Estuary calculated for the box model. Circled sources represent fluxes measured in this study (Chapters 2 and 3).

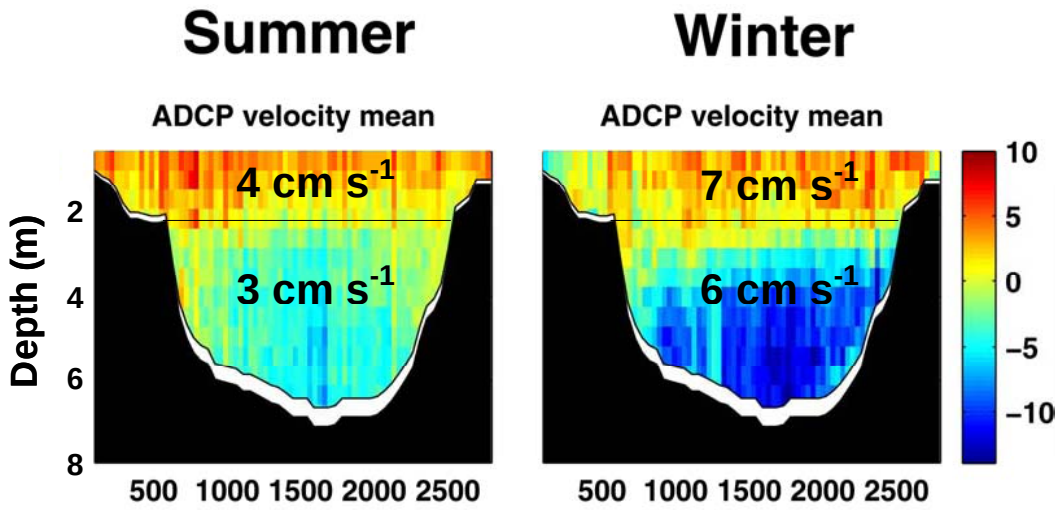


Figure 4.4. Mean velocity of flow for ADCP data collected between 1999-2001 at Cherry Point - Minnesott Beach transect (near the Wilkinson Point site of this study) in the Neuse River Estuary. The line represents the depth used to separate surface and bottom water flow to calculate an area for discharge. The mean velocity is represented by the color bar in cm s^{-1}, and the estimated velocity is printed for each season and surface/bottom water flow. The white area represents the depth missed by the ADCP (0.5 m) (modified from Reed et al. 2004). These data were used to estimate ammonium exchange between the mesohaline and lower Neuse River Estuary.

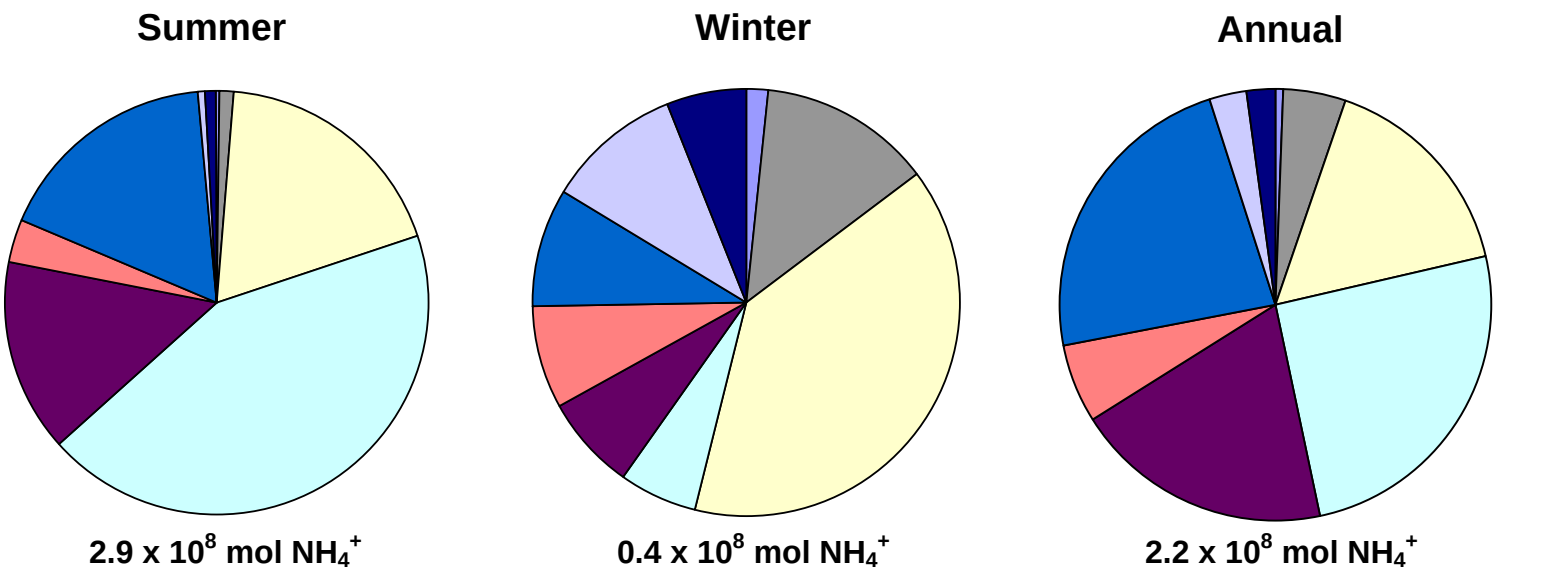


Figure 4.5. NH_4^+ sources, graphed as percent of total sources, to the Neuse River Estuary for summer mean (May-October), winter mean (November-April), and annual mean values. The total NH_4^+ inputs for each period are given in moles of NH_4^+.

5. CONCLUSIONS

Submarine groundwater discharge (SGD) can be an important source of nutrients to coastal environments, yet is poorly understood in many systems (e.g. Johannes 1980, Capone and Bausta, 1985, Burnett 2001). SGD is difficult to quantify because of spatial heterogeneity and temporal variability, and therefore, is often not included in nutrient budgets and loading models. In this study, use of two methodologies, porewater ^{222}Rn as a tracer and seepage meters, provided significant evidence of SGD occurring in nearshore sites of the NRE. The mean SGD rate in the NRE, based on ^{222}Rn estimates, was 9.1 cm d^{-1}, comparable to other coastal systems (Burnett et al. 2006). It is important to investigate nearshore environments with advective flow such as SGD because the location of the oxic/anoxic boundaries and saltwater/freshwater boundaries significantly affect organic matter degradation, NH_4^+ production, and other redox reactions. NRE sediments have been shown to be an important source of nutrients, specifically NH_4^+, to the overlying water, but previous research focused mostly on diffusive flux and did not consider advective flux, such as SGD. In this study, the rate of mean NH_4^+ flux from SGD in nearshore environments of the NRE was 12.3 ± 3.7 mmol m^{-2} d^{-1}, compared to the diffusive flux of 3.6 ± 1.1 mmol m^{-2} d^{-1}. The data indicate that advective NH_4^+ flux can have significant contributions in shallow estuarine systems such as the Neuse.

Sediments in NRE nearshore environments are extremely heterogeneous, making measurements and quantification difficult, but the sediments play an important role in nutrient cycling to the overlying water column and represent a major source of NH_4^+

supporting phytoplankton productivity. NH_4^+ was the predominant form of DIN in porewaters, and the data indicate that SGD advection is generating NH_4^+ fluxes as high as, or higher than from the organic-rich, mid-channel sediments. NH_4^+ does not accumulate in porewaters at nearshore sites, resulting in relatively low diffusive flux from sediments to the overlying water column. In addition to advection, other processes such as biological uptake and N transformations may also be influencing the NH_4^+ flux from sandy sediments.

Total DIN is often reported in published research rather than treating NH_4^+ and NO_3^- + NO_2^- separately, and such studies have described groundwater as a minor source of N loading to the NRE (US EPA 2008). Moreover, in research on the NRE and other estuaries, upstream discharge is commonly assumed to be the primary source of estuarine nutrient loading. Here, investigation of NH_4^+ fluxes indicated that SGD contributed significantly more NH_4^+ than riverine discharge during late summer-fall (June, August, September, October), whereas riverine inputs contributed higher NH_4^+ flux than SGD during winter (January) and spring (April). Thus, the importance of riverine inputs versus SGD varies seasonally: SGD can provide appreciable NH_4^+ supplies for late summer algal blooms, whereas riverine inputs would be expected to be a more important source in winter-spring.

Nutrient cycling and loading are distinct from the processes associated with groundwater discharge. The chemical reactions that occur in the subsurface may produce different N:P ratios compared to river discharge, which can affect primary production. Based on the N:P ratios of marine phytoplankton (16:1) (Redfield 1934) and water- column values (river: 18; estuary: 1 to > 200) (Day 1989), the concentration of N relative to P can influence phytoplankton assemblage composition and alter primary nutrient limiting algal. The N:P

ratio of SGD in the NRE was 42 - 73 over all sampling months. The greater flux of N relative to P can drive this estuary toward a P-limited system compared to the current N limitation, which would be expected to alter phytoplankton dynamics (Rudek et al. 1991, Mallin 1994).

Other eutrophic systems also have sustained significant increases in water-column NH_4^+ concentrations (e.g. Rocha et al. 1995, Burkholder et al. 2006, Dugdale et al. 2007), but many of the NH_4^+ sources remain poorly quantified. NH_4^+ is efficiently recycled and it is the preferred form of N over NO_3^- by phytoplankton (Middelburg et al. 2000), and several studies have demonstrated the importance of assessing NH_4^+ in estuarine environments (e.g. Rocha 1998, Middleburg and Nieuwenhuize 2000). In the Sado Estuary, intertidal sediment demonstrated significant NH_4^+ fluxes between times of atmospheric exposure and tidal flooding (Rocha 1998). Seventy five percent of the NH_4^+ pool, dissolved and adsorbed, was flushed from sediments by advective porewater exchange, demonstrating rapid remineralization of organic matter and high turnover rate, 37-43 d (Rocha 1998). Middleburg and Nieuwenhuize (2000) discovered more rapid turnover rates (0.1 – 27 d) of NH_4^+ in six European estuaries. As expected, NO_3^- had a longer residence time from 19 to 2160 d compared to NH_4^+ since NH_4^+ is the preferred N form of phytoplankton (Middleburg and Nieuwenhuize 2000). Also, NO_3^- had lower uptake rates, and therefore most NO_3^- flows through the estuaries unless it denitrified or buried (Middleburg and Nieuwenhuize 2000). These findings further suggest that significant NO_3^- loading will certainly impact an estuary, but a eutrophic estuary is mostly driven by NH_4^+ and its regenerative nature.

