

Abstract

David F. Harnsberger. URBAN CHANNEL INCISION, WATER TABLE DECLINE, AND NITRATE ATTENUATION IN FLOODPLAIN AQUIFERS, GREENVILLE, NC (Under the direction of Dr. Michael O'Driscoll) Department of Geological Sciences, March 2009

Water table decline in riparian areas has been linked to the incision of urban stream channels by increased stormwater runoff. The contact of riparian groundwater with shallow, organic-rich surface soils in riparian zones of both urban and agricultural watersheds may be affected by channel incision. Therefore, channel incision has notable implications for nitrate (NO_3^-) attenuation via denitrification and plant uptake in groundwater of riparian, floodplain areas of urban watersheds. In this study, three sediment cores (nine cores total; 3.5 to 6.9 m depth) were collected across transects in the floodplains of three progressively incised, low-order Coastal Plain streams. Standard loss on ignition (LOI) method was used to assess changes in percent organic matter (% OM) with depth for the full length of each core. Three well transects were installed in line with floodplain transects to determine if water table decline adjacent to incised Coastal Plain streams notably impacts the contact of floodplain groundwater and shallow organic matter (OM). The impact of water table decline on NO_3^- -attenuation in floodplain aquifers was also assessed. Water samples were collected monthly from eighteen monitoring wells (six per site) from October, 2007 to September, 2008 and were analyzed for nitrate-N (NO_3^- -N), ammonium-N (NH_4^+ -N), dissolved organic carbon (DOC), and dissolved oxygen (DO).

Results of this investigation suggest organic matter in riparian areas is not confined to the upper few centimeters of riparian sediment profiles in low-order Coastal Plain

watersheds. Buried soil horizons and isolated hotspots of OM were found in 8 of 9 cores at depths of 54 to 230 cm. Despite the occurrence of deep and laterally extensive peat layers at the urban and suburban sites, water table decline caused a notable reduction in contact between floodplain groundwater and shallow organic matter at the urban and suburban sites. Though groundwater-organic matter contact was reduced adjacent to incised channels, buried peats contributed high (> 6 mg/L) concentrations of DOC to floodplain groundwater. High DOC concentrations in association with low DO concentrations (< 1 mg/L) provided conditions suitable for denitrification across all three floodplain aquifers.

Median NO_3^- -attenuation (decrease, loss and/or retention) values ($N = 12/\text{site}$) were calculated as a percent difference in monthly NO_3^- -N concentrations between up-gradient and near-stream locations for each floodplain study site. NO_3^- -N concentrations were attenuated 99%, 58%, and 46% at the rural, suburban, and urban floodplain sites. This decrease in percentage NO_3^- -attenuation with increasing near-stream water table depth (0.82 m, 0.99 m, and 1.47 m for the rural, suburban, and urban sites) suggests that water table decline and impaired NO_3^- -attenuation across the urban and suburban floodplains may be related. Though near-stream NO_3^- -N concentrations were significantly higher at the incised study sites than at the rural site, they were low in comparison to near-stream concentrations in unbuffered agricultural settings of the US and Canada. Marked variability in groundwater discharge from each floodplain, caused by variable hydraulic conductivity of floodplain sediments at each site, prevented a clear relationship between water table decline and the loading of NO_3^- to surface water at each site.

URBAN CHANNEL INCISION, WATER TABLE DECLINE, AND NITRATE
ATTENUATION IN FLOODPLAIN AQUIFERS, GREENVILLE, NC

A Thesis

presented to

the Faculty of the Department of Geological Sciences

East Carolina University

In Partial Fulfillment

of the requirements for the Degree

Master of Science in Geology

By

David F. Harnsberger

2009

URBAN CHANNEL INCISION, WATER TABLE DECLINE, AND NITRATE
ATTENUATION IN FLOODPLAIN AQUIFERS, GREENVILLE, NC

by

David F. Harnsberger

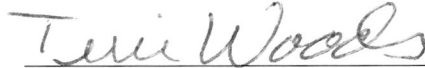
Approved By:

Director of Thesis



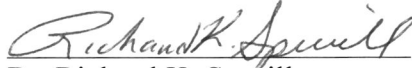
Dr. Michael A. O'Driscoll
Assistant Professor
ECU Dept. of Geological Sciences

Committee Member



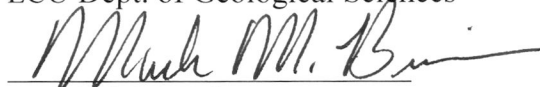
Dr. Terri Woods
Associate Professor
ECU Dept. of Geological Sciences

Committee Member



Dr. Richard K. Spruill
Associate Professor
ECU Dept. of Geological Sciences

Committee Member



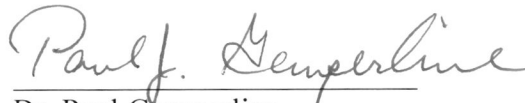
Dr. Mark M. Brinson
Professor
ECU Dept. of Biology

Chair of the ECU Dept.
of Geological Sciences



Dr. Stephen J. Culver

Dean of the
Graduate School



Dr. Paul Gemperline

Acknowledgements

First and foremost, I would like to thank my thesis advisor, Dr. Mike O'Driscoll. His support in helping to design the project, conduct field work, and provide edits on the many draft versions of preliminary work and this document has been invaluable.

Next, I would like to thank the NC Water Resources Research Institute (WRRI) and the NC Ecosystem Enhancement Program (EEP) for providing funding to purchase equipment and for helping to fund the water sample analyses.

Thirdly, I would like to extend a most formal thanks to my thesis committee. They provided valuable feedback on the original proposal of this project and helped me avoid major problems in the design and implementation of the original concept. Their feedback on the many drafts of this document has also been invaluable. Thanks specifically to Dr. Brinson for convincing me that I was not going to be able to core straight into the channel sediments of Fornes Branch, to Dr. Spruill for helping interpret the odd hydrology at the rural site and for his demand that the document be condensed, and to Dr. Woods for lending us her filtration equipment.

Also critical to the completion and success of this project were the many faculty and grad students of the ECU Geological Sciences Department. ECU Geological Sciences faculty that were instrumental include: John Woods, Jim Watson, Dare Merrit, Dr. Reide Corbett, Dr. JP Walsh, and Dr. Steve Culver. ECU grad students that deserve special thanks include: John DeLoatch, Jason Soban, Brion Byers, Kolt Johnson, Laura

McKenna, Reanna Camp, Lauren Metger, Emma Hardison, David Vandervelde, Brad Elkins, Dani Dominique, Rob Howard, David Lagomasino, and Andrew Dietsche.

Thanks specifically to Pete Parham for providing draft versions of the lateral transects from his work in the Coastal Plain of Eastern NC. Transects presented herein are based on his transects. Thanks to Becky Cooper for her help with the NO_3^- -N and NH_4^+ -N analyses, and to Jesse Chadwick at GUC for running 12 months of DOC analyses for us. Thanks also to the homeowners who provided access to their urban, floodplain riparian zones with little to no good understanding for what exactly we were up to.

Finally special thanks to my parents. Without their moral and financial support, I probably would not have been able to finish. Thank you parents!

Table of Contents

List of Figures.....	vi
List of Tables.....	viii
Introduction	1
Study Design	9
STUDY AREA AND GEOLOGIC SETTING	9
<i>Coastal Plain Geology</i>	9
<i>Coastal Plain Hydrology</i>	12
FLOODPLAIN GEOLOGY	14
WELL TRANSECTS AND TRANSECT STRATIGRAPHY	16
WATER CHEMISTRY	19
DATA ANALYSIS.....	22
Results	24
FLOODPLAIN HYDROGEOLOGY	24
FLOODPLAIN GROUNDWATER LEVELS AND TEMPERATURE.....	28
HYDRAULIC GRADIENTS AND GROUNDWATER DISCHARGE	32
GROUNDWATER AND SURFACE WATER CHEMISTRY	35
<i>Dissolved inorganic-N concentrations</i>	35
<i>DOC and DO concentrations</i>	43
<i>Chloride concentrations</i>	47
STATISTICAL RELATIONSHIPS	48
FLOODPLAIN NO ₃ ⁻ -ATTENUATION AND LOADING TO INCISED STREAM CHANNELS	52
Discussion.....	55
CHANGES IN ORGANIC MATTER WITH DEPTH	55
EFFECTS OF DECLINE ON OM CONTACT	55
EFFECTS OF WATER TABLE DECLINE ON NO ₃ ⁻ -ATTENUATION.....	58
COMPARISON TO PREVIOUS STUDIES	63
Conclusions and Management Recommendations.....	68
FLOODPLAIN N-REMOVAL IS AFFECTED BY DECLINING WATER TABLES	69

References	71
Appendix A: Summary Statistics of Measured Variables	80
Appendix B: Electroconductivity Response Logs.....	96
Appendix C: Sediment Core Logs.....	103
Appendix D: Percent Organic Matter Data	113
Appendix E: Hydrologic Data.....	116
Appendix F: Water Quality Data.....	119
Appendix G: Monthly Water Chemistry Data.....	121

List of Figures

Figure 1. Schematic of the nitrogen cycle showing plant and microbial processes that convert N between its various end members.	4
Figure 2. Study site location map showing well transect locations and study site subwatersheds.	10
Figure 3. Correlation of sediment electrical conductivity (EC) log with sediment core taken at the location of the near-stream well nest of the urban study site showing conductive response of peat, sandy sediments, and packed wet clay.	15
Figure 4. Sample layout diagram showing location, orientation, and spacing of well transect at the urban study site.	17
Figure 5. Hydrogeology of study transects at the urban, suburban and rural sites showing framework geology, seasonal high (marked ‘H’) water table on 4/12/2008, and seasonal low (marked ‘L’) water table on 10/5/2007.	25
Figure 6. Vertical distribution of % OM based LOI processing of samples from floodplain sediment cores of each study site.	27
Figure 7. Near-stream water table depths measured in deep, near-stream wells of each of the study sites from 9/14/2007 to 9/4/2008.	29
Figure 8. Monthly groundwater levels (m AMSL) from the shallow up-gradient (U) and near-stream (N) wells of the A) urban, B) suburban and C) rural sites.....	31
Figure 9. Monthly hydraulic gradient across the floodplains of the three study sites from 10/5/2007 to 9/5/2008.....	33
Figure 10. Monthly discharge of floodplain groundwater from 10/5/2007 to 9/5/2008 based on a 100 m cross-sectional stream reach.	34
Figure 11. Study site transects at the urban, suburban, and rural sites showing median nitrate-N and ammonium-N (mg/L) values measured in wells at the near-stream, floodplain, and up-gradient locations.	37
Figure 12. Shallow, deep, and in-stream nitrate-N concentrations from the A) urban, B) suburban, and C) rural floodplains for the one year study period.	38
Figure 13. Groundwater and surface water ammonium-N concentrations (mg/L) across the A) urban, B) suburban, and C) rural floodplains for the one year study period.	39

Figure 14. Median nitrate-N, median ammonium-N, and DON (mg/L) from 5/30/2008 in A) shallow and B) deep wells of the urban floodplain.	40
Figure 15. Median nitrate-N, median ammonium-N, and DON (mg/L) from 5/30/2008 in A) shallow and B) deep wells of the suburban floodplain.	41
Figure 16. Median nitrate-N, median ammonium-N, and DON (mg/L) from 5/30/2008 in A) shallow and B) deep wells of the rural floodplain.	42
Figure 17. Study site transects of the urban, suburban and rural sites showing median annual DOC, DO values from shallow and deep wells of the three study sites.	44
Figure 18. Plot of screen depth below water table vs. median DOC from groundwater samples over the duration of the study period.	45
Figure 19. Median well DO concentrations vs. screen depth for floodplain wells of each of the study sites.	46
Figure 20. Median well DO (ppm) concentrations vs. dist. (m) of wells from the stream edge at each site.	46
Figure 21. Correlations between nitrate-N and dissolved oxygen (DO) at the urban, suburban, and rural sites.	49
Figure 22. Correlations between nitrate-N and dissolved organic carbon (DOC) at the urban, suburban, and rural sites.	50
Figure 23. Monthly percent difference in NO_3^- -N concentrations (%) over twelve months of chemical data at the urban, suburban and rural sites.	53
Figure 24. Seasonality graphs showing variability in A) NO_3^- loading (g/mo), B) average near-stream NO_3^- -N concentrations (mg/L), and C) discharge (m^3/mo) across the three floodplains.	54

List of Tables

Table 1. Annual hydraulic gradients from up-gradient to near-stream wells across floodplains of each site.	33
Table 2. Descriptive statistics for annual discharge from each floodplain.	34
Table 3. Percent difference in median groundwater chloride concentrations (N = 6 months of chloride data) from up-gradient to near-stream wells across each floodplain..	47
Table 4. Pearson correlation coefficients for bivariate correlation of monthly groundwater (gw) levels (m AMSL) and monthly groundwater concentrations (mg/L) from shallow floodplain wells (N1 and N2 locations) of each site.	51
Table 5. Median NO ₃ ⁻ concentrations and percentage attenuation (- = loss, + = gain) in floodplain, riparian groundwater estimated from studies conducted in agricultural catchments of the central United States, eastern United States, and Canada.	65

Introduction

Anthropogenic activity in coastal watersheds has greatly altered the nitrogen (N) cycle and has significantly accelerated the delivery of N in both organic and inorganic forms to coastal water bodies (Anderson et al., 2002; Boyer et al., 2002; and Howarth et al., 2002). Eutrophication, and associated harmful algal blooms lead to fish kills, increased abundance of toxic algae species, and more frequent anoxic conditions of coastal water bodies (Anderson et al., 2002; Burkholder, 2000). Eutrophication continues to be the single largest pollution problem in coastal rivers and bays of the US (Howarth et al., 2002; National Research Council, 2000). For most coastal water systems, non-point source contribution of nutrients in the form of surface runoff and groundwater inputs from developed watersheds is the single largest contributor of N to coastal waters (Howarth et al., 2002).

Though agriculture has been shown to be a major source of N in many coastal watersheds (Howarth et al., 2002), a considerable body of evidence suggests that urban watersheds may also contribute elevated levels of N to receiving coastal waters (Boyer et al., 2002; Groffman et al., 2002; Paul and Meyer, 2001). Boyer et al. (2002) have suggested that even small shifts in land use in forested catchments can cause large increases in annual nitrogen export. In their study of 16 catchments across a latitudinal profile from Maine to Virginia, urban land use was shown to increase the mass of N applied to the surface area of a catchment. They demonstrated a positive correlation between “disturbed” land use and total N loading, indicating the importance of

urbanization, in addition to agriculture, as a large human-derived source of N to coastal watersheds.

In a review of urban land-use effects on streams, Walsh et al. (2005) recognized several symptoms of “the urban stream syndrome.” Most important to this study is the condition of elevated concentrations of in-stream nutrients. The sources of elevated in-stream nutrient concentrations in urban catchments include: 1) elevated wet and dry deposition of atmospheric N (Howarth et al., 2002; Anderson et al., 2002), 2) N-based fertilizer application (Boyer et al., 2002), 3) legacy pollutants (nutrients sourced in fertilizer from past agricultural land use) in urban groundwater (Walsh et al., 2005), 4) biological fixation of elevated atmospheric N (Boyer et al., 2002), and 5) import of N in food for humans and feed for animals (Boyer et al., 2002). Though considerable efforts have been made to reduce the amount of N in both organic and inorganic forms that is transferred to streams, N inputs due to sources such as atmospheric deposition and legacy pollutants are difficult and/or expensive to control (Walsh et al., 2005).