N_i supplied to the water column of the NRE has been assessed as an important nutrient source for phytoplankton. Haruthunian (1997), for example, focused on NH_4^+ flux across the sediment-water interface at three sites from the central part of the NRE channel and estimated that benthic N regeneration supplied 41% of the total N demand by phytoplankton in the mesohaline NRE annually. Over recent years, the Neuse River basin has experienced significant urbanization and natural habitats have decreased. Wastewater discharges and swine agriculture have been identified as the highest contributors of N to the Neuse surface waters (Rothenberger et al. 2009), contributing to the sustained eutrophication over the past decade resulting in major fish kills, harmful algal blooms, and oxygen deficits (Burkholder et al. 2006).

The importance of understanding NH_4^+ dynamics is also supported by the striking ammonium increases that have begun to be documented in other eutrophic estuaries (e.g. Rocha et al. 1995, Dugdale et al. 2007). Human disturbances, for example agriculture, manufacturing, burning of fossil fuels are increasing nutrient fluxes to surface waters of many rivers and estuaries (Nixon 1995). The mobilization of nutrients to coastal systems is a phenomenon occurring worldwide and questions still remain regarding synergistic and long-term effects (Cloern 2001).

The analysis of NH_4^+ sources and sinks in this study is valuable for understanding nutrient dynamics in a nitrogen-sensitive estuarine system and estuarine management practices overall. Overall, there was a higher input of NH_4^+ to the mesohaline NRE during summer (2.9×10^8 mol season^{-1}) compared to winter (0.4×10^8 mol season^{-1}). Since most of the physical and biochemical drivers vary seasonally, it is important to look at the system

fluxes using seasonal scenarios and not rely on annual averages. Advective and diffusive fluxes in NRE nearshore environments contributed 35% of the total NH_4^+ inputs during summer compared to 24% during winter. Diffusive and advective fluxes from nearshore environments contribute greater than 40% of the NH_4^+ on an annual basis, and overall, sediments in the NRE may supply greater than 70% of the NH_4^+ to the water column. In this study, the magnitude of the NH_4^+ flux in the nearshore environment provides evidence for permeable sediments and SGD making a significant contribution to nutrient cycling in the NRE. Initial estimates indicate SGD NH_4^+ fluxes account for 4-8% of the annual NH_4^+ supply to the estuary. Diffusive and advective fluxes in nearshore environments are two sources that should be considered when developing nutrient budgets in the NRE and other estuarine systems.

The water column of the NRE has sustained a ~500% increase in NH_4^+ over the past decade (Burkholder et al. 2006). The data from this study indicate that nearshore environments and SGD in these permeable areas are an important, previously overlooked source of NH_4^+ that has contributed to the documented significant increase in water-column NH_4^+. This study advances understanding about N sources to the NRE and, more generally, about the contribution of SGD to the NH_4^+ flux in shallow estuaries under accelerated eutrophication (National Research Council 2000). The insights from these data will help to define the role of SGD in N fluxes to coastal ecosystems. The data also provide a baseline for use in assessing the effects of future perturbations such as sea level rise, groundwater withdrawal, industrialized animal agriculture, and urbanization.

5.1 References

Burkholder, J.M., D.A. Dickey, C. Kinder, R.E. Reed, M.A. Mallin, G. Melia, M.R. McIver, L.B. Cahoon, C. Brownie, N. Deamer, J. Springer, H. Glasgow, D. Toms and J. Smith. 2006. Comprehensive trend analysis of nutrients and related variables in a large eutrophic estuary: A decadal study of anthropogenic and climatic influences. Limnology and Oceanography 51:463-487.

Burnett, W.C., Taniguchi, M., Oberdorfer, J., 2001. Measurement and significance of the direct discharge of groundwater into the coastal zone. J. Sea Res. 46, 109-116.

Capone, D.G., Bautista, M.F., 1985. A groundwater source of nitrate in nearshore marine sediments. Nature 313, 214-216.

Cloern, J.E. 2001. Our evolving conceptual model of the coastal eutrophications problem. Mar. Ecol. Prog. Ser. 210, 223-253.

Dugdale, R.C., Wilkerson, F.P., Hogue, V.E., Marchi, A., 2007. The role of ammonium and nitrate in spring bloom development in San Francisco Bay. Estuar. Coast. Shelf Sci. 73, 17-29.

Haruthunian, 1997. Seasonal and spatial variations in benthic organic nitrogen remineralization in the Neuse River Estuary, North Carolina. M.S. Thesis, UNC Chapel Hill, 70 pp.

Johannes, R.E., 1980. The ecological significance of submarine discharge of groundwater. Mar. Ecol. Prog. Ser. 3, 365-373.

Middelburg, J.J., Nieuwenhuize, J., 2001. Nitrogen isotope tracing of dissolved inorganic nitrogen behaviour in tidal estuaries. Estuar. Coast. Shelf Sci. 53, 385-391.

National Research Council (NRC), 2000. Clean coastal waters—understanding and reducing the effects of nutrient pollution. National Academy Press.

Nixon, S.W., 1995. Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia 41, 199-219.

Redfield, A.C., 1934. On the proportions of organic derivatives in seawater and their relation to the composition of plankton, pp. 177-192. In: Daniel, R.J., (Ed), 1934. James Johnson Memorial Volume, Liverpool Univ. Press, Liverpool.

Rocha, C., 1998. Rythmic ammonium regeneration and flushing in intertidal sediments of the Sado Estuary. Limnol. Ocean. 43, 823-831.

Rothenberger, M., J.M. Burkholder, C. Brownie, 2009b. Long-term effects of changing land use practices on surface water quality in a major lagoonal estuary. Environmental Management 44: 505-523.

Rudek, J.R., Paerl, H.W, Mallin, M.A., Bates, P.W., 1991. Seasonal and hydrologic control of phytoplankton nutrient limitation in the lower Neuse River Estuary, North Carolina. Mar. Ecol. Prog. Ser. 75, 133-142.

U.S. EPA. U.S. EPA's 2008 Report on the Environment (Final Report). 2008. U.S. Environmental Protection Agency, Washington, D.C., EPA/600/R-07/045F (NTIS PB2008-112484).

Appendices

Appendix A. List of ^{222}Rn activities (dpm L^{-1}) from each depth of the multi-level sampling piezometers. SD = standard deviation.

Date	Site	Piezometer	Dist. From shore (m)	Depth (cmbsf)	^{222}Rn (dpm L^{-1})	SD
6/13/2007	**MB**	WC		0		
6/13/2007	**MB**	1	3	10	87.3	
6/13/2007	**MB**	1	3	30	114.6	
6/13/2007	**MB**	1	3	60	48.2	
6/13/2007	**MB**	1	3	90	70.5	
6/13/2007	**MB**	1	3	120	88.6	
6/13/2007	**MB**	1	3	150	136.8	
6/13/2007	**MB**	1	3	210	112.3	
6/13/2007	**MB**	2	6	10	27.3	
6/13/2007	**MB**	2	6	20	67.7	
6/13/2007	**MB**	2	6	30	53.2	
6/13/2007	**MB**	2	6	50	58.5	
6/13/2007	**MB**	2	6	80	98.2	
6/13/2007	**MB**	3	9	10	32.8	
6/13/2007	**MB**	3	9	20	44.0	
6/13/2007	**MB**	3	9	30	61.6	
6/13/2007	**MB**	3	9	50	68.8	
6/13/2007	**MB**	3	9	80	41.8	
6/13/2007	**MB**	3	9	110	70.9	
6/13/2007	**MB**	3	9	140	64.3	
8/16/2007	**MB**	WC		0		
8/16/2007	**MB**	1	3	10	51.2	5.2
8/16/2007	**MB**	1	3	30	65.5	0.2
8/16/2007	**MB**	1	3	60	89.4	17.8
8/16/2007	**MB**	1	3	90	56.1	15.8
8/16/2007	**MB**	1	3	120	73.9	14.9
8/16/2007	**MB**	1	3	150	84.8	31.2
8/16/2007	**MB**	1	3	210	54.6	29.8
8/16/2007	**MB**	2	6	10	59.3	2.3
8/16/2007	**MB**	2	6	20	81.1	24.2
8/16/2007	**MB**	2	6	30	47.2	23.3
8/16/2007	**MB**	2	6	50	54.4	20.6
8/16/2007	**MB**	2	6	80	33.7	12.8
8/16/2007	**MB**	3	9	10	32.1	
8/16/2007	**MB**	3	9	20	25.4	8.6
8/16/2007	**MB**	3	9	30	32.5	18.3
8/16/2007	**MB**	3	9	50	44.9	13.1
8/16/2007	**MB**	3	9	80	34.4	4.9
8/16/2007	**MB**	3	9	110	31.0	5.9
8/16/2007	**MB**	3	9	140	73.9	9.9
1/16/2008	**MB**	WC		0	149.8	25.0
1/16/2008	**MB**	1	3	10	173.6	77.7
1/16/2008	**MB**	1	3	30	176.9	43.3
1/16/2008	**MB**	1	3	60	182.8	56.9
1/16/2008	**MB**	1	3	90	171.4	82.3
1/16/2008	**MB**	1	3	120	190.2	38.2

Date	Site	Piezometer	Dist. From shore (m)	Depth (cmbsf)	^{222}Rn (dpm/L)	SD
1/16/2008	**MB**	1	3	150	219.0	66.6
1/16/2008	**MB**	1	3	210	214.9	1.2
1/16/2008	**MB**	2	6	10	184.0	52.1
1/16/2008	**MB**	2	6	20	110.8	71.6
1/16/2008	**MB**	2	6	30	159.3	8.2
1/16/2008	**MB**	2	6	50	154.2	11.8
1/16/2008	**MB**	2	6	80	179.9	24.3
1/16/2008	**MB**	3	9	10	205.8	61.0
1/16/2008	**MB**	3	9	20	179.6	28.4
1/16/2008	**MB**	3	9	30	215.1	16.1
1/16/2008	**MB**	3	9	50	128.4	39.5
1/16/2008	**MB**	3	9	80	189.6	44.7
1/16/2008	**MB**	3	9	110	165.5	116.3
1/16/2008	**MB**	3	9	140	289.1	47.0
4/18/2008	**MB**	WC		0		
4/18/2008	**MB**	1	3	10	117.0	20.3
4/18/2008	**MB**	1	3	30	125.7	0.9
4/18/2008	**MB**	1	3	60	116.7	12.9
4/18/2008	**MB**	1	3	90	121.5	25.4
4/18/2008	**MB**	1	3	120	95.8	10.8
4/18/2008	**MB**	1	3	150	147.5	29.9
4/18/2008	**MB**	1	3	210	208.9	5.5
4/18/2008	**MB**	2	6	10		
4/18/2008	**MB**	2	6	20		
4/18/2008	**MB**	2	6	30		
4/18/2008	**MB**	2	6	50		
4/18/2008	**MB**	2	6	80		
4/18/2008	**MB**	3	9	10	95.6	26.1
4/18/2008	**MB**	3	9	20	102.6	7.8
4/18/2008	**MB**	3	9	30	124.1	19.7
4/18/2008	**MB**	3	9	50	131.3	46.6
4/18/2008	**MB**	3	9	80	93.3	13.5
4/18/2008	**MB**	3	9	110	83.1	14.3
4/18/2008	**MB**	3	9	140	133.1	51.8
8/18/2008	**MB**	WC		0		
8/18/2008	**MB**	1	3	10	51.5	9.5
8/18/2008	**MB**	1	3	30	77.9	10.9
8/18/2008	**MB**	1	3	60		
8/18/2008	**MB**	1	3	90	114.1	30.4
8/18/2008	**MB**	1	3	120	120.0	24.4
8/18/2008	**MB**	1	3	150	130.6	2.7
8/18/2008	**MB**	1	3	210		
8/18/2008	**MB**	2	6	10		
8/18/2008	**MB**	2	6	20		
8/18/2008	**MB**	2	6	30		
8/18/2008	**MB**	2	6	50		
8/18/2008	**MB**	2	6	80		
8/18/2008	**MB**	3	9	10	59.6	13.2
8/18/2008	**MB**	3	9	20	72.7	18.9
8/18/2008	**MB**	3	9	30	54.0	13.0
8/18/2008	**MB**	3	9	50	75.5	29.2

Date	Site	Piezometer	Dist. From shore (m)	Depth (cmbsf)	^{222}Rn (dpm/L)	SD
8/18/2008	**MB**	3	9	80	67.1	8.8
8/18/2008	**MB**	3	9	110		
8/18/2008	**MB**	3	9	140	117.2	25.9
6/21/2007	**CP**	MW			677.2	3.0
6/21/2007	**CP**	WC		0		
6/21/2007	**CP**	2	10	10	13.1	
6/21/2007	**CP**	2	10	20	256.8	
6/21/2007	**CP**	2	10	30	538.8	
6/21/2007	**CP**	2	10	50	929.8	
6/21/2007	**CP**	2	10	80	851.8	61.8
6/21/2007	**CP**	2	10	110	2097.9	4.0
6/21/2007	**CP**	2	10	140	3625.5	4.0
6/21/2007	**CP**	3	15	10	6.0	10.4
6/21/2007	**CP**	3	15	20	22.9	29.6
6/21/2007	**CP**	3	15	30	92.2	48.0
6/21/2007	**CP**	3	15	50	333.8	80.5
6/21/2007	**CP**	3	15	65	215.2	4.6
6/21/2007	**CP**	4	20	10	153.8	7.8
6/21/2007	**CP**	4	20	30	741.0	47.9
6/21/2007	**CP**	4	20	50	610.9	19.9
6/21/2007	**CP**	4	20	80	735.2	28.7
6/21/2007	**CP**	4	20	110	1759.9	68.6
6/21/2007	**CP**	4	20	150	3230.1	91.3
6/21/2007	**CP**	4	20	190	3746.6	27.4
6/21/2007	**CP**	4	20	230	3664.0	
8/9/2007	**CP**	MW			1074.1	29.5
8/9/2007	**CP**	WC		0	31.2	18.4
8/9/2007	**CP**	2	10	10	11.3	13.3
8/9/2007	**CP**	2	10	20	231.6	36.6
8/9/2007	**CP**	2	10	30	423.8	29.3
8/9/2007	**CP**	2	10	50	932.7	66.8
8/9/2007	**CP**	2	10	80	1191.4	99.7
8/9/2007	**CP**	2	10	110	2737.9	81.3
8/9/2007	**CP**	2	10	140	4375.3	55.4
8/9/2007	**CP**	3	15	10	26.4	16.9
8/9/2007	**CP**	3	15	20	46.4	18.5
8/9/2007	**CP**	3	15	30	103.1	9.2
8/9/2007	**CP**	3	15	50	312.6	78.6
8/9/2007	**CP**	3	15	65	192.1	32.2
8/9/2007	**CP**	4	20	10	400.6	45.1
8/9/2007	**CP**	4	20	30	980.9	123.5
8/9/2007	**CP**	4	20	50	818.7	29.9
8/9/2007	**CP**	4	20	80	781.7	65.8
8/9/2007	**CP**	4	20	110	2050.0	50.0
8/9/2007	**CP**	4	20	150	3605.8	395.8
8/9/2007	**CP**	4	20	190	4117.4	136.9
8/9/2007	**CP**	4	20	230	4002.3	167.1
10/12/2009	**CP**	MW			1070.9	62.5
10/12/2009	**CP**	WC		0	102.5	26.0
10/12/2009	**CP**	2	10	10	136.5	15.7

Date	Site	Piezometer	Dist. From shore (m)	Depth (cmbsf)	^{222}Rn (dpm/L)	SD
10/12/2009	**CP**	2	10	20	227.8	49.5
10/12/2009	**CP**	2	10	30	420.2	23.0
10/12/2009	**CP**	2	10	50	727.6	47.0
10/12/2009	**CP**	2	10	80	907.4	56.3
10/12/2009	**CP**	2	10	110	1803.7	113.1
10/12/2009	**CP**	2	10	140	3434.6	45.8
10/12/2009	**CP**	3	15	10	93.0	31.3
10/12/2009	**CP**	3	15	20	109.6	15.9
10/12/2009	**CP**	3	15	30	132.7	23.2
10/12/2009	**CP**	3	15	50	322.3	2.8
10/12/2009	**CP**	3	15	65	263.7	4.8
10/12/2009	**CP**	4	20	10	372.8	12.8
10/12/2009	**CP**	4	20	30	974.2	47.9
10/12/2009	**CP**	4	20	50	688.1	8.5
10/12/2009	**CP**	4	20	80	871.9	8.0
10/12/2009	**CP**	4	20	110	2230.8	127.2
10/12/2009	**CP**	4	20	150	3465.2	104.2
10/12/2009	**CP**	4	20	190	4056.5	87.0
10/12/2009	**CP**	4	20	230	4384.4	85.6
1/4/2009	**CP**	MW			1084.3	84.9
1/4/2009	**CP**	WC		0	293.2	85.3
1/4/2009	**CP**	2	10	10	55.4	3.7
1/4/2009	**CP**	2	10	20	291.7	24.6
1/4/2009	**CP**	2	10	30	562.7	84.2
1/4/2009	**CP**	2	10	50	981.5	84.7
1/4/2009	**CP**	2	10	80	762.4	7.5
1/4/2009	**CP**	2	10	110	2087.7	88.2
1/4/2009	**CP**	2	10	140	3368.0	53.1
1/4/2009	**CP**	3	15	10	96.5	15.0
1/4/2009	**CP**	3	15	20	132.3	13.3
1/4/2009	**CP**	3	15	30	184.5	34.4
1/4/2009	**CP**	3	15	50	366.8	6.5
1/4/2009	**CP**	3	15	65	273.3	3.6
1/4/2009	**CP**	4	20	10	471.1	12.1
1/4/2009	**CP**	4	20	30	1101.0	56.0
1/4/2009	**CP**	4	20	50	817.4	21.0
1/4/2009	**CP**	4	20	80	1573.3	23.1
1/4/2009	**CP**	4	20	110	2963.2	228.2
1/4/2009	**CP**	4	20	150	4418.8	246.4
1/4/2009	**CP**	4	20	190	5000.5	1.6
1/4/2009	**CP**	4	20	230	4252.5	916.4
4/29/2008	**CP**	MW			872.8	170.0
4/29/2008	**CP**	WC		0		
4/29/2008	**CP**	2	10	10	43.0	64.2
4/29/2008	**CP**	2	10	20	211.0	18.7
4/29/2008	**CP**	2	10	30	433.6	39.9
4/29/2008	**CP**	2	10	50	698.3	34.8
4/29/2008	**CP**	2	10	80	613.5	36.5
4/29/2008	**CP**	2	10	110	1643.3	96.0
4/29/2008	**CP**	2	10	140	3074.2	1.6
4/29/2008	**CP**	3	15	10	62.3	36.1