In addition to the sources of elevated nutrient concentrations in urban streams being numerous and highly variable, several pathways of migration from source to stream exist. Of primary concern to this study is the likelihood of increased concentrations of inorganic-N in urban groundwater. Dissolved inorganic-N in urban groundwater may be elevated due to: 1) N-based fertilizer application to residential yard space, 2) the persistence of legacy pollutants from past agricultural land uses, and 3) discharge, leakage, and overflow from sewage infrastructure.

NO_3^- is the species of inorganic-N that has received the most attention for its role in limiting or exacerbating eutrophic conditions in coastal water bodies (Howarth et al., 2002). Background NO_3^- -N concentrations in streams and groundwater systems vary spatially and temporally, related to regional N-deposition and ecosystem N-retention (Stoddard 1994). In a review of NO_3^- -N concentration data obtained from the U.S. Geological Survey's National Water-Data Storage and Retrieval System (WATSTORE), Madison and Burnett (1985) attempted to obtain a national perspective on the extent to which nitrate concentrations in groundwater of the United States had been elevated by anthropogenic activity. Data from 87,000 wells throughout the United States obtained from WATSTORE, and an additional 36,000 wells obtained from the Texas Natural Resource Information System (TNRIS) were analyzed. A concentration of more than 3 mg/L was arbitrarily defined as the average, background concentration of NO_3^- -N in groundwater of the US (Madison and Burnett, 1985). The use of this "background concentration" as an average NO_3^- -N concentration for unpolluted natural groundwaters of the US may be conservative, since 50% of samples assessed in Madison and Burnett's study had concentrations below detection limits (Spalding and Exner 1993; USEPA 1990). The maximum NO_3^- -N concentration established by the EPA as safe for drinking water (the Maximum Contaminant Level or MCL) is 10 mg/L (USEPA 2003).

The cycling of N in streams is closely linked to biologic processes in riparian areas and channel sediments (Figure 1). In riparian areas, N_2 fixation, which is mediated by N-fixing bacteria, may provide N-inputs to urban groundwater. N-fixing bacteria form symbiotic associations with plant roots and are free living (Duff and Triska, 2000). Most

of the N that is fixed by N-fixing bacteria is assimilated by riparian vegetation, and is later released to streams as throughfall, leachate from litterfall, or by decomposition of plant tissue (Duff and Triska, 2000; Wetzel, 1975). Organic matter (OM) in decomposed plant tissues of riparian soils is further decomposed by heterotrophic bacteria that convert organically bound N to NH_4^+ via the bacterially mediated process of ammonification. In aerobic soils, free NH_4^+ is converted to NO_3^- by nitrifying bacteria in a two step process called nitrification. First, NH_4^+ is converted to nitrite (NO_2^-), and then NO_2^- is converted to NO_3^- (Vepraskas and Faulkner, 2001).

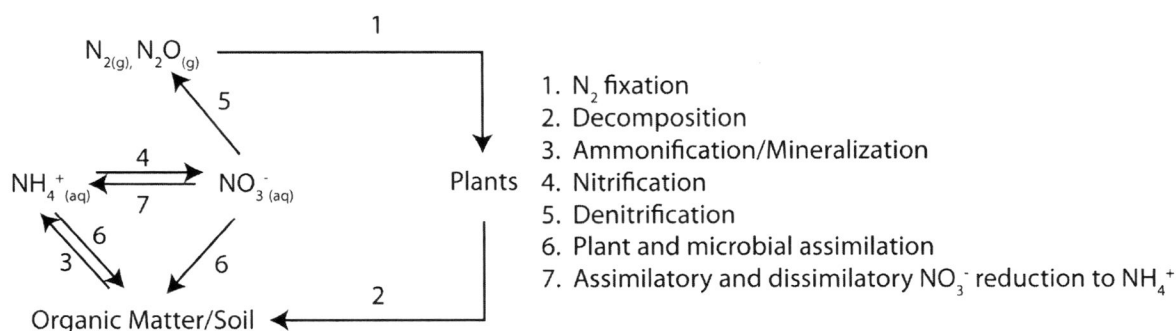


Figure 1. Schematic of the nitrogen cycle showing plant and microbial processes that convert N between its various end members. Only processes that occur specifically in floodplain, fresh water environments are shown.

Because NO_3^- that is produced by nitrifying bacteria is mobile and easily transported (Duff and Triska, 2000; Jones et al, 1995; Holmes et al., 1994) it often moves through floodplain sediments to anoxic sites, locations or zones of the floodplain environment where it can be denitrified. Denitrification is the bacterially mediated redox reaction where bacteria reduce NO_3^- to N_2 or N_2O gas as a result of electron transfer. In hydric soils (soils formed under conditions of saturation), DOC compounds leached from

organic substrates often provide electrons for denitrification (Vepraskas and Faulkner, 2001; Ponnampetuma, 1972). Denitrification is important in riparian zones because it is one of the only bacterially mediated processes in the nitrogen cycle that effectively removes N from groundwater and streams. Because redox conditions control denitrification, the occurrence of denitrification in floodplain groundwater is often limited to locations in floodplain aquifers where anoxic conditions exist (Vepraskas and Faulkner, 2001). Studies by Denver et al. (2004) and Bohlke et al. (2002) suggest that denitrification is inhibited when groundwater dissolved oxygen (DO) concentrations are $> 1.9 \text{ mg/L}$. NO_3^- in groundwater may also be assimilated back into plant and microbial biomass (microbial assimilation). In hypoxic environments, NO_3^- may be reduced to NH_4^+ by both assimilatory nitrate reduction to ammonium (ANRA), where NH_4^+ produced by the process is incorporated into cellular material, and dissimilatory nitrate reduction to ammonium (DNRA), where NH_4^+ produced by the process is excreted back to the hydric environment.

In floodplain aquifers where conditions fluctuate between oxic and anoxic, denitrification is often effective at removing $\text{NO}_3^- \text{N}$. NO_3^- for denitrification in floodplain aquifers is often: 1) imported by infiltrating rain water, 2) input by overbank flow from flooding stream channels, and/or 3) input by groundwater from upland areas of Coastal Plain watersheds (Denver et al. 2004; Bohlke and Denver, 1995). When NO_3^- enters a zone of anoxia and labile organic matter, denitrification is initiated. NO_3^- may also be generated by nitrification of NH_4^+ in oxic surface soils when precipitation introduces new water to the floodplain groundwater system. NO_3^- generated by

nitrification in shallow, oxic groundwater is denitrified when it is advectively transported by groundwater to anoxic microsites of the floodplain aquifer (Patrick and Tusneem, 1972) or when dry periods of relatively little precipitation in low-order watersheds allow floodplain aquifers to become anoxic (Bohlke et al. 2007).

Various studies have shown that high potential denitrification (DNP) rates in organic-rich soils are often confined to the upper few centimeters of the riparian sediment profile (Schoonover and Willard, 2003; Groffman et al., 2002; Burt et al., 1999; Groffman et al., 1996). More recent work by Gurwick et al. (2008) and Hill et al. (2004) suggests that organic-rich soils and associated high DNP can occur at depths of up to 300 cm in riparian sediment, though there is a question as to whether the carbon produced by buried soil horizons is available (labile) for microbial metabolic processing. Organic matter in surface and buried, organic-rich soils plays an important role for N-cycle dynamics in floodplain groundwater, for two main reasons: 1) it supplies floodplain groundwater with DOC (Baker et al., 2000; Hill, 2000; O'Brien et al., 1994; Dosskey and Bertsch, 1994) that can act as an electron donor to promote denitrification (Hill et al., 2004; Groffman et al., 2002; Burt et al., 1999), and 2) it provides NH_4^+ (via OM mineralization) to soil water and floodplain groundwater (Hill, 2000; McLain et al., 1994; McDowell et al., 1992) that can be nitrified under aerobic conditions to increase groundwater NO_3^- concentrations.

Stormwater runoff in urban watersheds has led to significant incision of stream channels in various geographic settings (Soban, 2007; Paul and Meyer, 2001; Henshaw and Booth, 2000). Stream channel incision, in turn, has caused significant decline of

water tables adjacent to incised stream channels (Hardison, 2008; Groffman et al., 2003; Groffman et al., 2002). The decline of water tables across riparian zones in urban catchments has been coined “riparian hydrologic drought” by Groffman et al. (2003), and has important implications for nitrate attenuation (the net percentage decrease in NO_3^- concentrations across a riparian zone that typically results from mechanisms that both increase and decrease NO_3^- concentrations) in urban, floodplain groundwater (Kaushal et al., 2008; Groffman et al., 2003; Groffman et al., 2002; Gold et al. 2001). The established effects of water table decline on hydrogeochemical conditions in floodplain sediments and aquifers are three-fold: 1) considerable alteration in the hydrologic and geochemical condition of unsaturated, surface soils (Groffman, 2003), 2) decreased contact of floodplain groundwater with organic-rich surface soils that have high denitrification potential (Bohlke et al., 2007; Groffman et al., 2003; Groffman et al., 2002; Gold et al. 2001), and 3) the preferential forcing of groundwater flow to deeper hydrologic flowpaths across floodplain aquifers, where nitrate derived from upland aquifers is less likely to be denitrified or taken up by riparian vegetation (Bohlke et al., 2007; Groffman et al., 2003; Gold et al., 2001).

In a study of the effects of water table decline on shallow soil chemistry, Groffman et al. (2002) suggested that urban hydrologic factors can increase the production and decrease the consumption of NO_3^- in urban settings. Schilling et al. (2006) have suggested that NO_3^- concentration increases in groundwater samples from wells across the floodplain of their study may have been caused by the leaching and transport of NO_3^-

from unsaturated soil during a single large storm event that occurred during the three months of their investigation.

The primary objective of this study was to determine the effects of water table decline on NO_3^- -attenuation in floodplain aquifers of incised urban streams of the Greenville area. Specifically, the following hypotheses were tested: 1) organic matter in riparian sediment profiles will be concentrated at shallow depths (0-30 cm), 2) water table decline adjacent to incised urban streams will reduce contact between floodplain groundwater and surface organic-rich soil, and 3) water table decline across floodplain aquifers adjacent to incised urban streams will cause less NO_3^- to be attenuated from floodplain aquifers.

Study Design

Study area and geologic setting

This study focused on floodplains at selected locations in the catchments of three low-order streams (small streams with very few tributaries) of the Tar River Basin, which have undergone various degrees of urban development. Fornes Branch (FB), Meeting House Branch (MHB), and Phillippi Branch (PB) (Figure 2) were classified as urban, suburban, and rural respectively based on the percent of surface area classified as impervious area (Total Impervious Area or TIA) in each catchment. TIA percentages were calculated for each catchment during a previous study using impervious cover data from the City of Greenville and the National Land Cover Database (Hardison, 2008) to be 37% (urban), 22.1% (suburban), and 4% (rural), respectively.

Coastal Plain Geology

The study area (Figure 2) resides within the Inner Coastal Plain of eastern North Carolina (NC). At the surface, the Coastal Plain is characterized by a series of relict coastal terraces that slope gently towards the sea separated by scarps that run parallel to the coast (Maddry, 1979). In the Greenville area, surface terraces are underlain by a vast, thick, and laterally extensive wedge of unconsolidated sediment that has been roughly categorized by Maddry (1979) into 5 hydrogeologic units: the Black Creek, Pee Dee, Beaufort, Castle Hayne, and Yorktown formations. Overlying the Yorktown is a relatively thin section (~ 10 m; Winner and Coble, 1996) of Quaternary sediment that includes the floodplain unit examined in this work.

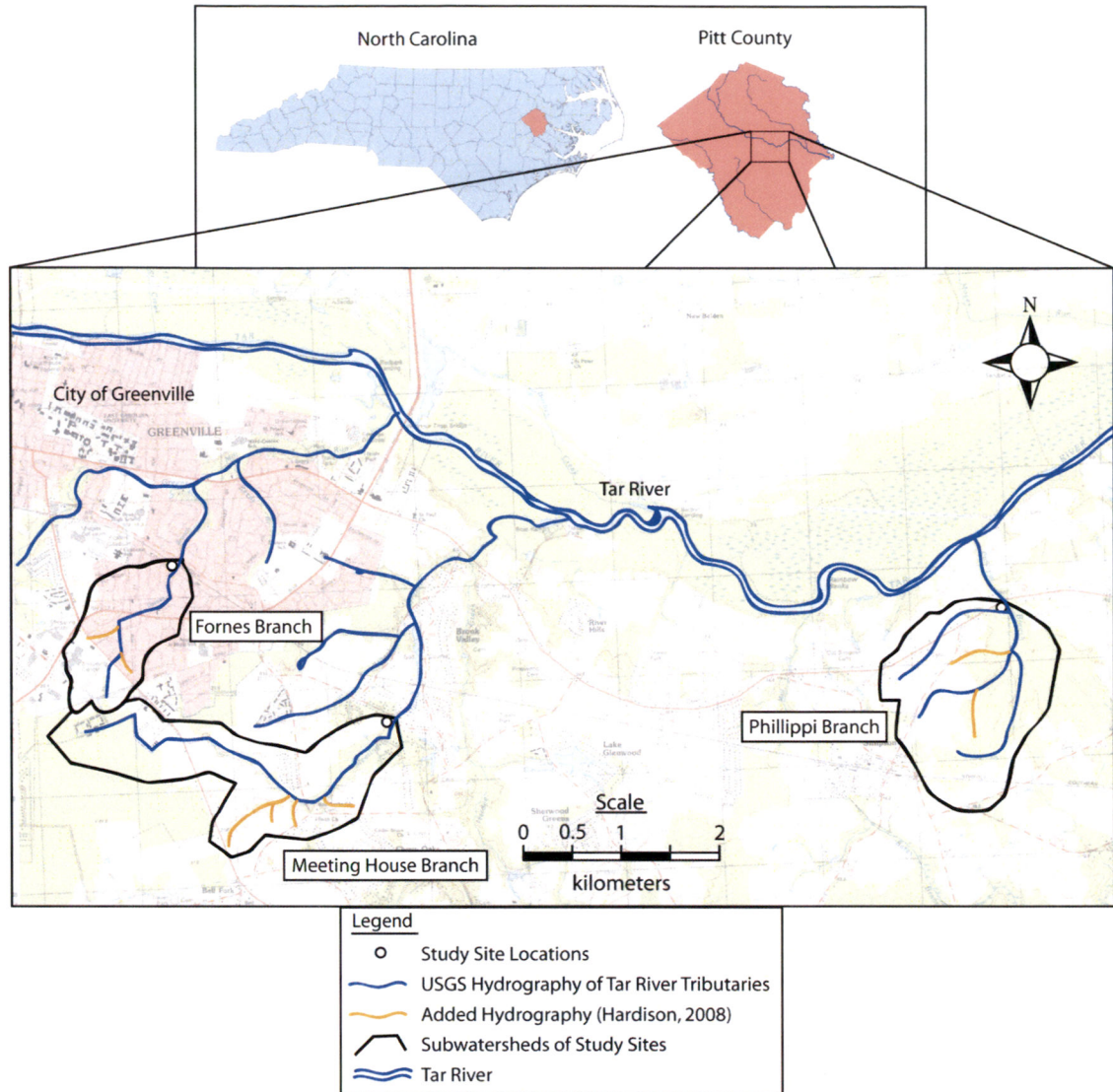


Figure 2. Study site location map showing well transect locations and study site subwatersheds. Hydrography added by Hardison (2008) is based on field observations. Background image is a cropped portion of the Greenville SE, 7.5" USGS Topographic Quadrangle, obtained using Terrain Navigator Pro 7.5.

The uppermost section of the Yorktown frequently occurs as a thick, bluish gray, low-permeability clay (Lautier, 2001). The continuity and lateral extent of the confining clay of the Yorktown is important to geochemical processing of nitrate in unconfined, floodplain aquifers. In eastern Pitt County, the area of this study, the Yorktown confining unit is composed of alternating silt and clay layers and is roughly 1 to 22 m thick, with an average thickness of 7 m (Winner and Coble, 1996). Maddry (1979) has suggested that the Yorktown was likely deposited during the transgressive portion of a single cyclostratigraphic cycle. Relict channel deposits offshore of Virginia and North Carolina that cut into and through the Yorktown (Shideler and Swift, 1972), suggest that during the regressive portion of the cyclostratigraphic cycle responsible for the deposition of the Yorktown, the silts and clays of the Yorktown were left exposed to erosion and fluvial seaward transport. Finally, Maddry suggests that during a more recent marine transgression, a thin section of terrigenous, clastic sediments was deposited by both marine and fluvial processes.

Maddry separates these Quaternary clastic sediments into 6 distinct stratigraphic units which he labels Q₁-Q₆. Q₁ and Q₂ are described as a transgressive sequence of sedimentary units that occur in interstream areas south of the Tar River and presumably away from the floodplain aquifers of this study. Q₃ is classified into four units based on stratigraphic descriptions that closely resemble the stratigraphy of sediment encountered during this study. Q_{3a} is described as a fine to coarse, sand unit with basal pebble-sized sediment and isolated clay-rich lenses. Dark to light green glauconite grains with cracks and spaces between grains filled with a dark-reddish-brown iron oxide occurred in the

sand of Q_{3a}. Q_{3b} and Q_{3c} are described as organic-rich clays and sands that contain abundant plant debris and occur in select locations of Eastern Pitt County. Q_{3d} is described as organic-rich sand that occurs at or near the surface with a maximum depth of burial of about two meters. Maddry suggests that the shallow depth of burial and fresh appearance of the plant remains in Q_{3d} provide evidence of it being a recent floodplain deposit less than 8000 years old. Maddry explains that Q₃ as a sequence was deposited in stream valleys tributary to the Tar River that are likely the same valleys filled by floodplain sediments encountered during this study.

Coastal Plain Hydrology

The hydrogeologic units of the Coastal Plain sediment wedge discussed above consist of permeable sand, gravel, and limestone aquifers separated by confining units composed of lower permeability clays (Winner and Coble, 1996). Recharge to these aquifers begins as rainfall that infiltrates to the surficial aquifer at interstream areas, moves down through underlying confining units, and then permeates back through the same confining units to discharge to floodplains and streams of the NC Coastal Plain (Winner and Coble, 1996). Annual rainfall estimates for the Greenville area suggest that approximately 137 cm of rain fall in Pitt County each year, with a mean annual air temperature of about 17.4 C (Southeast Regional Climate Center, 2007). Rainfall for the year of this study (110 cm; October, 2007 to October, 2008) was below average due to extreme drought conditions into the late summer and fall of 2007. Mean annual air temperature was 17.1 C.

The combined annual discharge of groundwater from deeper confined aquifers to surficial aquifers and large, high order streams and rivers is approximately 1.3 cm per

year (Heath, 1975). For a watershed in Pitt, Beaufort and Craven counties, estimated average annual discharge of groundwater from the confined Castle Hayne Limestone unit was approximately 2.0 cm per year (Winner and Coble, 1996; Winner and Simmons, 1977). Discharge from the surficial aquifer occurs as direct discharge and/or seepage into streams, lakes and drainage ditches, evapotranspiration from shallow surficial soils and sediment, and upwelling through basal sediments of large rivers and estuaries (Winner and Coble, 1996).

Coastal Plain streams and rivers can be described as low-gradient, meandering systems that often develop broad floodplains that are subjected to frequent and prolonged inundation (Hupp, 2000). Using a partial-duration series of average daily discharge, Sweet and Geratz (2003) estimated that the average recurrence interval of bankfull discharge flows for streams in the Southeastern Plain ecoregion of the NC Coastal Plain is about 0.19 year, or about 5 bankfull events per year. According to Hupp (2000), medium and large streams of the south-eastern Coastal Plain have a strong seasonal variation in discharge driven by seasonal variation in evapotranspiration and rainfall. Hupp (2000) identifies two distinctly different hydrological seasons for Coastal Plain streams in their natural state: 1) a low-flow season from about June through to October, which is often interrupted by tropical storms or hurricanes (Brinson, 2009, pers. comm.) and 2) a high-flow season from about November through May, when large parts of adjacent floodplains are often inundated.

Generally speaking, at least 40% of the average annual streamflow in the NC Coastal Plain is derived from groundwater (Harden and Spruill, 2008; Harden et al., 2003; Spruill et al., 1998; Winner and Simmons, 1977). Some studies of streams in the Coastal Plain streams have found the groundwater component of surface water discharge to be on the order of 90% (Hutchinson, 2007; Williams and Pinder, 1990). Several studies in agricultural settings of the Coastal Plain have shown that surface water quality (concentrations of nutrients and contaminants in surface water) are notably influenced by groundwater quality (Harden and Spruill, 2008; Spruill, 2004; Tesoriero et al. 2004; Denver et al. 2004).

Floodplain geology

Framework geology for floodplain transects at the study sites was established via a combination of sediment electrical conductivity logging and sediment core comparison. A GeoprobeTM electro-conductivity sensor was used in conjunction with a GeoprobeTM direct push sediment sampling rig to conduct conductivity surveys based on a 4-6 point grid layout that typically extended 20 m by 30 m (Appendix B). Sediment electrical conductivity logs and sediment cores were correlated to identify peat, sand, and clay layers in the floodplains of the study sites (Figure 3). The sandy surficial aquifer was targeted for installation of three wells per floodplain. Groundwater levels measured in wells were used to calculate direction of groundwater flow at each proposed study site via standard three-point solution (Heath, 2004).

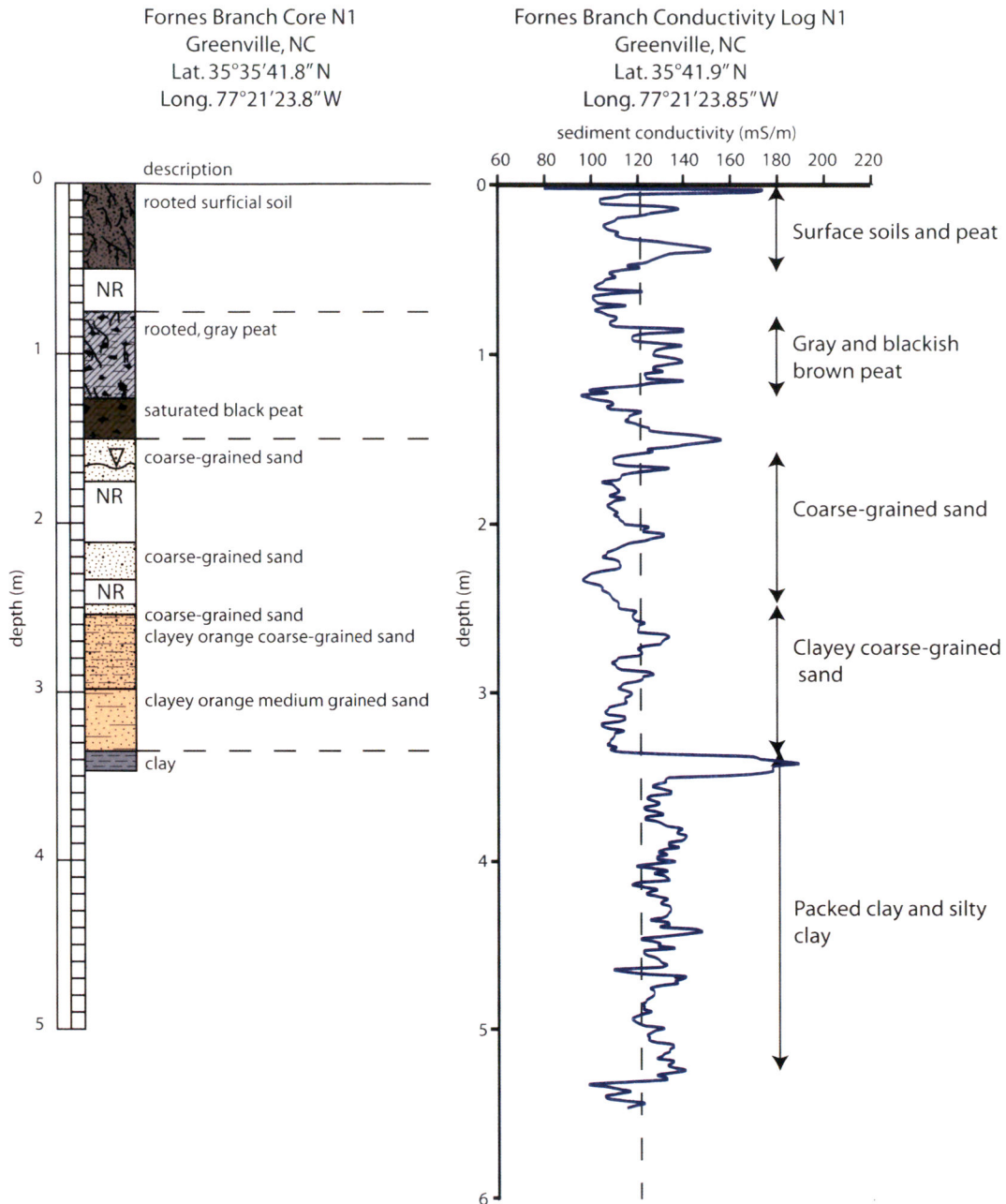


Figure 3. Correlation of sediment electrical conductivity (EC) log with sediment core taken at the location of the near-stream well nest of the urban study site showing conductive response of peat, sandy sediments, and packed wet clay. EC logs were used in conjunction with sediment cores to position well screens just below the water table and just above the confining unit for shallow and deep wells at each nest. Remaining EC logs are provided in Appendix B.

Well transects and transect stratigraphy

After calculating direction of groundwater flow according to standard three point procedure (Heath, 2004), nested well transects were established at each of the proposed study sites along distinct groundwater flowpaths. Transects extended from the floodplain edge or a short distance into the upland-floodplain interface to within 6 (± 1) meters of the stream edge at each of the study sites. Three nests of two wells each were installed across each of the floodplains. Nests were located 6 (± 1), 20 (± 1), and 34 (± 1) m from the banks at the urban (Figure 4) and rural sites and 5, 15, and 25 meters from the banks at the suburban site. Each nest consisted of wells constructed from PVC pipe (3.2 cm inner diameter) with 50 cm screens installed at variable depths between 1.7 and 6.5 m below ground, depending on the thickness of the unconfined aquifer. Wells at the N1 nest locations (Figure 4) closest to each stream are referred to hereafter as “near-stream” wells; wells at the floodplain, N2 locations are referred to as “floodplain” wells; and wells at the floodplain edge/upland, N3 locations are “up-gradient”.

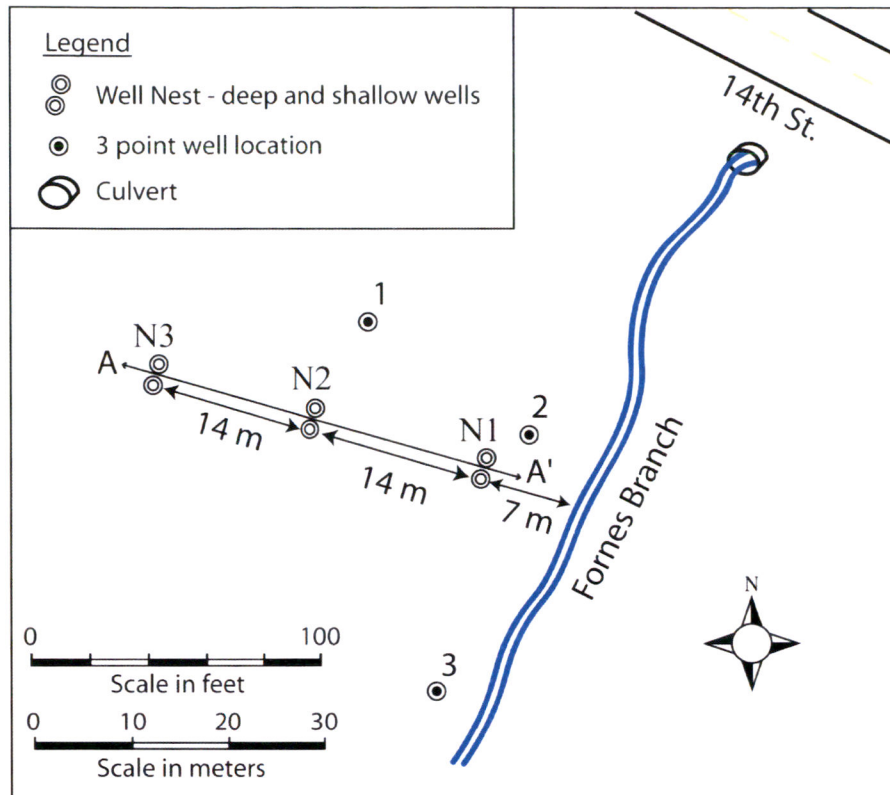


Figure 4. Sample layout diagram showing location, orientation, and spacing of well transect at the urban study site. Well nests consist of shallow and deep wells screened just below floodplain water tables and just above confining unit in sandy sediments of the unconfined aquifer. Wells at the N1 location are “near-stream” wells, wells at the N2 location are “floodplain” wells, and wells at the N3 location are “up-gradient” for the remainder of this manuscript. Spacing of wells for the calculation of groundwater flow direction is also shown.

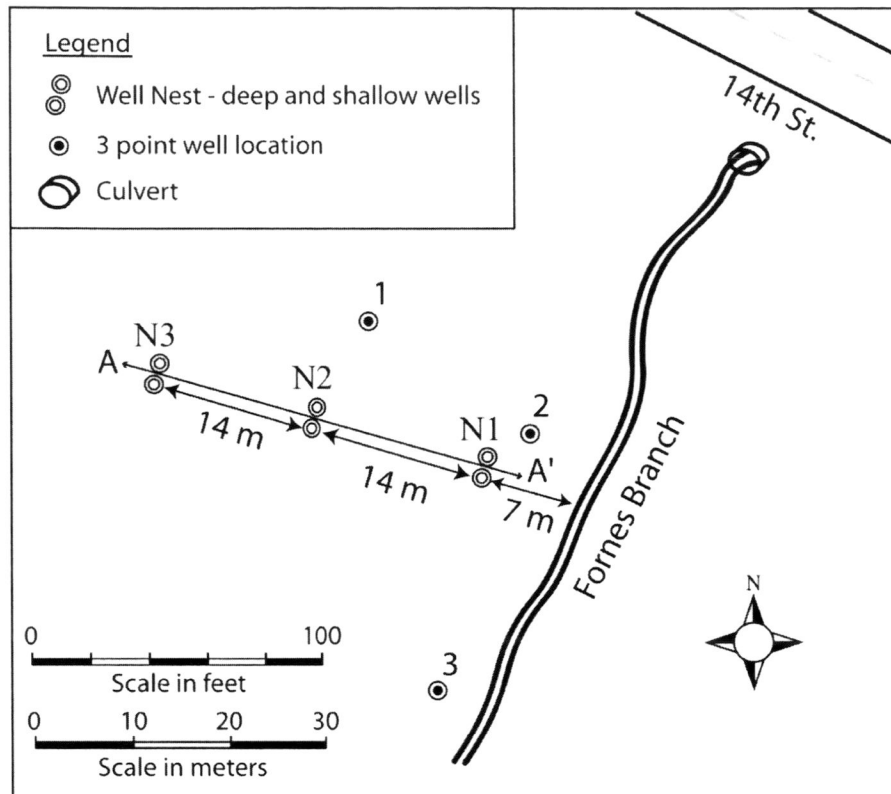


Figure 4. Sample layout diagram showing location, orientation, and spacing of well transect at the urban study site. Well nests consist of shallow and deep wells screened just below floodplain water tables and just above confining unit in sandy sediments of the unconfined aquifer. Wells at the N1 location are “near-stream” wells, wells at the N2 location are “floodplain” wells, and wells at the N3 location are “up-gradient” for the remainder of this manuscript. Spacing of wells for the calculation of groundwater flow direction is also shown.