Date	Site	Piezometer	Dist. From shore (m)	Depth (cmbsf)	^{222}Rn (dpm/L)	SD
4/29/2008	**CP**	3	15	20	31.1	6.9
4/29/2008	**CP**	3	15	30	178.0	32.9
4/29/2008	**CP**	3	15	50	317.5	34.3
4/29/2008	**CP**	3	15	65	219.6	28.4
4/29/2008	**CP**	4	20	10	373.2	0.9
4/29/2008	**CP**	4	20	30	1139.3	20.5
4/29/2008	**CP**	4	20	50	1025.1	24.1
4/29/2008	**CP**	4	20	80	1056.2	10.3
4/29/2008	**CP**	4	20	110	2163.1	59.8
4/29/2008	**CP**	4	20	150	3399.0	122.4
4/29/2008	**CP**	4	20	190	3851.7	62.7
4/29/2008	**CP**	4	20	230	3999.4	100.6
9/28/2008	**CP**	MW			1197.5	31.6
9/28/2008	**CP**	WC		0		
9/28/2008	**CP**	2	10	10		
9/28/2008	**CP**	2	10	20		
9/28/2008	**CP**	2	10	30		
9/28/2008	**CP**	2	10	50		
9/28/2008	**CP**	2	10	80		
9/28/2008	**CP**	2	10	110		
9/28/2008	**CP**	2	10	140		
9/28/2008	**CP**	3	15	10	4.0	17.5
9/28/2008	**CP**	3	15	20	45.7	18.9
9/28/2008	**CP**	3	15	30	152.5	28.4
9/28/2008	**CP**	3	15	50	231.0	84.9
9/28/2008	**CP**	3	15	65	232.8	56.1
9/28/2008	**CP**	4	20	10	187.0	3.9
9/28/2008	**CP**	4	20	30	1137.4	83.6
9/28/2008	**CP**	4	20	50	790.4	17.4
9/28/2008	**CP**	4	20	80	489.6	12.5
9/28/2008	**CP**	4	20	110	1629.5	39.4
9/28/2008	**CP**	4	20	150	3510.7	102.9
9/28/2008	**CP**	4	20	190	4306.1	131.9
9/28/2008	**CP**	4	20	230	4566.1	15.4
6/27/2007	**WP**	WC		0		
6/27/2007	**WP**	1	7	10	73.0	
6/27/2007	**WP**	1	7	20	161.6	40.3
6/27/2007	**WP**	1	7	30	172.2	21.9
6/27/2007	**WP**	1	7	50	179.4	3.9
6/27/2007	**WP**	1	7	80	239.6	11.8
6/27/2007	**WP**	1	7	110	431.7	13.5
6/27/2007	**WP**	1	7	150	406.8	34.6
6/27/2007	**WP**	2	10	10		
6/27/2007	**WP**	2	10	20		
6/27/2007	**WP**	2	10	30		
6/27/2007	**WP**	2	10	50		
6/27/2007	**WP**	2	10	80	350.0	38.5
6/27/2007	**WP**	2	10	110	384.0	6.5
6/27/2007	**WP**	2	10	150	367.1	12.4
8/1/2007	**WP**	WC		0		

Date	Site	Piezometer	Dist. From shore (m)	Depth (cmbsf)	^{222}Rn (dpm/L)	SD
8/1/2007	**WP**	1	7	10	64.1	2.8
8/1/2007	**WP**	1	7	20	57.0	37.3
8/1/2007	**WP**	1	7	30	104.3	17.9
8/1/2007	**WP**	1	7	50	221.1	17.2
8/1/2007	**WP**	1	7	80	299.3	33.2
8/1/2007	**WP**	1	7	110	359.2	25.0
8/1/2007	**WP**	1	7	150	382.9	35.4
8/1/2007	**WP**	2	10	10	208.9	11.7
8/1/2007	**WP**	2	10	20	227.6	29.4
8/1/2007	**WP**	2	10	30	247.7	36.1
8/1/2007	**WP**	2	10	50	335.7	7.1
8/1/2007	**WP**	2	10	80	327.0	33.9
8/1/2007	**WP**	2	10	110	380.9	55.7
8/1/2007	**WP**	2	10	150	313.8	42.9
10/1/2007	**WP**	WC		0		
10/1/2007	**WP**	1	7	10	100.1	16.9
10/1/2007	**WP**	1	7	20	230.6	8.6
10/1/2007	**WP**	1	7	30	244.0	6.8
10/1/2007	**WP**	1	7	50	248.4	6.9
10/1/2007	**WP**	1	7	80	368.5	9.0
10/1/2007	**WP**	1	7	110	429.0	21.1
10/1/2007	**WP**	1	7	150	371.8	9.8
10/1/2007	**WP**	2	10	10	282.8	5.5
10/1/2007	**WP**	2	10	20	190.0	14.1
10/1/2007	**WP**	2	10	30	178.3	4.0
10/1/2007	**WP**	2	10	50	298.2	2.6
10/1/2007	**WP**	2	10	80	369.0	12.5
10/1/2007	**WP**	2	10	110	391.1	17.7
10/1/2007	**WP**	2	10	150	330.1	21.0
9/18/2008	**WP**	WC		0		
9/18/2008	**WP**	1	7	10	0.0	26.1
9/18/2008	**WP**	1	7	20	203.6	21.3
9/18/2008	**WP**	1	7	30	115.8	72.4
9/18/2008	**WP**	1	7	50	156.6	30.0
9/18/2008	**WP**	1	7	80	174.7	34.0
9/18/2008	**WP**	1	7	110	173.7	4.3
9/18/2008	**WP**	1	7	150	378.0	25.9
9/18/2008	**WP**	2	10	10	294.1	98.6
9/18/2008	**WP**	2	10	20	244.5	110.0
9/18/2008	**WP**	2	10	30	301.7	55.6
9/18/2008	**WP**	2	10	50	306.1	7.8
9/18/2008	**WP**	2	10	80	373.5	56.0
9/18/2008	**WP**	2	10	110	335.5	25.8
9/18/2008	**WP**	2	10	150	356.9	3.8

Appendix B. List of porewater physical and chemical parameters for each depth sampled.

Date	Site	Piezometer	Depth (cmbsf)	Temp °C	DO (mg L^{-1})	Conductivity (mS)	Salinity
6/13/2007	**MB**	WC	0	27.2	3.6	3.4	1.7
6/13/2007	**MB**	1	10	26.1		1.7	0.8
6/13/2007	**MB**	1	30	24.4	0.8	1.6	0.8
6/13/2007	**MB**	1	60	22.7	0.3	1.6	0.8
6/13/2007	**MB**	1	90	22.0	0.6	1.8	0.8
6/13/2007	**MB**	1	120	20.9	0.3	1.5	0.8
6/13/2007	**MB**	1	150	21.2	0.2	1.5	0.8
6/13/2007	**MB**	1	210	20.1	0.2	1.1	0.6
6/13/2007	**MB**	2	10	27.5	0.1	2.3	1.1
6/13/2007	**MB**	2	20	27.6	0.1	2.3	1.1
6/13/2007	**MB**	2	30	26.6	0.3	1.7	0.8
6/13/2007	**MB**	2	50	24.7	0.2	1.5	0.8
6/13/2007	**MB**	2	80	24.5	0.2	1.3	0.7
6/13/2007	**MB**	3	10				
6/13/2007	**MB**	3	20				
6/13/2007	**MB**	3	30				
6/13/2007	**MB**	3	50				
6/13/2007	**MB**	3	80	24.1	0.3	1.4	0.7
6/13/2007	**MB**	3	110	24.1	0.4	1.4	0.7
6/13/2007	**MB**	3	140	24.3	0.3	1.4	0.7
8/16/2007	**MB**	WC	0	30.2	6.9	5.4	2.9
8/16/2007	**MB**	1	10	27.8	0.7	1.9	1.0
8/16/2007	**MB**	1	30	25.9	0.9	1.6	0.8
8/16/2007	**MB**	1	60	24.7	0.7	1.5	0.8
8/16/2007	**MB**	1	90	24.0	0.7	1.5	0.8
8/16/2007	**MB**	1	120	23.5	0.8	1.5	0.7
8/16/2007	**MB**	1	150	23.1	0.7	1.5	0.8
8/16/2007	**MB**	1	210	22.5		1.2	0.6
8/16/2007	**MB**	2	10	29.6	0.1	4.3	2.3
8/16/2007	**MB**	2	20	29.4	0.1	3.2	1.7
8/16/2007	**MB**	2	30	29.0	0.2	4.9	2.6
8/16/2007	**MB**	2	50	27.6	0.9	1.5	0.7
8/16/2007	**MB**	2	80	26.6	0.8	1.3	0.7
8/16/2007	**MB**	3	10	29.2	0.9	1.5	0.7
8/16/2007	**MB**	3	20	28.6	0.9	1.4	0.7
8/16/2007	**MB**	3	30	28.4	0.9	1.4	0.7
8/16/2007	**MB**	3	50	27.7	0.8	1.4	0.7
8/16/2007	**MB**	3	80	27.0	0.9	1.4	0.7
8/16/2007	**MB**	3	110	26.7		1.4	0.7
8/16/2007	**MB**	3	140	26.0	1.0	1.3	0.7
1/16/2008	**MB**	WC	0	10.9	8.8	1.8	0.9
1/16/2008	**MB**	1	10	15.6	1.0	1.5	0.8
1/16/2008	**MB**	1	30	17.1	1.0	1.5	0.8
1/16/2008	**MB**	1	60	17.4	0.9	1.4	0.7
1/16/2008	**MB**	1	90	17.7	0.7	1.4	0.7
1/16/2008	**MB**	1	120	17.7	0.9	1.4	0.7
1/16/2008	**MB**	1	150	18.0	0.8	1.5	0.7
1/16/2008	**MB**	1	210	17.9	0.7	1.3	0.6

Date	Site	Piezometer	Depth (cmbsf)	Temp °C	DO (mg L^{-1})	Conductivity (mS)	Salinity
1/16/2008	**MB**	2	10	13.6	0.7	1.5	0.8
1/16/2008	**MB**	2	20	13.5	0.6	1.4	0.7
1/16/2008	**MB**	2	30	13.9	0.8	2.4	1.3
1/16/2008	**MB**	2	50	14.9	1.2	1.3	0.6
1/16/2008	**MB**	2	80	15.7	0.9	1.2	0.6
1/16/2008	**MB**	3	10	14.9	0.9	1.3	0.7
1/16/2008	**MB**	3	20	14.7	0.7	1.3	0.7
1/16/2008	**MB**	3	30	14.8	0.4	1.3	0.7
1/16/2008	**MB**	3	50	15.0	0.8	1.3	0.7
1/16/2008	**MB**	3	80	15.9	0.8	1.4	0.7
1/16/2008	**MB**	3	110	16.2	0.8	1.3	0.7
1/16/2008	**MB**	3	140	16.4	0.8	1.2	0.6
							0.0
4/18/2008	**MB**	WC	0	16.8	6.0	0.4	0.2
4/18/2008	**MB**	1	10	19.3	0.5	0.0	
4/18/2008	**MB**	1	30	18.5	0.7	1.5	0.8
4/18/2008	**MB**	1	60	18.1	0.6	1.4	0.7
4/18/2008	**MB**	1	90	18.4	0.6	1.4	0.7
4/18/2008	**MB**	1	120	17.9	0.3	1.5	0.7
4/18/2008	**MB**	1	150	17.6	0.3	1.5	0.7
4/18/2008	**MB**	1	210	17.6	0.5	1.3	0.6
4/18/2008	**MB**	2	10			0.0	
4/18/2008	**MB**	2	20			0.0	
4/18/2008	**MB**	2	30			0.0	
4/18/2008	**MB**	2	50			0.0	
4/18/2008	**MB**	2	80			0.0	
4/18/2008	**MB**	3	10	19.0	0.4	1.3	0.6
4/18/2008	**MB**	3	20	18.1	0.3	1.3	0.6
4/18/2008	**MB**	3	30	18.1	0.4	1.3	0.6
4/18/2008	**MB**	3	50	17.9	0.4	1.3	0.7
4/18/2008	**MB**	3	80	18.4	0.6	1.3	0.6
4/18/2008	**MB**	3	110	18.7	0.4	1.3	0.6
4/18/2008	**MB**	3	140	18.0	0.3	1.1	0.6
8/18/2008	**MB**	WC	0	28.8	3.5	17.1	11.0
8/18/2008	**MB**	1	10	29.5	0.3	7.1	3.9
8/18/2008	**MB**	1	30	27.5	0.4	1.6	0.8
8/18/2008	**MB**	1	60				
8/18/2008	**MB**	1	90	25.6	0.3	1.5	0.7
8/18/2008	**MB**	1	120	24.5	0.2	1.5	0.8
8/18/2008	**MB**	1	150	24.6	0.3	1.4	0.7
8/18/2008	**MB**	1	210				
8/18/2008	**MB**	2	10				
8/18/2008	**MB**	2	20				
8/18/2008	**MB**	2	30				
8/18/2008	**MB**	2	50				
8/18/2008	**MB**	2	80				
8/18/2008	**MB**	3	10	28.8	0.9	1.8	0.9
8/18/2008	**MB**	3	20	28.4	0.5	1.4	0.7
8/18/2008	**MB**	3	30	28.4	0.4	1.3	0.6
8/18/2008	**MB**	3	50	27.6	0.3	1.2	0.6
8/18/2008	**MB**	3	80	27.4	0.3	1.3	0.7
8/18/2008	**MB**	3	110				

Date	Site	Piezometer	Depth (cmbsf)	Temp °C	DO (mg L^{-1})	Conductivity (mS)	Salinity
8/18/2008	**MB**	3	140	26.4	0.5	1.1	0.6
6/21/2007	**CP**	MW		27.5	2.6	0.5	0.2
6/21/2007	**CP**	WC	0	30.3	7.3	18.8	10.0
6/21/2007	**CP**	2	10	27.9	0.4	16.6	9.1
6/21/2007	**CP**	2	20	27.5	0.6	13.0	7.1
6/21/2007	**CP**	2	30	26.3	0.3	10.9	6.0
6/21/2007	**CP**	2	50	26.5	0.3	8.7	4.7
6/21/2007	**CP**	2	80	26.6	0.7	9.7	5.2
6/21/2007	**CP**	2	110	27.2	0.7	7.6	4.0
6/21/2007	**CP**	2	140	24.9	0.6	4.7	2.5
6/21/2007	**CP**	3	10	27.4	0.4	17.2	9.5
6/21/2007	**CP**	3	20	27.1	0.3	17.1	9.5
6/21/2007	**CP**	3	30	26.5	0.5	16.5	9.1
6/21/2007	**CP**	3	50	26.0	0.5	11.8	6.5
6/21/2007	**CP**	3	65	26.0	0.3	11.8	6.6
6/21/2007	**CP**	4	10	28.9	0.3	14.1	7.5
6/21/2007	**CP**	4	30	26.9	0.2	3.3	1.7
6/21/2007	**CP**	4	50	26.3	0.3	4.8	2.4
6/21/2007	**CP**	4	80	25.6	0.3	7.0	3.8
6/21/2007	**CP**	4	110	24.5	0.4	2.1	1.1
6/21/2007	**CP**	4	150	23.9	1.1	0.7	0.3
6/21/2007	**CP**	4	190	22.9	1.3	0.6	0.3
6/21/2007	**CP**	4	230	25.7	0.3	0.7	0.3
8/9/2007	**CP**	MW		22.8	1.7	0.5	0.2
8/9/2007	**CP**	WC	0	33.9	3.4	27.4	16.6
8/9/2007	**CP**	2	10	32.4	1.1	26.4	16.0
8/9/2007	**CP**	2	20	30.6	0.5	23.2	13.9
8/9/2007	**CP**	2	30	30.5	0.4	18.7	11.0
8/9/2007	**CP**	2	50	30.1	0.6	10.8	6.1
8/9/2007	**CP**	2	80	29.3	0.6	12.9	7.4
8/9/2007	**CP**	2	110	28.8	0.8	8.8	4.9
8/9/2007	**CP**	2	140	27.4	0.8	5.8	3.1
8/9/2007	**CP**	3	10	31.6	0.3	26.7	16.2
8/9/2007	**CP**	3	20	30.8	0.5	26.6	16.2
8/9/2007	**CP**	3	30	30.6	0.5	26.5	16.1
8/9/2007	**CP**	3	50	29.9	0.6	23.9	14.4
8/9/2007	**CP**	3	65	30.2	0.5	24.0	14.4
8/9/2007	**CP**	4	10	31.1	0.5	7.3	4.0
8/9/2007	**CP**	4	30	30.6	0.6	2.7	1.4
8/9/2007	**CP**	4	50	29.7	0.5	5.3	2.8
8/9/2007	**CP**	4	80	28.7	0.5	7.8	4.3
8/9/2007	**CP**	4	110	27.5	0.5	1.6	0.8
8/9/2007	**CP**	4	150	27.0	0.9	0.7	0.3
8/9/2007	**CP**	4	190	26.4	1.6	0.7	0.4
8/9/2007	**CP**	4	230	27.7	1.1	0.6	0.3
10/12/2009	**CP**	MW		21.7	2.1	0.5	0.3
10/12/2009	**CP**	WC	0	20.4	5.8	26.1	16.0
10/12/2009	**CP**	2	10	20.5	1.1	23.3	15.5
10/12/2009	**CP**	2	20	21.3	1.2	24.2	14.7
10/12/2009	**CP**	2	30	22.1	1.0	24.9	15.2
10/12/2009	**CP**	2	50	22.6	1.3	21.6	13.0

Date	Site	Piezometer	Depth (cmbsf)	Temp °C	DO (mg L^{-1})	Conductivity (mS)	Salinity
10/12/2009	**CP**	2	80	23.7	1.4	21.8	13.1
10/12/2009	**CP**	2	110	22.8	2.1	23.8	14.4
10/12/2009	**CP**	2	140	23.4	1.5	18.1	10.7
10/12/2009	**CP**	3	10	20.8	4.2	26.1	16.0
10/12/2009	**CP**	3	20	20.9	1.3	25.1	15.3
10/12/2009	**CP**	3	30	21.6	1.2	26.4	16.2
10/12/2009	**CP**	3	50	23.5	1.0	26.7	16.4
10/12/2009	**CP**	3	65	23.3	1.4	26.7	16.4
10/12/2009	**CP**	4	10	22.1	1.6	13.3	7.7
10/12/2009	**CP**	4	30	22.6	1.2	5.6	3.0
10/12/2009	**CP**	4	50	23.5	1.1	9.5	5.3
10/12/2009	**CP**	4	80	24.2	1.2	9.5	1.2
10/12/2009	**CP**	4	110	24.1	1.2	2.3	0.4
10/12/2009	**CP**	4	150	23.8	1.4	0.8	0.3
10/12/2009	**CP**	4	190	23.7	1.9	0.6	0.3
10/12/2009	**CP**	4	230	22.4	2.6	1.0	0.5
1/4/2009	**CP**	MW		11.1	5.5	0.5	0.2
1/4/2009	**CP**	WC	0	6.0	10.9	24.9	15.0
1/4/2009	**CP**	2	10	5.2	6.6	26.3	15.9
1/4/2009	**CP**	2	20	5.8	1.0	23.1	13.8
1/4/2009	**CP**	2	30	6.7	1.1	18.7	11.0
1/4/2009	**CP**	2	50	8.6	1.2	19.3	11.4
1/4/2009	**CP**	2	80	10.2	1.1	23.2	14.0
1/4/2009	**CP**	2	110	10.9	1.5	15.4	9.0
1/4/2009	**CP**	2	140	12.7	1.2	16.5	9.7
1/4/2009	**CP**	3	10	6.6	4.7	25.7	15.5
1/4/2009	**CP**	3	20	6.5	1.3	26.8	16.3
1/4/2009	**CP**	3	30	7.3	1.1	27.5	16.8
1/4/2009	**CP**	3	50	10.4	1.1	26.8	16.4
1/4/2009	**CP**	3	65	9.8	1.0	28.2	17.3
1/4/2009	**CP**	4	10	7.9	1.3	8.4	4.7
1/4/2009	**CP**	4	30	9.0	1.3	3.1	1.6
1/4/2009	**CP**	4	50	10.3	1.3	8.4	4.7
1/4/2009	**CP**	4	80	12.1	1.3	5.2	2.8
1/4/2009	**CP**	4	110	12.9	1.5	0.8	0.4
1/4/2009	**CP**	4	150	13.9	1.5	0.6	0.3
1/4/2009	**CP**	4	190	14.5	2.0	0.6	0.3
1/4/2009	**CP**	4	230	13.2	2.4	0.6	0.3
4/29/2008	**CP**	MW		18.0	2.4	0.5	0.2
4/29/2008	**CP**	WC	0	21.4	6.0	19.3	11.5
4/29/2008	**CP**	2	10	18.5	4.9	18.9	11.2
4/29/2008	**CP**	2	20	19.3	0.9	16.3	9.4
4/29/2008	**CP**	2	30	19.2	0.6	15.5	9.1
4/29/2008	**CP**	2	50	19.9	0.8	14.9	8.7
4/29/2008	**CP**	2	80	19.4	0.8	19.4	11.6
4/29/2008	**CP**	2	110	19.0	0.9	19.0	11.3
4/29/2008	**CP**	2	140	18.2	1.0	13.6	7.9
4/29/2008	**CP**	3	10	19.5	5.3	19.6	11.7
4/29/2008	**CP**	3	20	19.7	4.3	18.9	11.2
4/29/2008	**CP**	3	30	19.4	3.0	17.6	10.4
4/29/2008	**CP**	3	50	19.4	2.7	22.5	13.6