Groundwater levels in transect wells were monitored monthly to estimate hydraulic gradients and to quantify groundwater contact with surface soil at each site. One groundwater logger in the shallow, near-stream well at each site recorded changes in floodplain groundwater levels at 0.5 hour increments. Monthly fluctuations in water table levels in shallow wells of each site were compared to depth of surface soils to quantify loss of contact between groundwater and organic-rich soil for the duration of the study period.

Ground-water discharge (Q) from floodplain sediments was estimated from monthly head measurements collected from October 5, 2007 to September 5, 2008. Darcy's law ($Q=KA \, dh/dl$) was used to quantify groundwater discharge, where K was the median site hydraulic conductivity, A was the cross-sectional area of the surficial aquifer at a site, and dh/dl was the hydraulic gradient across each floodplain. Cross-sectional area was determined for a 100 m length of floodplain sediment and an aquifer thickness based on monthly calculation of the height of the water table above the impermeable confining unit at the floodplain, N2 well locations of each transect (monthly aquifer thickness = depth to confining unit – water table depth in the shallow N2 well for a given month). Discharge estimates presented in this study represent an estimate of groundwater discharge to a 100 m length of each stream from floodplains adjacent to each of the study sites. Notable variation in K within floodplains of this study and throughout the catchments of each stream may cause discharge estimates presented in this manuscript to vary measurably from actual discharge at both the floodplains of this study and other discharge locations within each watershed. Slug tests were used to estimate floodplain K in all 6 wells at

each site (18 total) (Fetter, 1994; Bouwer and Rice, 1976). Monthly nitrate loading from the edge of each floodplain was calculated by multiplying the average near-stream nitrate concentration (average of concentrations from the shallow and deep near-stream wells at each site) by the monthly groundwater discharge calculated for a 100 m reach of each floodplain study site.

A single sediment core was taken at each well nest location (3 cores per site) for detailed stratigraphic analysis. The average core length was 4.5 m with a total of 60.2 m of sediment collected for this study. Organic profiles of stream cores were established by sampling cores at 25 cm increments from the floodplain surface to the core base and then processing discrete sediment samples according to standard loss on ignition technique (Soil and Plant Analysis Council, 1999). Percent Organic Matter (% OM) results were paired with simple lithologic descriptions of distinct sediment layers to establish detailed transects of the riparian stratigraphy at each study site.

Water chemistry

Groundwater and stream samples were collected monthly from October, 2007 through September, 2008. Three well volumes were purged from wells prior to sample collection. Surface water samples were collected normal to well transects during each monthly site visit. Surface water and groundwater samples were collected using small bailers and 200 mL opaque plastic bottles (NO_3^- -N and NH_4^+ -N), or amber glass bottles (DOC). Samples were stored in a cooler, and transported back to the Ragsdale geology lab where they were filtered (0.45 μm) and stored overnight at 4 C prior to analysis. In

rare cases where collected samples were heavily sediment-laden, samples were run first through a 1.25 μm 934-AH glass fiber filter, then through a 0.7 μm APFF glass fiber filter, and finally through the 0.45 μm membrane filter. Pre-filters were rinsed twice with ultra-pure DI water to prepare them for the pre-filtration process.

Monthly NO_3^- -N and NH_4^+ -N concentrations, and Kjeldahl-N concentrations for the sampling date of 5/30/2008 were measured at the Central Environmental Laboratory of East Carolina University (ECU) by Dr. Rebecca Cooper. NO_3^- -N concentrations were analyzed using a Westco Scientific SmartChem 200 analyzer according to SmartChem Method 375-100E-2-Rev.A-02-0906: “Nitrate-Nitrite in water, wastewater, soil extracts and other aqueous samples” (Westco Scientific, 2006a) with a lower limit of detection of 0.02 mg/L N. NH_4^+ -N concentrations were analyzed according to Method 4500-NH3-F: “Phenate Method” (APHA, 1998) with a lower limit of detection of 0.0014 mg/L N. Samples for Kjeldahl-N collected on 5/30/2008 were digested using a Westco Scientific AD4020 block digester and were then analyzed by a Westco Scientific SmartChem 200 analyzer according to SmartChem Method 390-200E-Rev.A-0906: “Total Kjeldahl Nitrogen (TKN) in Water, Waste Water, Soil Extracts and other aqueous samples” modified from Westco Scientific (2006b) for use with the AD4020 colorimetric, block digester. The lower limit of detection for this method was 0.10 mg/L TKN. DON values (mg/L) presented in the results section, were calculated by subtracting corresponding NH_4^+ -N concentrations from the assessed TKN values since $\text{TKN} = \text{DON} + \text{NH}_4^+$ -N (Westco Scientific, 2006b). In order to confirm the precision of the analytical techniques, 10 replicate sample pairs collected on 4/14/2008 were analyzed for NO_3^- -N and NH_4^+ -N

concentrations. Mean difference of the paired analyses indicated that, NO_3^- -N and NH_4^+ -N concentrations reported in this manuscript are within 0.002 mg/L and 0.001 mg/L N of each other respectively.

DOC concentrations were measured by Mr. Jesse Chadwick using a Teckmar Dorhmann Phoenix 8000 TOC analyzer at the main drinking water treatment plant of Greenville Utilities Commission (GUC). DOC was analyzed according to the method: *UV Persulfate procedure Method 5310C* (APHA, 2005) with a lower limit of detection of 0.02 mg/L. Samples analyzed for NO_3^- -N, NH_4^+ -N, Kjeldahl-N, and DOC with concentrations lower than the limit of detection are reported as 0.00 mg/L. Replicate analysis of groundwater samples (N = 8 pairs) collected on 11/14/2007 indicated that DOC concentrations reported in this manuscript are within 0.1 mg/L of each other on average.

Chloride (Cl^-), DO, and specific conductivity (SC) were measured using field meters. Chloride concentrations were obtained using a Nexsens WQ-Cl Smart USB ion-specific chloride electrode with a manufacturer's lower detection limit of 1.8 ppm. Dissolved oxygen (DO), specific conductivity (SC), and groundwater temperature (GT) were measured in-situ during monthly collection trips using YSI EcoSense DO200 and EC300 field meters with detection ranges of 0 to 20.00 ppm and 0.0 to 499.9 $\mu\text{S}/\text{cm}$, respectively. Analyzed samples with concentrations lower than the limit of detection are reported as 0.00 ppm for Cl^- and DO and 0.00 $\mu\text{S}/\text{cm}$ for SC.

Data analysis

Monthly difference in NO_3^- and Cl^- concentrations (estimated as a percent) at each site were estimated for groundwater flowpaths ranging in length from 20 to 28 m. Monthly percent differences were estimated for each floodplain according to the following equation:

$$\frac{(\text{near - stream } \text{NO}_3^- \text{ concentration} - \text{up - gradient } \text{NO}_3^- \text{ concentration})}{\text{up - gradient } \text{NO}_3^- \text{ concentration}} * 100\%$$

where:

near-stream NO_3^- concentration = NO_3^- or Cl^- concentration averaged from the near-stream (N1) shallow and deep wells at a site for a given month.

up-gradient NO_3^- concentration = NO_3^- or Cl^- concentration averaged from the up-gradient (N3) shallow and deep wells at a site for a given month, and

Median concentrations for the year were used to calculate annual percent difference in NO_3^- concentrations, hereafter referred to as NO_3^- -attenuation. Positive percent difference in constituent concentrations represents an increase in concentrations across a particular floodplain, where negative values represent a concentration decrease.

The influence of dilution on observed decreases in NO_3^- concentrations across each floodplain aquifer was determined by measuring percent difference in Cl^- concentrations from up-gradient to near-stream wells, since Cl^- is generally considered non-reactive in most fresh groundwater systems (Hill 2000; Altman and Parizek, 1995).

Bivariate correlation and Mann-Whitney-U comparisons were completed using Minitab v.15.1. Linear, and power regressions were completed using Microsoft Excel 2003. Twenty-two data sets grouped on specific hydrologic and chemical variables such as near-stream groundwater depth, and near-stream nitrate concentrations at each site were tested for normal distribution via a standard Anderson-Darling normality test. Of the 22 sets tested, only five data sets were determined to be normally distributed, none of which repeated for a single variable across all three sites. Thus, non-parametric Mann-Whitney-U comparison was used to determine if the medians of the hydrologic and chemical data sets were significantly different. Where bivariate correlations are presented, both Pearson correlation coefficient (r) and p-values are reported to distinguish bivariate results from Mann-Whitney-U results, which are represented with a single p-value. For both analyses, only p values ≤ 0.05 were considered statistically significant.

Results

Floodplain hydrogeology

The floodplain sediment distribution and groundwater flowpaths for the three study site transects based on floodplain sediment cores (Appendix C) are shown in Figure 5. Sediments of the unconfined aquifers at the three sites can be divided into five main groups: 1) rooted surficial soil and gravel, 2) clayey sand, 3) sandy loam, 4) peat, 5) coarse- to fine-grained sand, 6) densely packed clay. The regional clay that serves as a confining unit was encountered at all sites and ranged from 2.8 m depth at the near-stream nest of the urban site to 5.9 m depth at up-gradient nest of the rural site, with a median depth of 3.3 m (Figure 5). Saturated sandy aquifers at the three sites ranged in thickness from 1.3-2 m at the near-stream wells to upwards of 4.3 m at the up-gradient wells of the suburban site (Figure 5). The sand of these floodplain aquifers was typically overlain by 5-170 cm of organic-rich sediment at the surface, depending on the occurrence of buried peat across each floodplain. A subsurface peat layer occurred at both the urban and suburban sites. The peat at the urban site ranged in thickness from about 1 m at the N1 core to 1.8 m at the N3 core, was light gray to brownish black, ranged in % OM from about 4-49%, and contained abundant plant debris including roots and stems to 0.5 cm diameter. The peat at the suburban site was thinner, and less extensive being 1 meter thick at the N1 core and pinching out between cores N2 and N3. Peat at the suburban site was similar in color to peat at the urban site from light gray to black. It had a range of % OM from 2-26%, and plant roots and stems to 0.6 cm diameter.

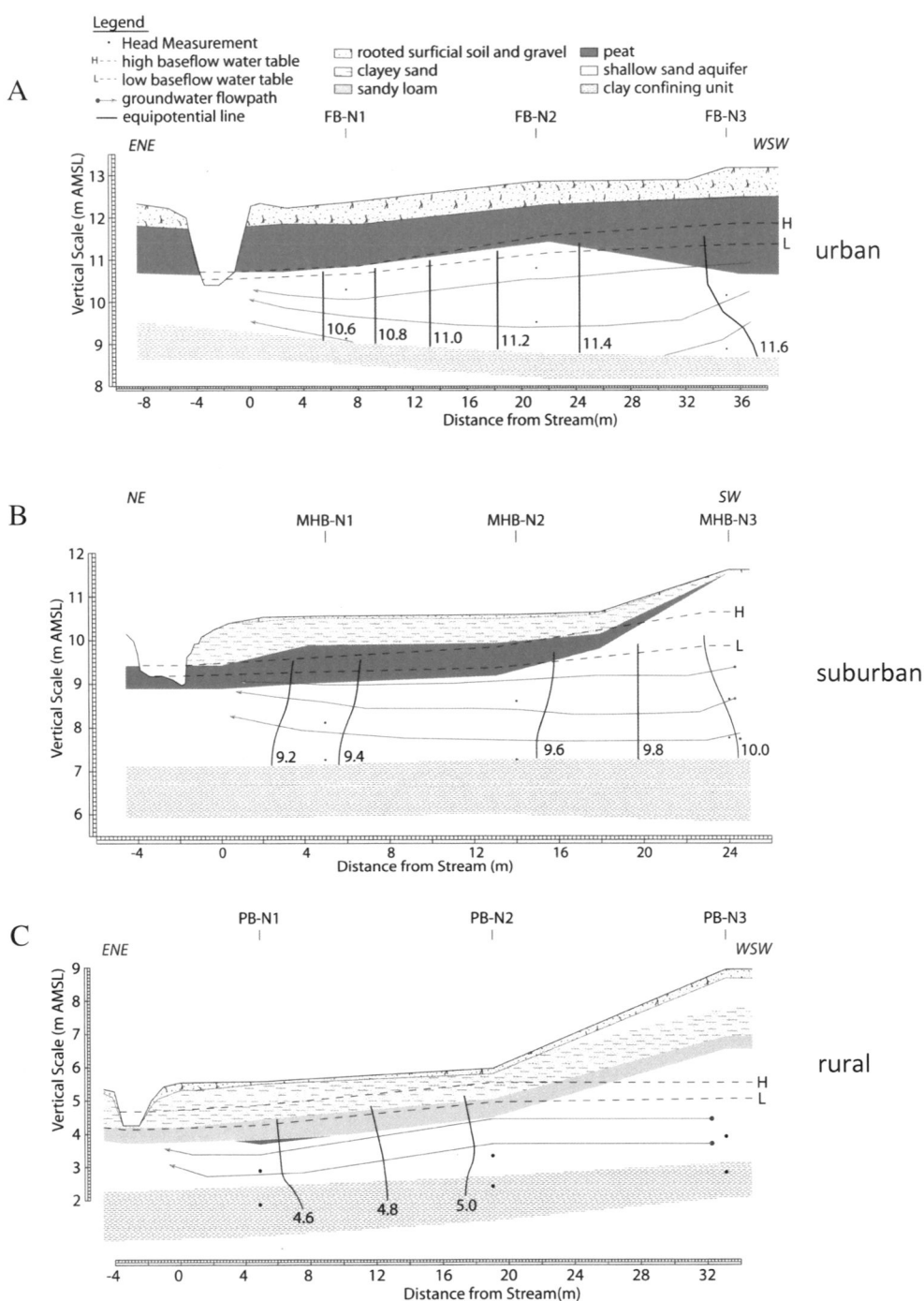


Figure 5. Hydrogeology of study transects at the urban, suburban and rural sites showing framework geology, seasonal high (marked ‘H’) water table on 4/12/2008, and seasonal low (marked ‘L’) water table on 10/5/2007. Also shown are well screen locations (black dots), and hydraulic head contours (m) for 1/8/2008. Labels above each transect show well nest locations. Arrows indicate inferred groundwater flowpaths.

Peats at both floodplains contained woody debris including fossilized bark, and thin sticks to 1 cm diameter that provide evidence of a forested floodplain environment. Peats were also interbedded from base to surface with thin lenses of fine-grained sand that were likely deposited by floods. An AMS radiocarbon date (1000 ± 40 Before Present (BP)) for the top of the peat layer at the suburban transect (MHB-N2, 0.8 m depth, Figure 5) yielded a 2σ calendar year calibration of 980 to 1060 Cal AD (“Anno Domini” - in the year of the lord). The 2σ calendar year calibration was calculated using the INTCAL04 calibration database (2004) as described by Talma and Vogel (1993).

Across each floodplain the greatest organic matter content (% OM) occurred at depths of 1 m or greater (Figure 6). Because of the absence of a thick peat layer at the rural site, floodplain sediments at the rural site showed less % OM at than the floodplain sediments at the urban and suburban sites. Very shallow soil layers (0-20 cm) showed slightly elevated % OM at all three sites (Figure 6). This pattern is less pronounced at the urban site, where shallow organic-rich soil grades directly into the underlying peat. A slight increase in % OM was observed in the samples taken from the confining unit of all three sites (Figure 6). The % OM peaks seen from 2-2.5 m at the suburban site (Fig. 5B, MHB-N1) and from 1.7 to 2 m at the rural site (Fig. 5C, PB-N1) represent isolated “hot-spots” of organic matter where woody debris and organic litter were sampled directly.