Date	Site	Piezometer	Depth (cmbsf)	Temp °C	DO (mg L^{-1})	Conductivity (mS)	Salinity
4/29/2008	**CP**	3	65	19.9	2.2	20.6	12.3
4/29/2008	**CP**	4	10	19.9	3.1	8.5	4.7
4/29/2008	**CP**	4	30	19.1	3.0	1.3	0.7
4/29/2008	**CP**	4	50	19.2	2.8	4.4	2.3
4/29/2008	**CP**	4	80	18.8	2.5	3.8	2.0
4/29/2008	**CP**	4	110	18.0	3.0	0.8	0.4
4/29/2008	**CP**	4	150	17.5	3.3	0.6	0.3
4/29/2008	**CP**	4	190	17.4	4.0	0.8	0.4
4/29/2008	**CP**	4	230	17.6	4.7	0.3	0.2
9/28/2008	**CP**	MW		24.7	4.2	0.4	0.2
9/28/2008	**CP**	WC	0	22.7	5.9	25.0	15.2
9/28/2008	**CP**	2	10				
9/28/2008	**CP**	2	20				
9/28/2008	**CP**	2	30				
9/28/2008	**CP**	2	50				
9/28/2008	**CP**	2	80				
9/28/2008	**CP**	2	110				
9/28/2008	**CP**	2	140				
9/28/2008	**CP**	3	10	23.7	3.7	25.2	15.3
9/28/2008	**CP**	3	20	22.9	2.5	24.6	14.9
9/28/2008	**CP**	3	30	23.2	1.2	22.5	13.6
9/28/2008	**CP**	3	50	23.7	0.9	28.8	17.8
9/28/2008	**CP**	3	65	23.7	0.9	26.4	16.2
9/28/2008	**CP**	4	10	23.1	1.6	10.3	17.5
9/28/2008	**CP**	4	30	23.3	1.7	6.1	3.3
9/28/2008	**CP**	4	50	23.7	2.1	14.1	8.2
9/28/2008	**CP**	4	80	23.9	1.6	17.0	10.0
9/28/2008	**CP**	4	110	24.2	1.3	14.9	8.7
9/28/2008	**CP**	4	150	24.6	1.5	2.1	1.1
9/28/2008	**CP**	4	190	24.6	1.8	1.2	0.6
9/28/2008	**CP**	4	230	25.4	2.8	1.7	0.8
6/27/2007	**WP**	WC	0	29.6	5.8	21.1	11.5
6/27/2007	**WP**	1	10	29.6	1.3	17.4	9.3
6/27/2007	**WP**	1	20	28.5	1.3	13.8	7.4
6/27/2007	**WP**	1	30	27.2	0.9	13.1	7.1
6/27/2007	**WP**	1	50	26.6	0.8	14.6	8.2
6/27/2007	**WP**	1	80	25.9	0.7	13.5	7.6
6/27/2007	**WP**	1	110	25.4	0.2	14.6	8.4
6/27/2007	**WP**	1	150	27.7	0.3	14.3	8.2
6/27/2007	**WP**	2	10	28.7	0.7	15.7	8.5
6/27/2007	**WP**	2	20	27.5	0.3	14.9	8.2
6/27/2007	**WP**	2	30	26.9	0.2	15.2	8.9
6/27/2007	**WP**	2	50	26.0	0.8	15.0	8.5
6/27/2007	**WP**	2	80	25.7	0.8	15.5	8.9
6/27/2007	**WP**	2	110	24.5	0.3	12.7	7.3
6/27/2007	**WP**	2	150	24.3	1.0	13.6	12.9
8/1/2007	**WP**	WC	0	YSI broke			
8/1/2007	**WP**	1	10				
8/1/2007	**WP**	1	20				
8/1/2007	**WP**	1	30				

Date	Site	Piezometer	Depth (cmbsf)	Temp °C	DO (mg L^{-1})	Conductivity (mS)	Salinity
8/1/2007	**WP**	1	50				
8/1/2007	**WP**	1	80				
8/1/2007	**WP**	1	110				
8/1/2007	**WP**	1	150				
8/1/2007	**WP**	2	10				
8/1/2007	**WP**	2	20				
8/1/2007	**WP**	2	30				
8/1/2007	**WP**	2	50				
8/1/2007	**WP**	2	80				
8/1/2007	**WP**	2	110				
8/1/2007	**WP**	2	150				
10/1/2007	**WP**	WC	0	18.6	7.3	29.2	18.1
10/1/2007	**WP**	1	10	19.7	2.2	26.6	16.3
10/1/2007	**WP**	1	20	19.6	1.3	21.8	13.2
10/1/2007	**WP**	1	30	20.1	1.1	20.6	12.4
10/1/2007	**WP**	1	50	20.8	0.7	22.4	13.5
10/1/2007	**WP**	1	80	21.5	0.6	23.6	14.3
10/1/2007	**WP**	1	110	21.6	0.4	26.2	16.0
10/1/2007	**WP**	1	150	21.7	0.2	27.1	16.7
10/1/2007	**WP**	2	10	20.2	0.7	22.7	13.7
10/1/2007	**WP**	2	20	20.7	0.6	26.4	16.2
10/1/2007	**WP**	2	30	21.2	0.2	26.2	16.0
10/1/2007	**WP**	2	50	21.3	1.6	25.9	15.9
10/1/2007	**WP**	2	80	22.0	1.1	25.7	15.7
10/1/2007	**WP**	2	110	21.9	1.0	23.5	14.2
10/1/2007	**WP**	2	150	22.0	0.5	25.3	15.4
9/18/2008	**WP**	WC	0	26.8	4.7	29.4	18.2
9/18/2008	**WP**	1	10	26.8	2.2	29.0	17.9
9/18/2008	**WP**	1	20	26.2	1.4	27.1	16.6
9/18/2008	**WP**	1	30	26.4	0.9	28.0	17.1
9/18/2008	**WP**	1	50	26.8	1.1	28.2	17.3
9/18/2008	**WP**	1	80	27.0	0.7	29.1	18.0
9/18/2008	**WP**	1	110	27.0	0.6	31.9	19.8
9/18/2008	**WP**	1	150	26.7	0.5	32.6	20.3
9/18/2008	**WP**	2	10	26.6	0.5	26.8	16.4
9/18/2008	**WP**	2	20	26.6	0.7	27.3	16.7
9/18/2008	**WP**	2	30	26.8	0.3	26.7	16.3
9/18/2008	**WP**	2	50	27.0	0.6	26.8	16.4
9/18/2008	**WP**	2	80	27.0	0.6	28.3	17.4
9/18/2008	**WP**	2	110	26.8	0.7	30.0	18.5
9/18/2008	**WP**	2	150	26.4	0.6	30.2	18.7

Appendix C. Porewater nutrient concentrations for each depth sampled.

Date	Site	Piezometer	Depth (cmbsf)	NH4+ (uM)	NO3- (uM)	SRP (uM)	TP (uM)	TOC (ppm)	TKN ($\mu g\ L^{-1}$)
6/13/2007	**MB**	WC	0	7.5	0.3	0.3	1.0	9.0	776
6/13/2007	**MB**	1	10	185.6		6.0	3.5	25.3	3276
6/13/2007	**MB**	1	30	163.0		6.5	3.4	26.3	2918
6/13/2007	**MB**	1	60	133.1		6.4	4.1	25.6	2622
6/13/2007	**MB**	1	90	136.4		5.9	2.8	25.2	2638
6/13/2007	**MB**	1	120	169.6		5.2	3.0	27.4	2940
6/13/2007	**MB**	1	150	218.7		5.4	3.0	29.3	3729
6/13/2007	**MB**	1	210	71.7		4.1	2.5	25.0	1762
6/13/2007	**MB**	2	10	134.6		3.9		18.5	2244
6/13/2007	**MB**	2	20	139.9		3.0	3.3	23.3	2397
6/13/2007	**MB**	2	30	162.2		6.2	3.9	26.0	2664
6/13/2007	**MB**	2	50	137.5		9.0	4.6	28.4	2799
6/13/2007	**MB**	2	80	129.6		7.9	5.0	28.4	2676
6/13/2007	**MB**	3	10	142.7	0.2		3.1	22.1	1676
6/13/2007	**MB**	3	20	179.9	0.0		5.2	23.1	2992
6/13/2007	**MB**	3	30	241.8	0.0		6.4	26.5	4163
6/13/2007	**MB**	3	50	146.5	0.0		2.2		2459
6/13/2007	**MB**	3	80	251.5	0.0			28.8	4146
6/13/2007	**MB**	3	110	154.6	0.0			28.3	3692
6/13/2007	**MB**	3	140	222.6	0.0		2.3	28.0	2924
8/16/2007	**MB**	WC	0	1.5	0.3	0.9			904
8/16/2007	**MB**	1	10	171.1		2.7	2.8	21.7	3025
8/16/2007	**MB**	1	30	162.7		4.3	5.6	24.8	3571
8/16/2007	**MB**	1	60	156.8		3.1	3.6	25.9	3179
8/16/2007	**MB**	1	90			3.3	3.2	26.3	3089
8/16/2007	**MB**	1	120	166.0		3.4		26.7	3354
8/16/2007	**MB**	1	150	241.5		3.2	3.5	29.0	4290
8/16/2007	**MB**	1	210	89.4		2.6	2.7	24.1	1887
8/16/2007	**MB**	2	10	130.5		2.7	4.9	20.4	3096
8/16/2007	**MB**	2	20	173.8		3.4	4.7	21.2	3331
8/16/2007	**MB**	2	30	179.9		4.6	4.1	19.2	3461
8/16/2007	**MB**	2	50	147.7		4.6	5.4	25.2	3258