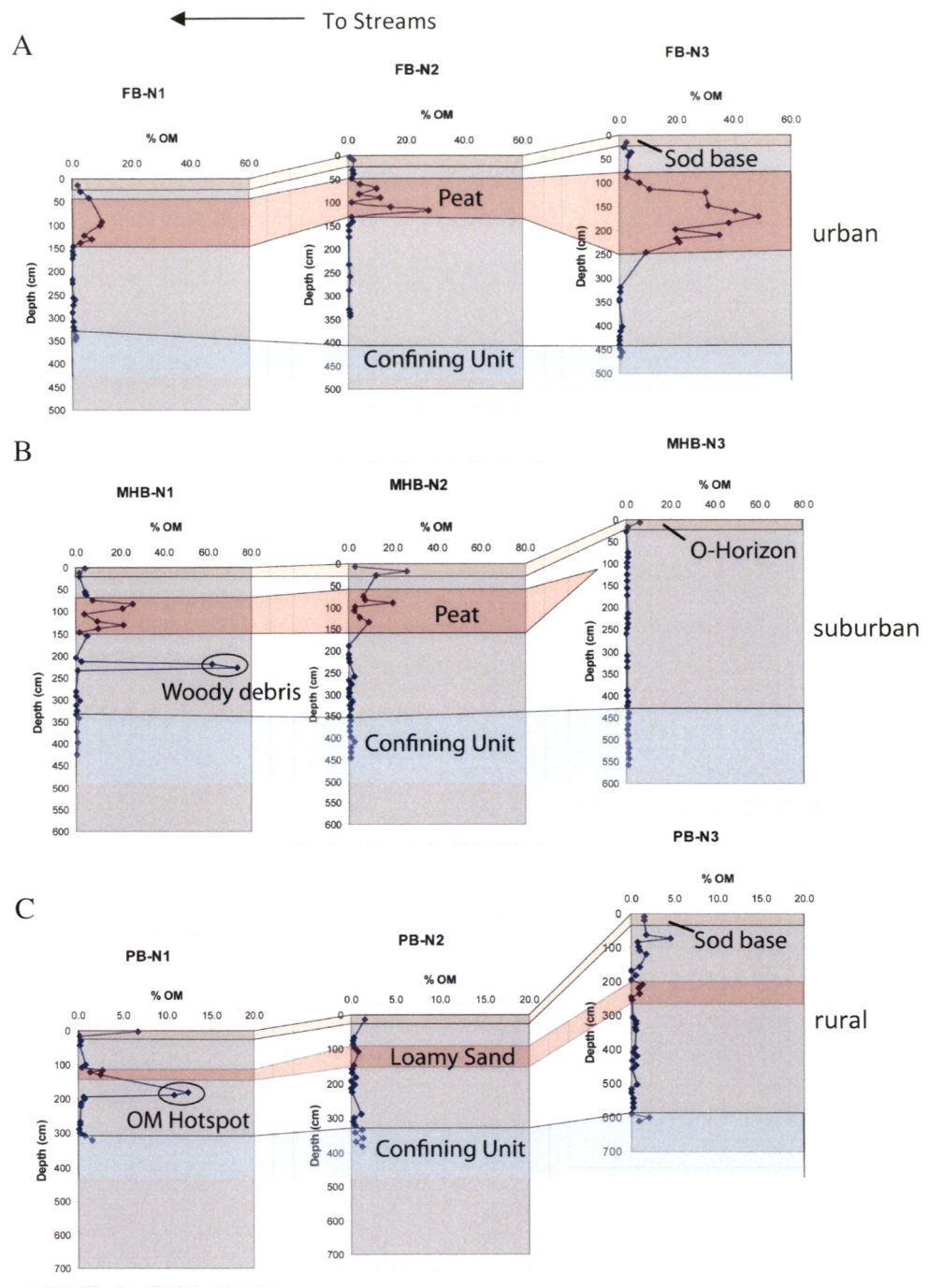


Figure 6. Vertical distribution of % OM based LOI processing of samples from floodplain sediment cores of each study site. Cores are spaced 14 m apart at the urban and rural sites and 10 m apart at the suburban site. X-axis at the rural site is scaled down relative to the axes of the other sites to show depths where % OM was high at the rural site despite generally low % OM relative to the urban and suburban sites.

The urban site had the highest median % OM of 1.2 % (Appendix A1). The maximum % OM measured for a single sample was 73.3 % measured at the suburban site at 222 cm depth, where woody debris was encountered. % OM increased with distance from the stream channel at the urban site and decreased with distance from the stream channel at the suburban and rural sites (Appendix A1).

Mean and median hydraulic conductivity (K) for the floodplain sediments at each of the wells (n = 18) were within an order of magnitude of each other (Appendix A2). Hydraulic conductivities ranged from $10^{-4.7}$ m/s at the deep near-stream well of the suburban site to $10^{-7.8}$ m/s at the deep near-stream well of the rural site. The maximum K is characteristic of medium-grained sand and the minimum K is characteristic of silt (Heath, 2004). Though K was highly variable within and across sites, the median K at the urban site ($10^{-6.6}$ m/s) was significantly lower ($p = 0.0328$) than the median K at the suburban site ($10^{-6.2}$ m/s). Median K values at the urban and suburban sites were not significantly different from the median K at the rural site ($10^{-6.0}$ m/s).

Floodplain groundwater levels and temperature

The median, near-stream groundwater depth (9/14/2007 to 9/4/2008) as measured by near-stream loggers at the urban (U) site (1.47 m) was 0.48 m deeper than the water table at the suburban (S) site (0.99 m; $p = 0.000$), and 0.65 m deeper than the near-stream water table at the rural site (0.82 m; $p = 0.000$) (Appendix A4; Figure 7). Over the one year study, the near-stream water table showed a measurably smaller range and standard

deviation at the urban site (0.74 m, 0.08 m) than at the suburban site (1.02 m, 0.12 m) and the rural site (1.31 m, 0.25 m) (Appendix A4).

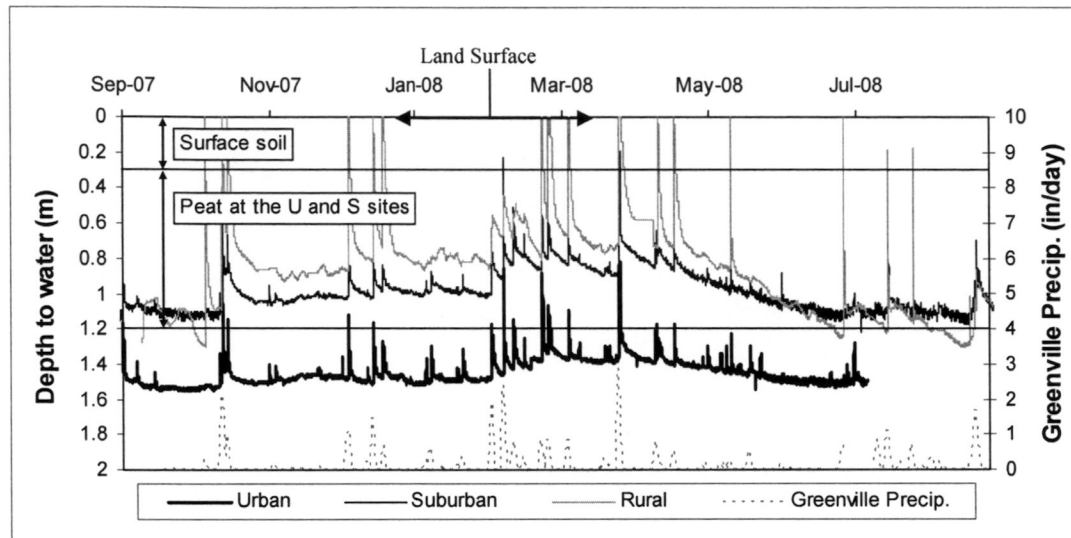


Figure 7. Near-stream water table depths measured in deep, near-stream wells of each of the study sites from 9/14/2007 to 9/4/2008. Urban data from 7/15/2008 to 9/4/2008 is missing due to a logger failure. Both seasonal and storm-induced changes in depth are consistent across the three sites.

Near-stream groundwater at the rural site saturates shallow surface soils completely on a near monthly basis, whereas near-stream groundwater at the suburban site and the urban site never fully saturates shallow surface soil (Figure 7). The Pitt County Soil Survey suggests that combined O-horizon and A-horizon soils, where organic matter is generally concentrated, typically range from about 10-30 cm in thickness for the region where Pitt County resides (Karnowski et al., 1974). The % OM data from surface soil of this study is consistent with this range. Thus, with a conservative estimate of 30 cm as the base of O- and A-horizon soils, near-stream groundwater at the urban site made no contact with shallow organic-rich soil, one half-hour of contact at the suburban site, and

234 hours of contact at the rural site, during the one year period of the study. In addition to loss of contact with surface organic soils, comparison of water table extremes of this study (seasonal high and low groundwater levels) to cross-sections of floodplain geology suggests significant loss of contact between near-stream groundwater and shallow peat at the incised study sites (Figures 5A and 5B).

Monthly groundwater levels (m Above Mean Sea Level (AMSL)) in shallow up-gradient wells at the three study sites showed a smaller annual range at the urban site (0.5 m) than at the suburban (0.8 m) and rural (0.6 m) sites respectively (Appendix A7, Figure 8). The annual groundwater level range was smaller at near-stream wells where monthly measurements at the urban site showed less than 0.1 m change for the total duration of the study period (Appendix A7, Figure 8). Seasonally, floodplain groundwater levels were relatively constant through the fall of 2007, increased into the late winter of 2007 and spring of 2008, and decreased into the summer of 2008 (Figure 7). Less seasonal variation was observed in near-stream wells of the urban and suburban sites than at the rural site (Figure 8).

Median groundwater temperature ($N = 72$ measurements/site) for the twelve months of data collected at each site was significantly higher at the urban site (18.6 C) than it was at the suburban (17.3 C, $p = 0.00$) and rural sites (17.2 C, $p < 0.01$) respectively (Appendix A8). Temperature did not vary significantly with depth or position across the three floodplain study sites (Appendix A9).

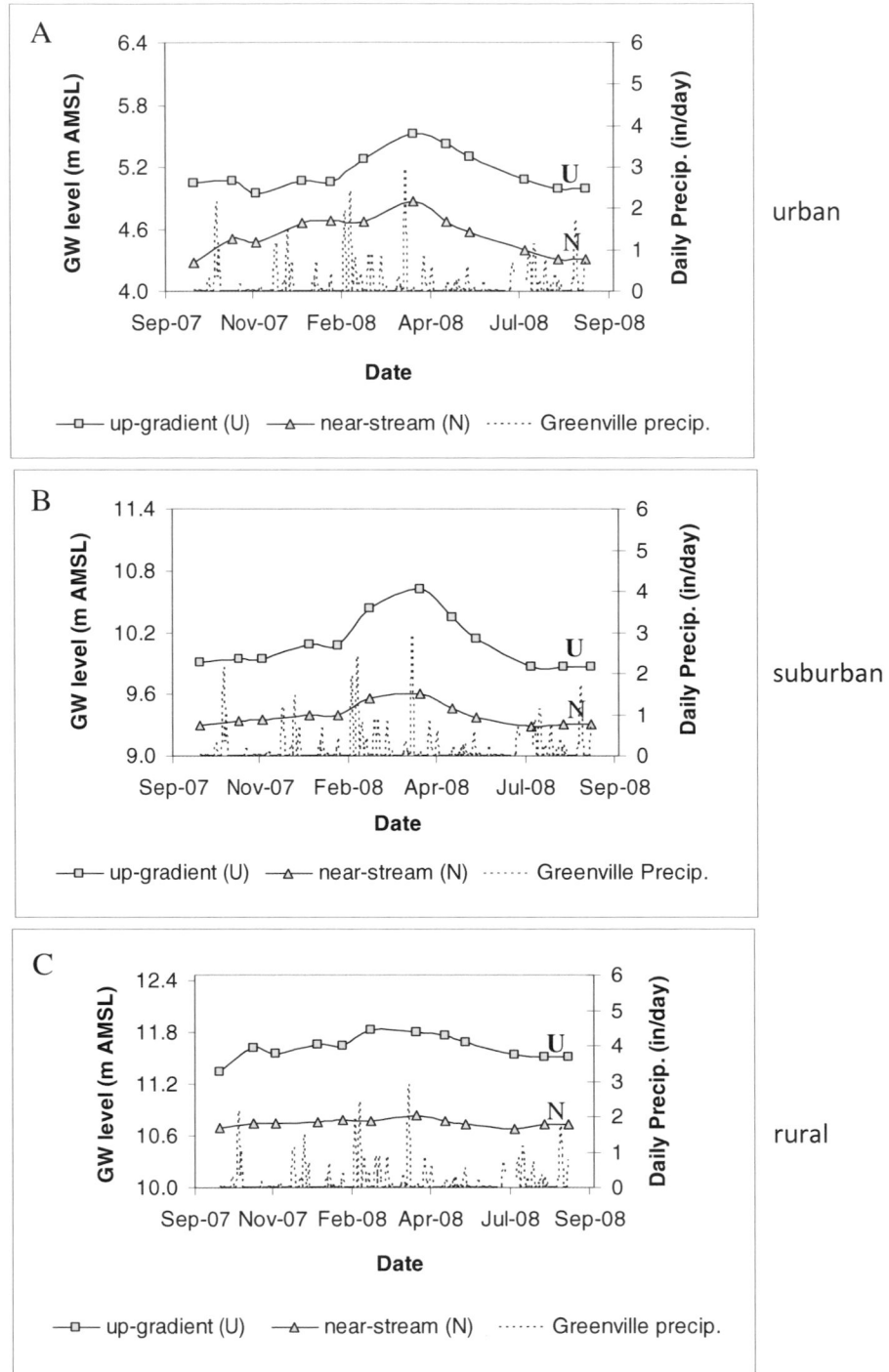


Figure 8. Monthly groundwater levels (m AMSL) from the shallow up-gradient (U) and near-stream (N) wells of the A) urban, B) suburban and C) rural sites.

Hydraulic gradients and groundwater discharge

Hydraulic gradients were steeper at the urban and suburban sites than at the rural site (Table 1, Figure 9). Annual groundwater discharge, based on median hydraulic conductivity and monthly hydraulic gradient at each transect, was significantly lower at the urban site ($5.0 \text{ m}^3/\text{month}$) than at the suburban site ($12.3 \text{ m}^3/\text{month}$; $p = 0.000$) and the rural site ($14.4 \text{ m}^3/\text{month}$; $p = 0.000$; Table 2). Median annual groundwater discharge was not significantly different between the suburban and rural sites ($p > 0.05$). The annual range in total discharge at the urban site ($3 \text{ m}^3/\text{month}$) was considerably lower than the range at the other sites (Table 2). Seasonal variation in hydraulic gradient and groundwater levels controlled variation in discharge (Figures 9 and 10).

Seasonally, peak groundwater discharge at the suburban and rural sites lagged behind peak discharge at the urban site. Discharge peaked in late February at the urban site, early April at the suburban site, and early May at the rural site (Figure 10). The urban and the suburban sites showed little change in discharge through the fall of 2007, a time when discharge at the rural site showed significant and steep decline. All three sites showed a significant increase in discharge as a response to heavy rains in February of 2008, but the urban site showed no discharge response to frequent late winter and spring showers. All three sites experienced a measurable decrease in discharge from the spring of 2008 to the summer of 2008 (Figure 10).

Table 1. Annual hydraulic gradients from up-gradient to near-stream wells across floodplains of each site.

		dh/dl (m/m)		
		Site		
		<i>urban</i>	<i>suburban</i>	<i>rural</i>
annual	N	12	12	12
	Median	0.031	0.032	0.024
	Maximum	0.038	0.051	0.028
	Minimum	0.023	0.028	0.013
	Range	0.015	0.023	0.014
	Standard Deviation	0.004	0.008	0.005

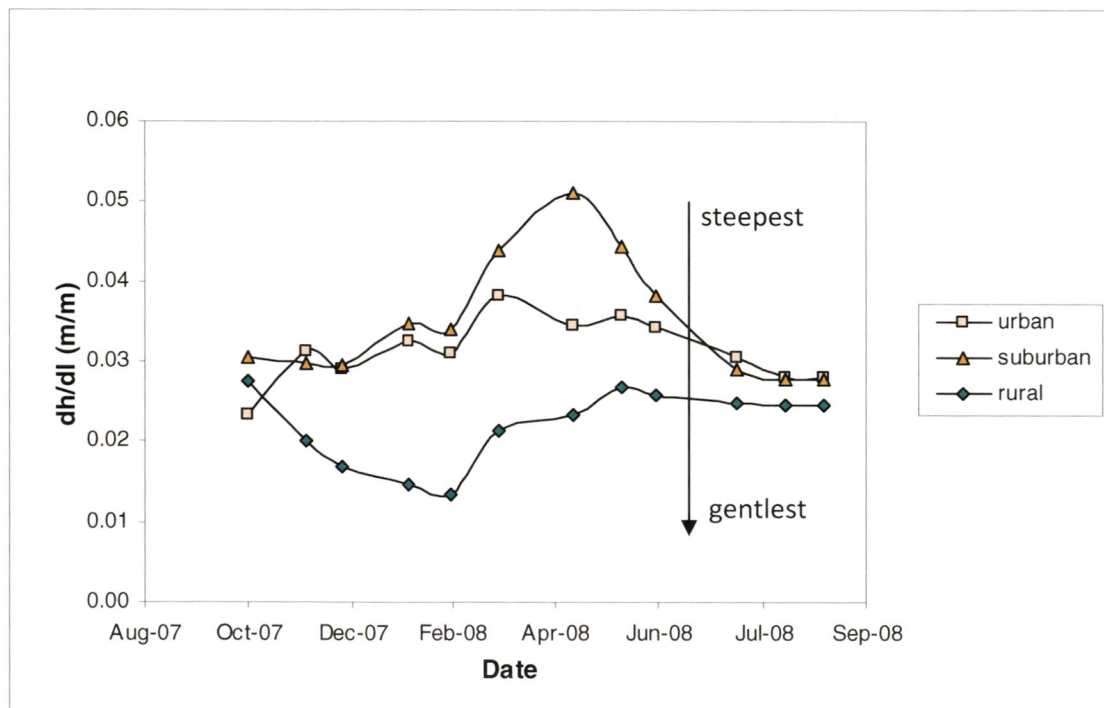
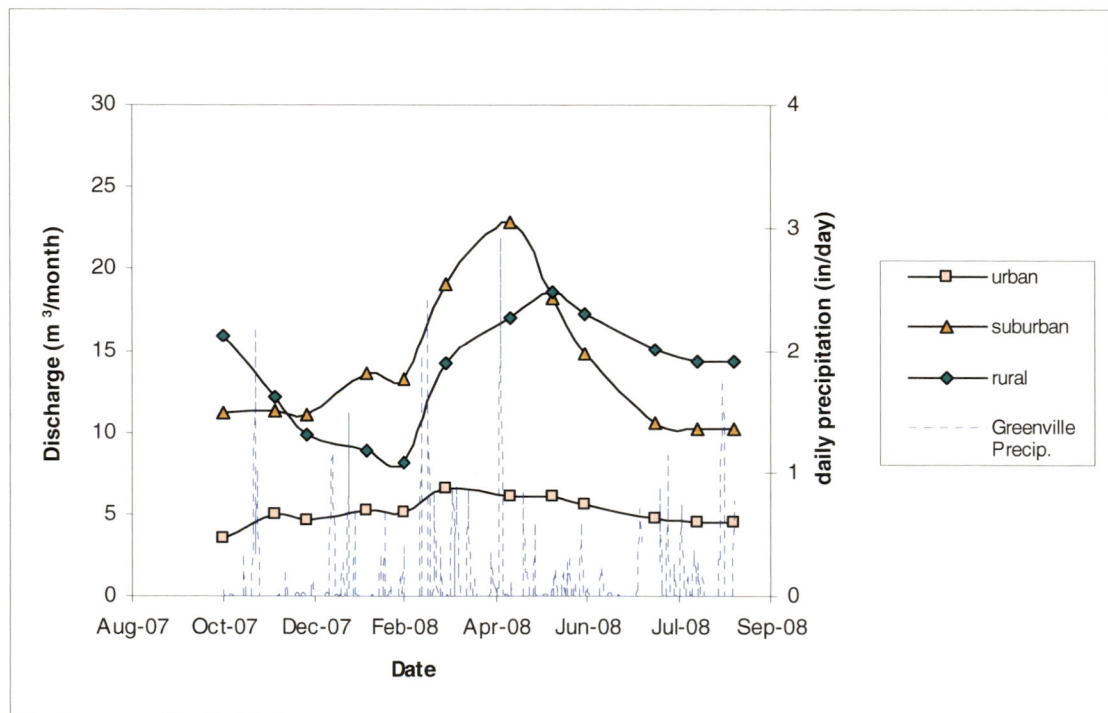


Figure 9. Monthly hydraulic gradient across the floodplains of the three study sites from 10/5/2007 to 9/5/2008.

Table 2. Descriptive statistics for annual discharge from each floodplain.

		Discharge (m^3/mo)		
		Site		
		<i>urban</i>	<i>suburban</i>	<i>rural</i>
annual	N	12	12	12
	Median	5.0	12.3	14.4
	Minimum	3.5	10.2	8.1
	Maximum	6.5	22.8	18.6
	Range	3.0	12.6	10.5

**Figure 10.** Monthly discharge of floodplain groundwater from 10/5/2007 to 9/5/2008 based on a 100 m cross-sectional stream reach. Dashed line represents daily precipitation (in/day) in Greenville during the course of the study period.

Groundwater and surface water chemistry

Dissolved inorganic-N concentrations

Generally, groundwater NO_3^- -N concentrations were < 1 mg/L, in all wells but the up-gradient shallow and deep wells of the rural site (Figure 11). A septic system buried approximately 20 meters west-southwest (WSW) of the up-gradient wells (landowner Christopher Graves, pers. comm., 2008) at the rural site presumably acted as the dominant source of nitrate concentrations greater than 8 mg/L measured in the shallow floodplain and up-gradient wells at the rural site. Median groundwater nitrate concentrations ($N = 12$) were significantly lower in shallow wells at the urban ($p = 0.0000$) and suburban ($p = 0.0021$) sites than in deeper wells (Appendix A10; Figures 12A and 12B). Concentrations were significantly higher ($p = 0.0005$) in the shallow wells relative to deep wells at the rural site (Appendix A10; Figure 12C). Median, near-stream NO_3^- -N concentrations in groundwater ($N = 24/\text{site}$) were generally less than 0.2 mg/L, and were significantly less than median surface water concentrations ($N = 12/\text{site}$) at each site (Appendix A11; Figure 11).

Groundwater NH_4^+ -N concentrations were generally < 0.2 mg/L (Figure 11; Appendices A12 and A13). Higher concentrations were found in the shallow wells of the urban floodplain and the near-stream wells of the rural floodplain (Figures 11 and 13). NH_4^+ -N concentrations decreased significantly from the shallow floodplain well of the urban site to the shallow near-stream well ($p < 0.001$) and increased significantly from the floodplain to the near-stream wells at the rural site ($p < 0.001$). DON

concentrations were generally less than 1 mg/L at all three study sites and remained stable or declined along lateral hydrologic flowpaths for the single date they were collected and assessed (Appendix A14, Figures 14-16). In general, DON and NH_4^+ -N remained stable or declined across each floodplain as NO_3^- -N concentrations declined (Figures 14-16).

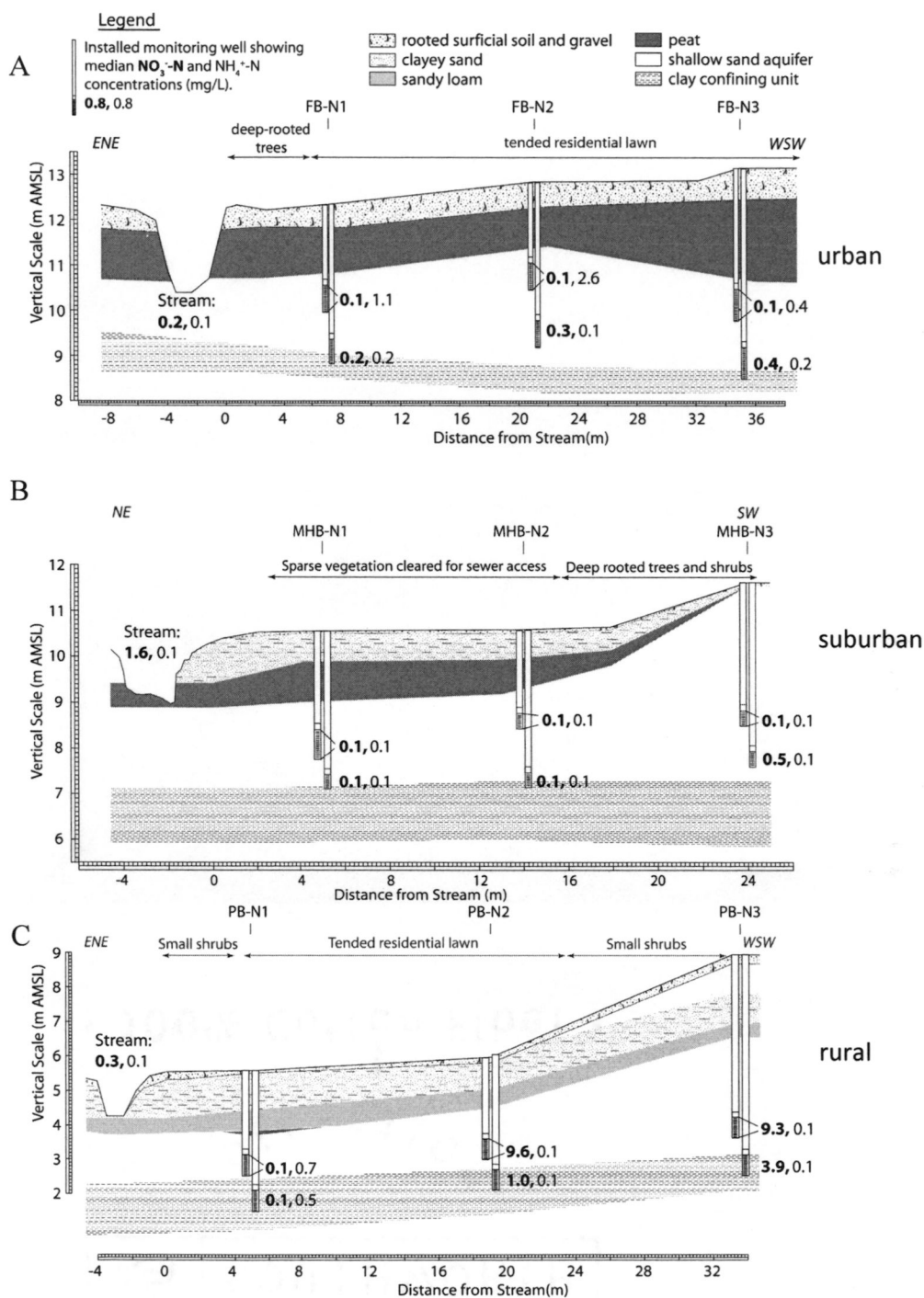


Figure 11. Study site transects at the urban, suburban, and rural sites showing median nitrate-N and ammonium-N (mg/L) values measured in wells at the near-stream, floodplain, and up-gradient locations.

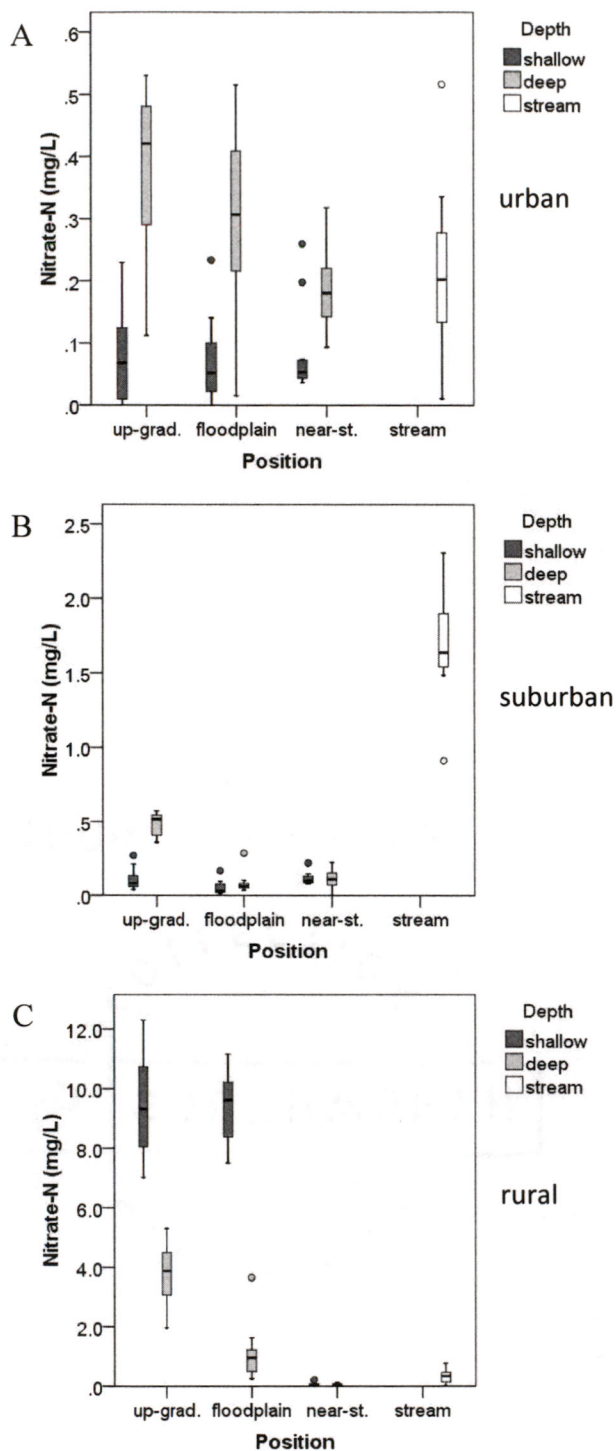


Figure 12. Shallow, deep, and in-stream nitrate-N concentrations from the A) urban, B) suburban, and C) rural floodplains for the one year study period.