Date	Site	Piezometer	Depth (cmbsf)	NH4+ (uM)	NO3- (uM)	SRP (uM)	TP (uM)	TOC (ppm)	TKN ($\mu g\ L^{-1}$)
8/16/2007	**MB**	2	80	141.2		4.6	3.8	1.6	
8/16/2007	**MB**	3	10	223.6		6.7	6.9	24.9	4510
8/16/2007	**MB**	3	20			7.7		27.3	5004
8/16/2007	**MB**	3	30	246.3		6.5	5.8	25.9	3700
8/16/2007	**MB**	3	50	221.0		4.7	4.3		4194
8/16/2007	**MB**	3	80	253.6		3.9	3.1	25.4	4531
8/16/2007	**MB**	3	110	232.3		3.3	1.0	24.4	4381
8/16/2007	**MB**	3	140			3.0		25.0	3257
1/16/2008	**MB**	WC	0	10.1	8.9	0.3	1.5		735
1/16/2008	**MB**	1	10	135.1	0.5		3.4		
1/16/2008	**MB**	1	30	124.2	0.2	3.0	3.1		
1/16/2008	**MB**	1	60	121.8	0.2	3.1	3.2		
1/16/2008	**MB**	1	90	122.4	0.3	2.3	2.7		
1/16/2008	**MB**	1	120	138.0	0.2	3.1	3.6		
1/16/2008	**MB**	1	150	211.8	0.2	4.0			
1/16/2008	**MB**	1	210	71.5	0.1	3.0	2.0		
1/16/2008	**MB**	2	10	109.7		2.4	3.3		
1/16/2008	**MB**	2	20	112.0			2.9		
1/16/2008	**MB**	2	30	131.8		4.6	3.2		
1/16/2008	**MB**	2	50	110.8		1.7	3.5		
1/16/2008	**MB**	2	80	117.5			3.1		
1/16/2008	**MB**	3	10	157.2		1.2	4.1		2626
1/16/2008	**MB**	3	20	177.7			4.4		3952
1/16/2008	**MB**	3	30	183.2			3.8		3762
1/16/2008	**MB**	3	50	171.4			2.9		3319
1/16/2008	**MB**	3	80	210.6		17.8	2.5		4131
1/16/2008	**MB**	3	110	197.3			2.5		3383
1/16/2008	**MB**	3	140	141.6		3.0	1.8		2684
4/18/2008	**MB**	WC	0	2.5			1.0		
4/18/2008	**MB**	1	10	123.0			2.2		
4/18/2008	**MB**	1	30	112.0			2.9		
4/18/2008	**MB**	1	60	104.2			4.1		
4/18/2008	**MB**	1	90	112.6			2.9		

Date	Site	Piezometer	Depth (cmbsf)	NH4+ (uM)	NO3- (uM)	SRP (uM)	TP (uM)	TOC (ppm)	TKN ($\mu g\ L^{-1}$)
4/18/2008	**MB**	1	120	138.4			3.0		
4/18/2008	**MB**	1	150	205.6			2.9		
4/18/2008	**MB**	1	210	76.9			2.3		
4/18/2008	**MB**	2	10						
4/18/2008	**MB**	2	20						
4/18/2008	**MB**	2	30						
4/18/2008	**MB**	2	50						
4/18/2008	**MB**	2	80						
4/18/2008	**MB**	3	10	138.2			3.1		
4/18/2008	**MB**	3	20	145.6			3.4		
4/18/2008	**MB**	3	30	151.6			4.4		
4/18/2008	**MB**	3	50	150.5			3.4		
4/18/2008	**MB**	3	80	188.2			2.5		
4/18/2008	**MB**	3	110	175.3			2.2		
4/18/2008	**MB**	3	140	125.0			1.8		
8/18/2008	**MB**	WC	0	1.2	0.2				
8/18/2008	**MB**	1	10	345.1	0.1				
8/18/2008	**MB**	1	30	141.4	0.0				
8/18/2008	**MB**	1	60		0.0				
8/18/2008	**MB**	1	90	144.9	0.0				
8/18/2008	**MB**	1	120		0.0				
8/18/2008	**MB**	1	150	196.4	0.0				
8/18/2008	**MB**	1	210		0.0				
8/18/2008	**MB**	2	10						
8/18/2008	**MB**	2	20						
8/18/2008	**MB**	2	30						
8/18/2008	**MB**	2	50						
8/18/2008	**MB**	2	80						
8/18/2008	**MB**	3	10	139.9	0.0				
8/18/2008	**MB**	3	20	157.0	0.0				
8/18/2008	**MB**	3	30	160.3	0.0				
8/18/2008	**MB**	3	50	153.4	0.0				
8/18/2008	**MB**	3	80	185.5	0.0				
8/18/2008	**MB**	3	110	196.2	0.0				

Date	Site	Piezometer	Depth (cmbsf)	NH4+ (uM)	NO3- (uM)	SRP (uM)	TP (uM)	TOC (ppm)	TKN ($\mu g\ L^{-1}$)
8/18/2008	**MB**	3	140	120.5	0.0				
6/21/2007	**CP**	MW		2.0	0.5	0.4		1.1	118
6/21/2007	**CP**	WC	0	0.7	0.0	0.7		7.8	512
6/21/2007	**CP**	2	10	52.8	0.0	0.5	0.8	8.6	900
6/21/2007	**CP**	2	20	39.4	0.3	0.3	1.3	5.6	697
6/21/2007	**CP**	2	30	31.1	0.0	0.2	0.7	4.1	420
6/21/2007	**CP**	2	50	19.9	0.0	0.1	0.7	3.5	213
6/21/2007	**CP**	2	80	25.5	0.0	0.2	2.0	3.0	409
6/21/2007	**CP**	2	110	16.9	0.0	0.2	1.8	3.0	223
6/21/2007	**CP**	2	140	12.2	0.1	0.1	1.1	1.7	126
6/21/2007	**CP**	3	10	88.7	0.0	0.8	1.1	8.8	1711
6/21/2007	**CP**	3	20	64.1	0.0	1.5	1.3	7.7	1117
6/21/2007	**CP**	3	30	45.5	0.4	1.7	3.5	7.7	1042
6/21/2007	**CP**	3	50	45.8	0.1	0.4	1.9	5.9	824
6/21/2007	**CP**	3	65	45.6	0.0	1.0	1.0	5.8	814
6/21/2007	**CP**	4	10	53.2	0.0	4.0	2.8	6.7	1154
6/21/2007	**CP**	4	30	27.3	0.0	0.3	2.2	2.7	504
6/21/2007	**CP**	4	50	20.4	0.0	0.2	1.9	1.7	249
6/21/2007	**CP**	4	80	21.5	0.0	0.1	1.0	1.6	287
6/21/2007	**CP**	4	110	9.9	0.0	0.4	1.6	2.6	138
6/21/2007	**CP**	4	150	10.4	0.4	0.5	1.9	1.4	183
6/21/2007	**CP**	4	190	9.0	0.5	0.3	1.8	1.2	151
6/21/2007	**CP**	4	230	15.0	0.4	0.4	4.7	2.0	282
8/9/2007	**CP**	MW		2.0	0.4	0.5	2.3	7.4	34
8/9/2007	**CP**	WC	0	0.7		0.9	2.3	1.3	713
8/9/2007	**CP**	2	10	52.8		0.9	1.3	7.5	527
8/9/2007	**CP**	2	20	39.4		0.3	0.9	6.2	638
8/9/2007	**CP**	2	30	31.1		0.3	0.8	5.2	738
8/9/2007	**CP**	2	50	19.9		0.1	0.5	3.3	426
8/9/2007	**CP**	2	80	25.5		0.1	0.9	2.6	509
8/9/2007	**CP**	2	110	16.9		0.1	1.2	3.7	251
8/9/2007	**CP**	2	140	12.2		0.3	1.0	2.2	116
8/9/2007	**CP**	3	10	88.7		1.5	2.3	9.0	1162

Date	Site	Piezometer	Depth (cmbsf)	NH4+ (uM)	NO3- (uM)	SRP (uM)	TP (uM)	TOC (ppm)	TKN ($\mu g\ L^{-1}$)
8/9/2007	**CP**	3	20	64.1		1.6	2.1	7.2	1056
8/9/2007	**CP**	3	30	45.5		1.8	2.1	7.7	1016
8/9/2007	**CP**	3	50	45.8		0.4	1.5	6.9	611
8/9/2007	**CP**	3	65	45.6		0.3	1.0	7.0	955
8/9/2007	**CP**	4	10	77.9	0.0	0.0	2.2	4.6	1507
8/9/2007	**CP**	4	30	22.2	0.0	0.6	1.4	2.4	365
8/9/2007	**CP**	4	50	17.9	0.0	0.3	1.7	1.8	436
8/9/2007	**CP**	4	80	15.0	0.0	0.1	0.9	2.1	228
8/9/2007	**CP**	4	110	6.6	0.0	0.2	1.4	1.3	91
8/9/2007	**CP**	4	150	3.8	0.0	0.4	0.9	0.9	78
8/9/2007	**CP**	4	190	5.0	0.0	0.3	1.4	1.2	86
8/9/2007	**CP**	4	230	5.3	0.3	0.3	3.1	0.9	131
10/12/2009	**CP**	MW		0.9	0.5	0.4	4.5	2.7	91
10/12/2009	**CP**	WC	0	1.6	0.0	0.3	1.4	23.2	768
10/12/2009	**CP**	2	10	11.9		0.7	1.1	6.6	634
10/12/2009	**CP**	2	20	26.6		0.3	1.0	5.9	520
10/12/2009	**CP**	2	30	26.6		0.2	0.9	6.0	
10/12/2009	**CP**	2	50	27.7		0.1	0.5	3.7	599
10/12/2009	**CP**	2	80	31.0		0.2	0.8	3.5	657
10/12/2009	**CP**	2	110	22.9		0.1	1.3	3.6	529
10/12/2009	**CP**	2	140	15.6		0.3	1.0	2.3	189
10/12/2009	**CP**	3	10	2.4		0.5	1.2	7.5	608
10/12/2009	**CP**	3	20	12.6		1.1	1.4	7.1	552
10/12/2009	**CP**	3	30	15.3		1.3	1.8	6.3	
10/12/2009	**CP**	3	50	30.7		0.2	1.2	6.2	661
10/12/2009	**CP**	3	65	24.1		0.2	0.8	5.8	291
10/12/2009	**CP**	4	10	21.8	0.0	0.7	1.5	5.5	571
10/12/2009	**CP**	4	30	12.9	0.0	0.2	1.4	2.1	269
10/12/2009	**CP**	4	50	19.1	0.0	0.1	1.3	2.3	
10/12/2009	**CP**	4	80	11.7	0.1	0.2	1.2	2.1	233
10/12/2009	**CP**	4	110	3.7	0.0	0.1	1.4	1.9	80
10/12/2009	**CP**	4	150	1.8	0.5	0.1	0.8	1.3	
10/12/2009	**CP**	4	190	0.6	0.4	0.1	1.0	1.0	46
10/12/2009	**CP**	4	230	0.8	0.4	0.2	1.6	2.0	136