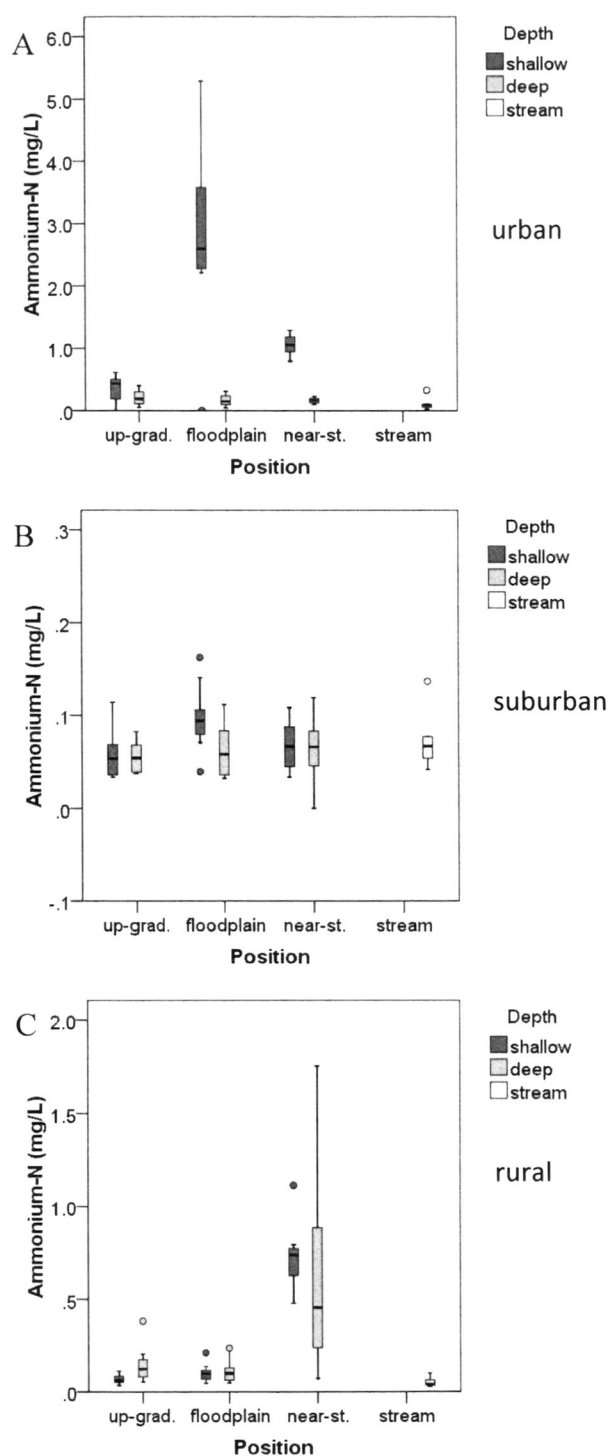


Figure 13. Groundwater and surface water ammonium-N concentrations (mg/L) across the A) urban, B) suburban, and C) rural floodplains for the one year study period.

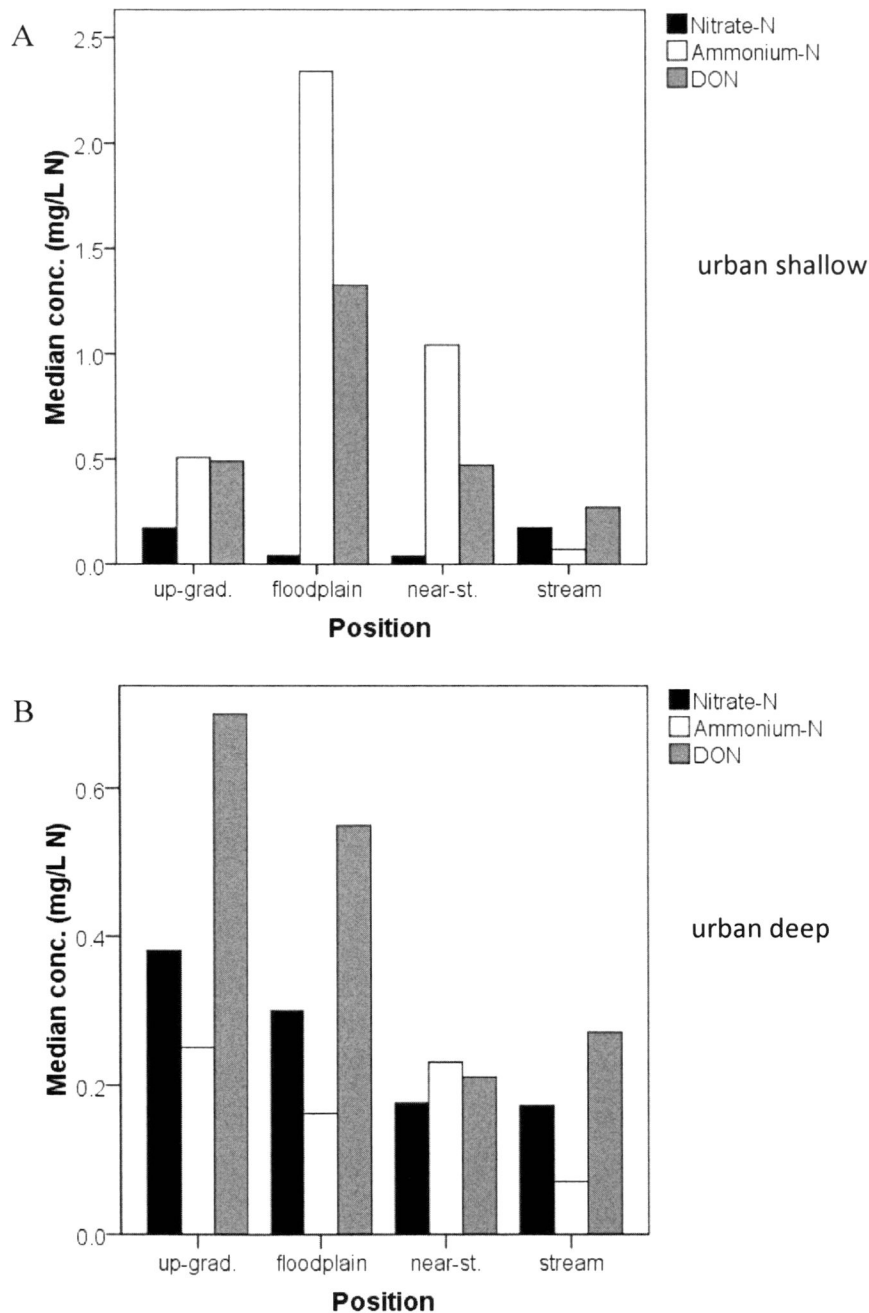


Figure 14. Median nitrate-N, median ammonium-N, and DON (mg/L) from 5/30/2008 in A) shallow and B) deep wells of the urban floodplain.

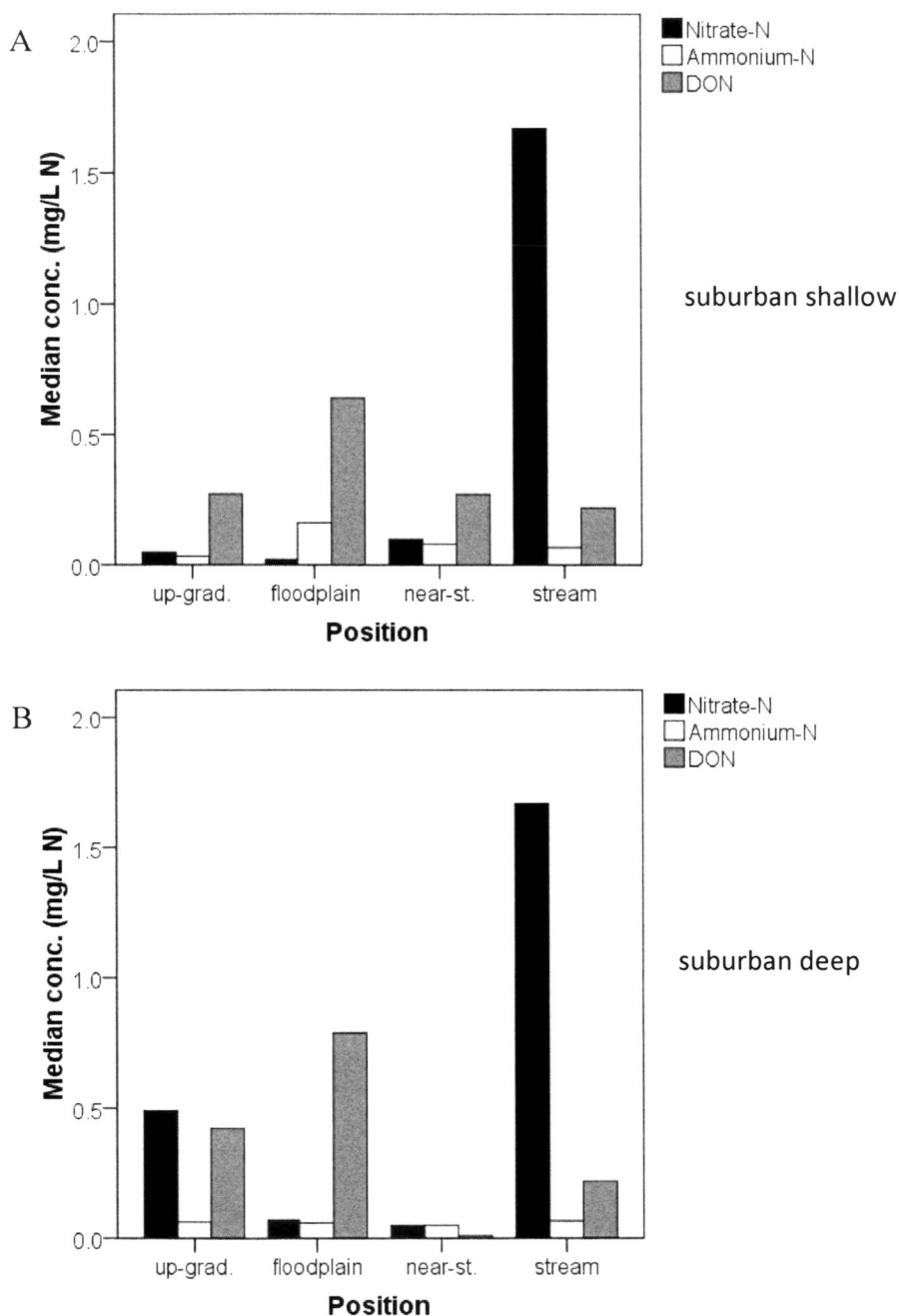


Figure 15. Median nitrate-N, median ammonium-N, and DON (mg/L) from 5/30/2008 in A) shallow and B) deep wells of the suburban floodplain.

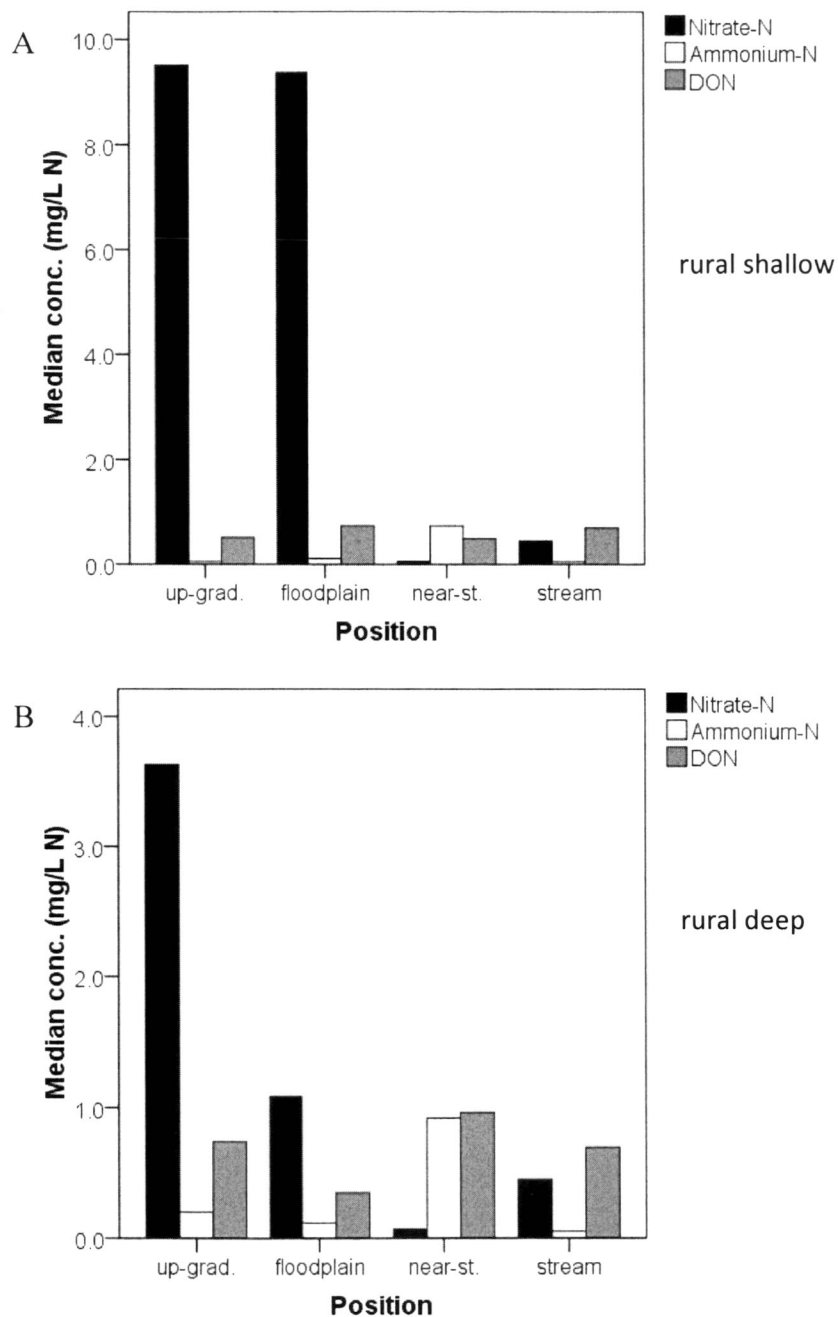


Figure 16. Median nitrate-N, median ammonium-N, and DON (mg/L) from 5/30/2008 in A) shallow and B) deep wells of the rural floodplain.

DOC and DO concentrations

Median dissolved organic carbon (DOC) concentrations were greater than 1.1 mg/L throughout the unconfined aquifers of all three study sites (Figure 17). DOC concentrations were variable across the floodplain, but generally decreased with depth below organic-rich sediment layers (Figure 17). Examples of this distribution are the high DOC concentrations of 6.2, 14.2, and 4.2 mg/L at the shallow wells of the urban site and the 2.1, 5.1 mg/L median concentrations determined at the shallow, floodplain wells of the suburban site. DOC concentrations showed a significant inverse relationship with well-screen depth below the water table across the three sites (Figure 18, $R^2 = 0.46$). Concentrations were significantly higher in the shallow wells of the urban and suburban sites than in the deeper wells ($p = 0.000$ and $p = 0.0018$ respectively). Finally, DOC concentrations were significantly higher at the urban site than at the suburban ($p < 0.005$) and the rural ($p = 0.056$) sites, respectively.

DOC concentrations also varied systematically with lateral groundwater flow (Figure 17). Concentrations decreased significantly along: 1) shallow flow from the shallow N2 to N1 wells at the urban site ($p = 0.0016$), 2) deep flow from the deep N3 to the deep N1 wells at the urban site ($p = 0.0244$), 3) and shallow flow from the shallow N2 to N1 wells of the suburban site ($p = 0.0131$). DOC increased significantly between the shallow N2 and N1 wells of the rural site ($p = 0.0302$) likely due to contact with “hot-spots” of woody plant debris buried in floodplain sands of the rural site.