Date	Site	Piezometer	Depth (cmbsf)	NH4+ (uM)	NO3- (uM)	SRP (uM)	TP (uM)	TOC (ppm)	TKN ($\mu g\ L^{-1}$)
1/4/2009	**CP**	MW		3.5	0.4	0.3	2.5		68
1/4/2009	**CP**	WC	0	1.6		0.1	0.6		491
1/4/2009	**CP**	2	10	9.8		0.4	0.6		
1/4/2009	**CP**	2	20	22.4		0.2	0.8		
1/4/2009	**CP**	2	30	23.3		0.2	0.7		
1/4/2009	**CP**	2	50	13.8		0.1	0.6		
1/4/2009	**CP**	2	80	26.2		0.3	0.7		
1/4/2009	**CP**	2	110	10.0		0.2	1.3		
1/4/2009	**CP**	2	140	9.2		0.4	1.2		
1/4/2009	**CP**	3	10	7.0		0.3	0.7		
1/4/2009	**CP**	3	20	14.8		0.8	1.1		
1/4/2009	**CP**	3	30	22.7		1.2	1.6		
1/4/2009	**CP**	3	50	19.0		0.2	1.0		
1/4/2009	**CP**	3	65	22.4		0.2	0.8		
1/4/2009	**CP**	4	10	8.2	0.3	0.4	1.1		234
1/4/2009	**CP**	4	30	5.3	0.2	0.3	2.1		126
1/4/2009	**CP**	4	50	6.8		0.2	1.1		125
1/4/2009	**CP**	4	80	2.9	0.3	0.4	1.0		44
1/4/2009	**CP**	4	110	3.8	0.3	0.3	1.3		11
1/4/2009	**CP**	4	150	1.8	0.4	0.2	0.7		35
1/4/2009	**CP**	4	190	1.6	0.5	0.1	0.9		45
1/4/2009	**CP**	4	230	2.2	0.4	0.2	1.0		24
4/29/2008	**CP**	MW		0.1			0.9		
4/29/2008	**CP**	WC	0	3.7			1.3		
4/29/2008	**CP**	2	10	3.7	0.1		2.2		
4/29/2008	**CP**	2	20	17.0	0.1		1.0		
4/29/2008	**CP**	2	30	20.3	0.1		1.4		
4/29/2008	**CP**	2	50	10.1	0.1		0.3		
4/29/2008	**CP**	2	80	19.1	0.1		0.5		
4/29/2008	**CP**	2	110	19.0	0.1		0.6		
4/29/2008	**CP**	2	140	10.0	0.5		0.6		
4/29/2008	**CP**	3	10	2.9					
4/29/2008	**CP**	3	20	6.9			0.8		
4/29/2008	**CP**	3	30	22.4			1.7		
4/29/2008	**CP**	3	50	23.1			2.2		

Date	Site	Piezometer	Depth (cmbsf)	NH4+ (uM)	NO3- (uM)	SRP (uM)	TP (uM)	TOC (ppm)	TKN ($\mu g\ L^{-1}$)
4/29/2008	**CP**	3	65	21.8			0.6		
4/29/2008	**CP**	4	10	23.7	0.1		1.4		
4/29/2008	**CP**	4	30	3.7	0.0		2.2		
4/29/2008	**CP**	4	50	3.3	0.0		0.6		
4/29/2008	**CP**	4	80	4.3	0.0		0.6		
4/29/2008	**CP**	4	110	2.6	0.0		0.6		
4/29/2008	**CP**	4	150	0.6	0.3		0.7		
4/29/2008	**CP**	4	190	1.2	0.3		1.0		
4/29/2008	**CP**	4	230	18.8	0.3		2.2		
9/28/2008	**CP**	MW		0.6					
9/28/2008	**CP**	WC	0	1.0					
9/28/2008	**CP**	2	10						
9/28/2008	**CP**	2	20						
9/28/2008	**CP**	2	30						
9/28/2008	**CP**	2	50						
9/28/2008	**CP**	2	80						
9/28/2008	**CP**	2	110						
9/28/2008	**CP**	2	140						
9/28/2008	**CP**	3	10	1.2					
9/28/2008	**CP**	3	20	4.3					
9/28/2008	**CP**	3	30	19.2					
9/28/2008	**CP**	3	50	23.4					
9/28/2008	**CP**	3	65	22.3					
9/28/2008	**CP**	4	10	9.3					
9/28/2008	**CP**	4	30	8.6					
9/28/2008	**CP**	4	50	19.7					
9/28/2008	**CP**	4	80	30.1					
9/28/2008	**CP**	4	110	12.9					
9/28/2008	**CP**	4	150	2.9					
9/28/2008	**CP**	4	190	1.3					
9/28/2008	**CP**	4	230	2.2					
6/27/2007	**WP**	WC	0	1.0					
6/27/2007	**WP**	1	10	97.5	0.0	4.5	3.5	7.8	1817

Date	Site	Piezometer	Depth (cmbsf)	NH4+ (uM)	NO3- (uM)	SRP (uM)	TP (uM)	TOC (ppm)	TKN ($\mu g\ L^{-1}$)
6/27/2007	**WP**	1	20	132.4	0.0	5.8	5.2	7.1	1862
6/27/2007	**WP**	1	30	97.9	0.0	4.8	3.8	6.9	1525
6/27/2007	**WP**	1	50	104.2	0.0	5.5	3.5	7.0	1526
6/27/2007	**WP**	1	80	144.9	0.0	6.0	4.3	7.8	2012
6/27/2007	**WP**	1	110	135.2	0.0	4.4	3.9	7.4	1892
6/27/2007	**WP**	1	150	116.9	0.0	3.9	3.1	6.8	1733
6/27/2007	**WP**	2	10	176.6	0.0	5.9	4.4	7.2	2514
6/27/2007	**WP**	2	20	148.6	0.0	0.4	3.5	7.0	2172
6/27/2007	**WP**	2	30	136.2	0.0	2.0	4.5	7.3	1980
6/27/2007	**WP**	2	50	146.7	0.0	4.0	3.7	7.4	2047
6/27/2007	**WP**	2	80	139.9	0.0	4.5	3.7	7.1	1956
6/27/2007	**WP**	2	110	133.4	0.0	4.3	3.3	6.7	1843
6/27/2007	**WP**	2	150	132.3	0.0	3.6	3.3	7.3	1813
8/1/2007	**WP**	WC	0	1.4			2.0	6.9	716
8/1/2007	**WP**	1	10	80.9		3.5	4.1	6.3	1772
8/1/2007	**WP**	1	20	60.4		3.0		5.9	1888
8/1/2007	**WP**	1	30	91.8		2.3	4.2	6.4	1992
8/1/2007	**WP**	1	50	79.1		3.5	3.2	5.7	1977
8/1/2007	**WP**	1	80	58.6		3.8	5.3	6.4	1923
8/1/2007	**WP**	1	110	109.8		3.6	4.4	6.4	1652
8/1/2007	**WP**	1	150	86.0		3.7	3.3		2115
8/1/2007	**WP**	2	10	130.2		3.5	3.5	6.8	1317
8/1/2007	**WP**	2	20	134.1		2.5	4.1	6.3	1083
8/1/2007	**WP**	2	30	159.4		4.6	3.7	6.2	1231
8/1/2007	**WP**	2	50	152.4		3.1		6.7	1053
8/1/2007	**WP**	2	80	139.2		4.7	3.8	6.3	1335
8/1/2007	**WP**	2	110	149.1		4.2	3.9	6.3	1608
8/1/2007	**WP**	2	150	151.8		3.3	3.9	6.2	
10/1/2007	**WP**	WC	0		0.1	0.3	0.9	8.1	642
10/1/2007	**WP**	1	10		0.0	1.5	2.0	6.5	850
10/1/2007	**WP**	1	20		0.0	3.0	3.7	5.8	1432
10/1/2007	**WP**	1	30		0.0	3.8	3.8	6.0	928
10/1/2007	**WP**	1	50		0.0	2.3	5.2	5.3	1187

Date	Site	Piezometer	Depth (cmbsf)	NH4+ (uM)	NO3- (uM)	SRP (uM)	TP (uM)	TOC (ppm)	TKN ($\mu g\ L^{-1}$)
10/1/2007	**WP**	1	80		0.0	4.6	4.3	6.8	1514
10/1/2007	**WP**	1	110		0.0	3.6	4.2	6.2	1434
10/1/2007	**WP**	1	150		0.0	4.1	3.7	5.8	1293
10/1/2007	**WP**	2	10		0.0	2.8	3.8	5.7	2118
10/1/2007	**WP**	2	20		0.0	2.5	3.4	5.9	
10/1/2007	**WP**	2	30		0.0	1.6	2.3	6.0	1605
10/1/2007	**WP**	2	50		0.0	2.7	3.3	5.8	
10/1/2007	**WP**	2	80		0.0	2.5	2.7	7.5	1918
10/1/2007	**WP**	2	110		0.0	2.6	2.9	6.2	1939
10/1/2007	**WP**	2	150		0.0	2.9	3.8	6.2	1348
9/18/2008	**WP**	WC	0	2.0	0.0				
9/18/2008	**WP**	1	10	27.5	0.0				
9/18/2008	**WP**	1	20	112.8	0.0				
9/18/2008	**WP**	1	30	86.4	0.0				
9/18/2008	**WP**	1	50	92.8	0.0				
9/18/2008	**WP**	1	80	108.5	0.0				
9/18/2008	**WP**	1	110	69.9	0.0				
9/18/2008	**WP**	1	150	103.9	0.0				
9/18/2008	**WP**	2	10	142.0					
9/18/2008	**WP**	2	20	148.6					
9/18/2008	**WP**	2	30	121.7					
9/18/2008	**WP**	2	50	118.2					
9/18/2008	**WP**	2	80	115.7					
9/18/2008	**WP**	2	110	115.6					
9/18/2008	**WP**	2	150	132.3					