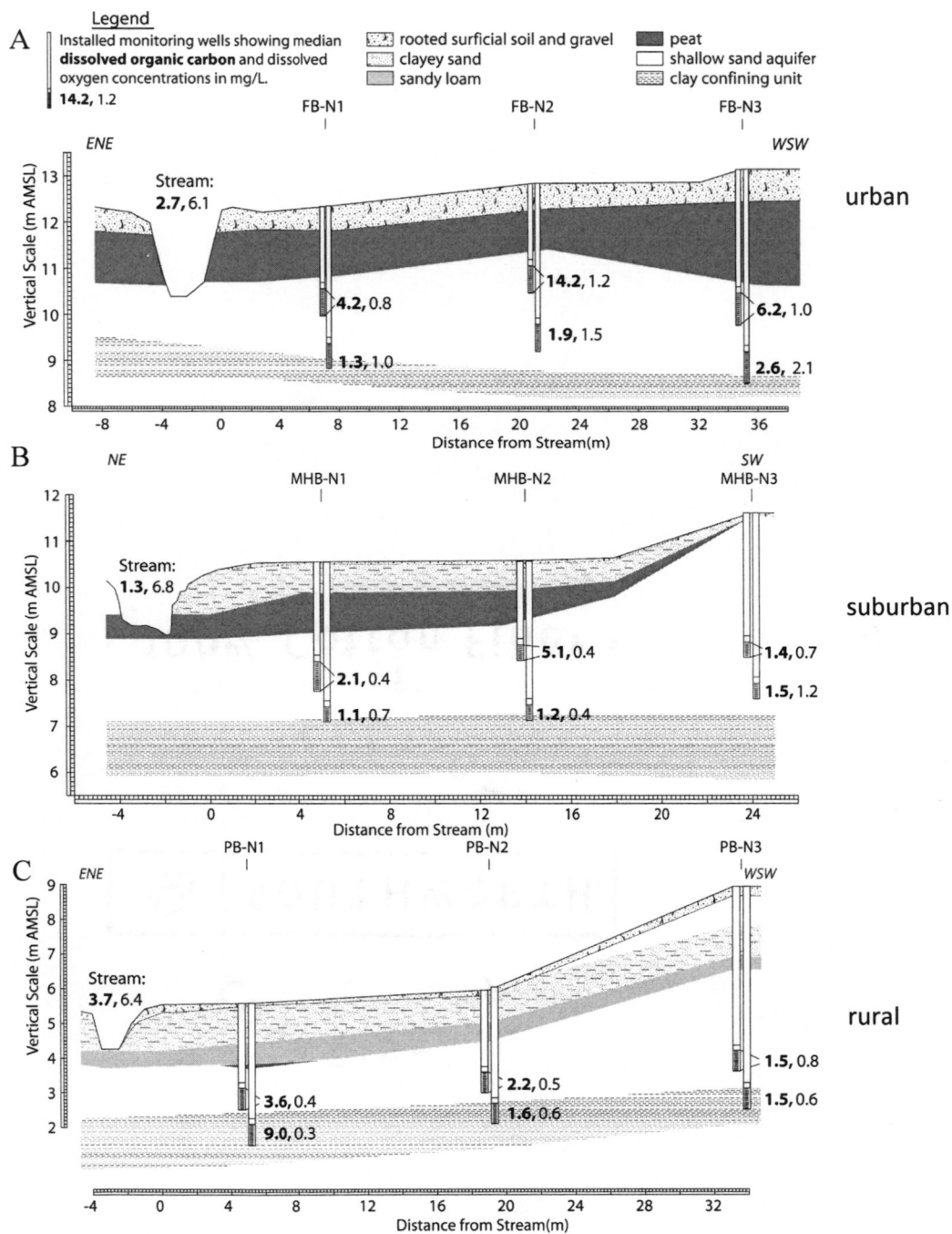


Figure 17. Study site transects of the urban, suburban and rural sites showing median annual DOC, DO values from shallow and deep wells of the three study sites.

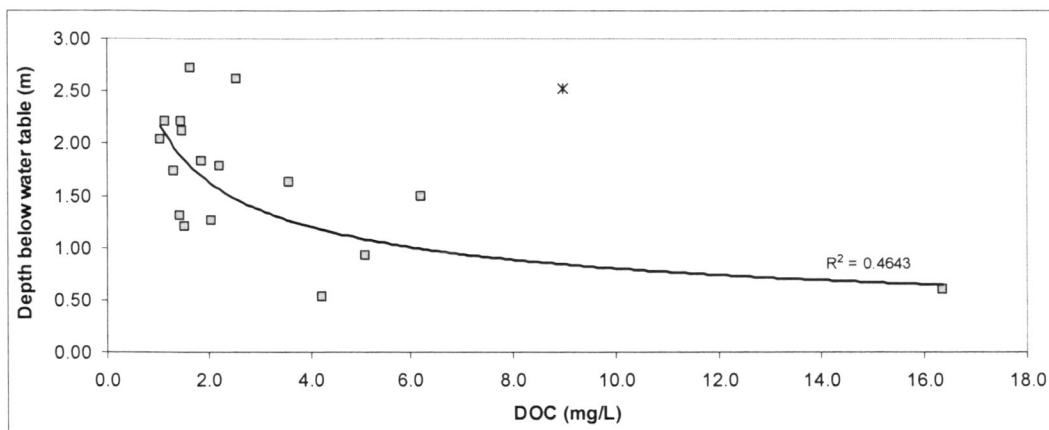


Figure 18. Plot of screen depth below water table vs. median DOC from groundwater samples over the duration of the study period. The value marked * is an outlier from the deep near-stream wells of the rural site, where high DOC concentrations may represent contribution of dissolved organic carbon from underlying marine sediments.

DO concentrations increased significantly with depth at the urban and suburban sites respectively (Figure 19, $R^2 = 0.58$ and 0.63 respectively). Across the floodplain, groundwater DO concentrations also decreased with proximity to the edge of each stream channel (Figure 20). Median annual groundwater DO concentration was significantly higher at the urban site (1.0 ppm) than at both the suburban site (0.7 ppm, $p = 0.000$) and the rural site (0.5 ppm, $p = 0.000$).

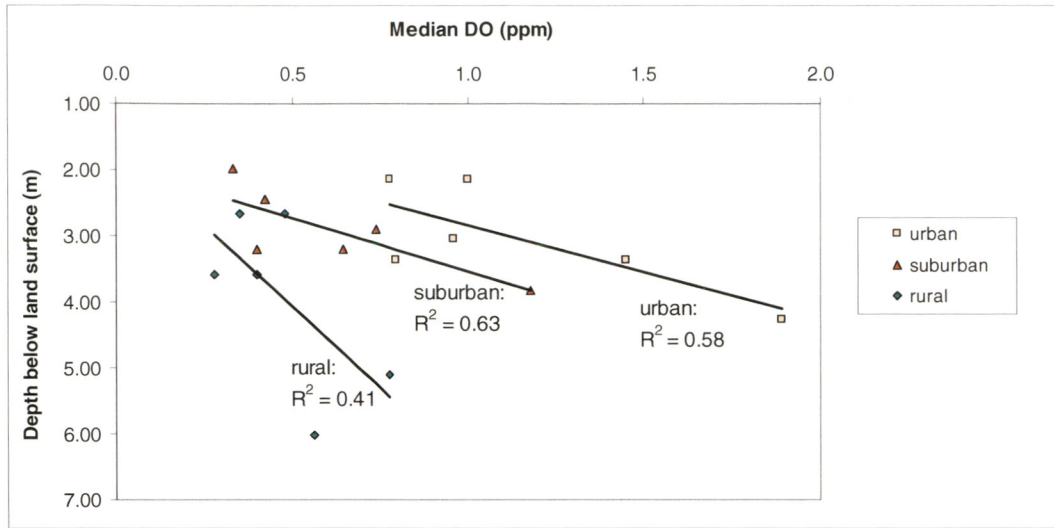


Figure 19. Median well DO concentrations vs. screen depth for floodplain wells of each of the study sites. R^2 values were 0.58, 0.63, and 0.41 for the urban, suburban and rural sites respectively.

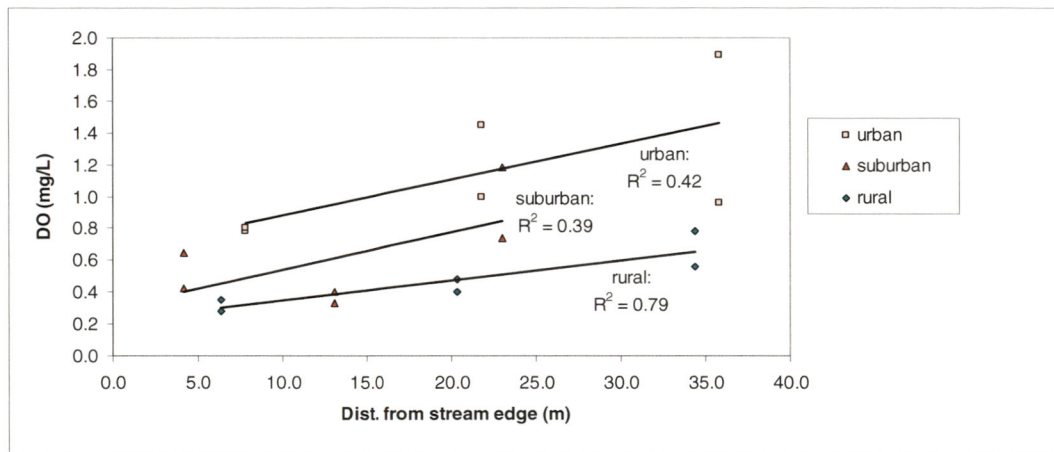


Figure 20. Median well DO (ppm) concentrations vs. dist. (m) of wells from the stream edge at each site. R^2 values of 0.42, 0.39, and 0.79 for the urban, suburban and rural sites respectively suggest median well DO concentrations increase with distance from the stream edge at each site.

Chloride concentrations

Groundwater chloride (Cl^-) concentrations ranged from 6.8-40 mg/L in the floodplain aquifers of this study (Appendix A18). Monthly percent difference in Cl^- concentrations from the up-gradient wells to the down-gradient wells across each floodplain were slight and inconsistent in comparison to percent difference in NO_3^- concentrations (Table 3). A slight decrease in median Cl^- concentrations was observed at the urban site (-17%), with a notable increase in concentrations at the suburban site (30%) and a notable decrease in concentrations at the rural site (-30%).

Table 3. Percent difference in median groundwater chloride concentrations (N = 6 months of chloride data) from up-gradient to near-stream wells across each floodplain.

			Chloride conc. (mg/L)		
			Position		
		Sample Depth	up-grad.	near-st.	% difference
			Median	Median	
Site	urban	average	11.3	9.4	-16.6
	suburban	average	15.0	19.4	29.8
	rural	average	28.5	19.9	-30.4

Statistical relationships

Correlation of NO_3^- -N concentrations with the concentrations of the other measured constituents revealed positive correlations between NO_3^- -N and DO and inverse correlations between NO_3^- -N and DOC. Strong positive relationships were observed between NO_3^- -N and DO at the urban site ($r = 0.48$, $p < 0.01$) and the suburban site ($r = 0.58$, $p < 0.01$) (Figures 21A and 21B)), with no significant relationship between the two constituents at the rural site ($r = 0.15$, $p = 0.28$) (Figure 21C). Significant inverse relationships were observed between NO_3^- -N and DOC at the urban site ($r = -0.38$, $p = 0.01$), suburban site ($r = -0.24$, $p = 0.040$), and rural sites ($r = -0.37$, $p = 0.01$) (Figure 22). NO_3^- concentrations were high along deep flowpaths at the urban and suburban sites with corresponding high DO concentrations and low DOC concentrations relative to concentrations of all three constituents in shallow wells (Figures 11 and 17). Such vertical stratification of concentrations was reversed at the rural site, where up-gradient septic discharge maintained markedly high nitrate concentrations in shallow up-gradient wells, and both DO and DOC values were notably low relative to the urban floodplains.

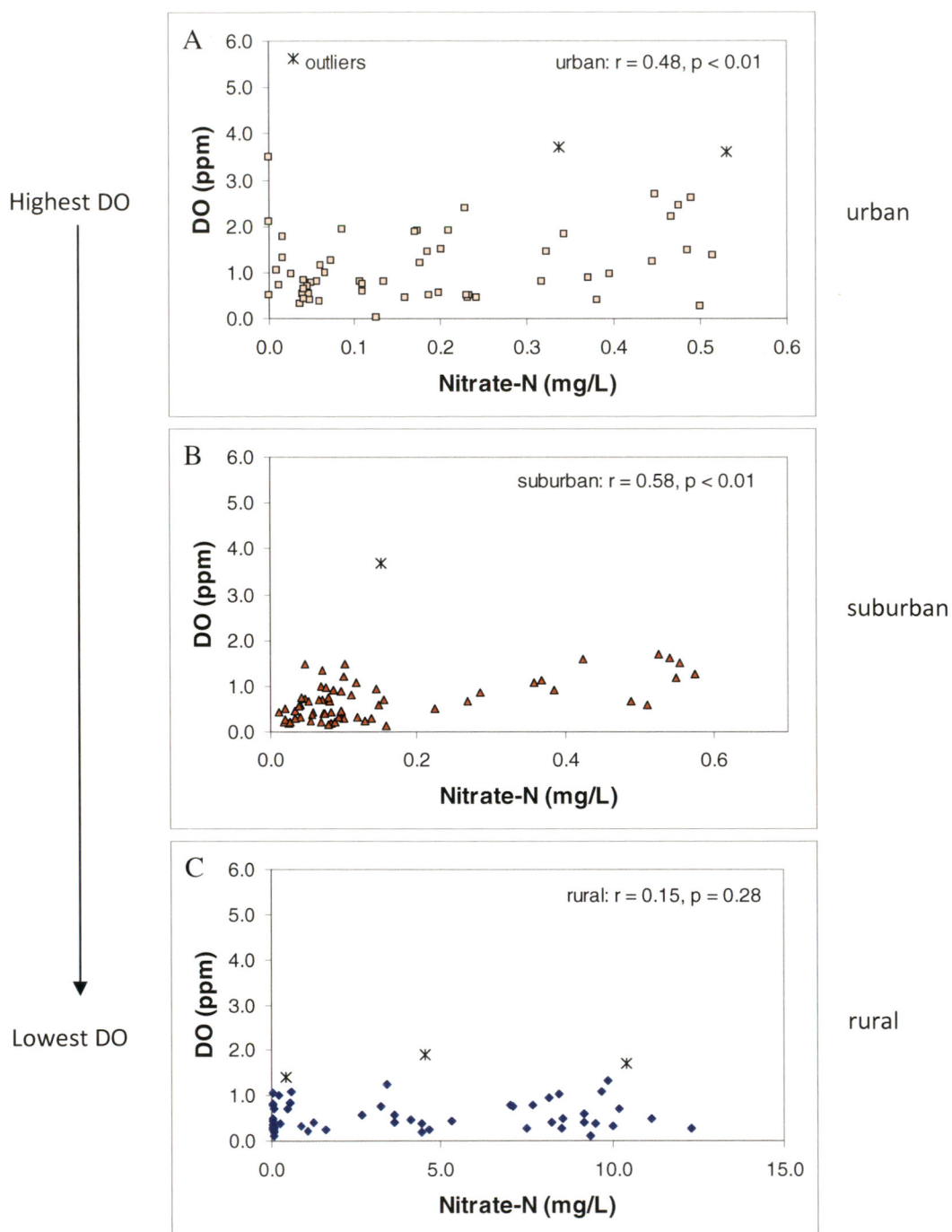


Figure 21. Correlations between nitrate-N and dissolved oxygen (DO) at the urban, suburban, and rural sites. Correlation between constituents at the rural site was complicated by the relatively constant contribution of up-gradient nitrate-N by a nearby septic tank. Outliers were excluded to highlight the general relationship.

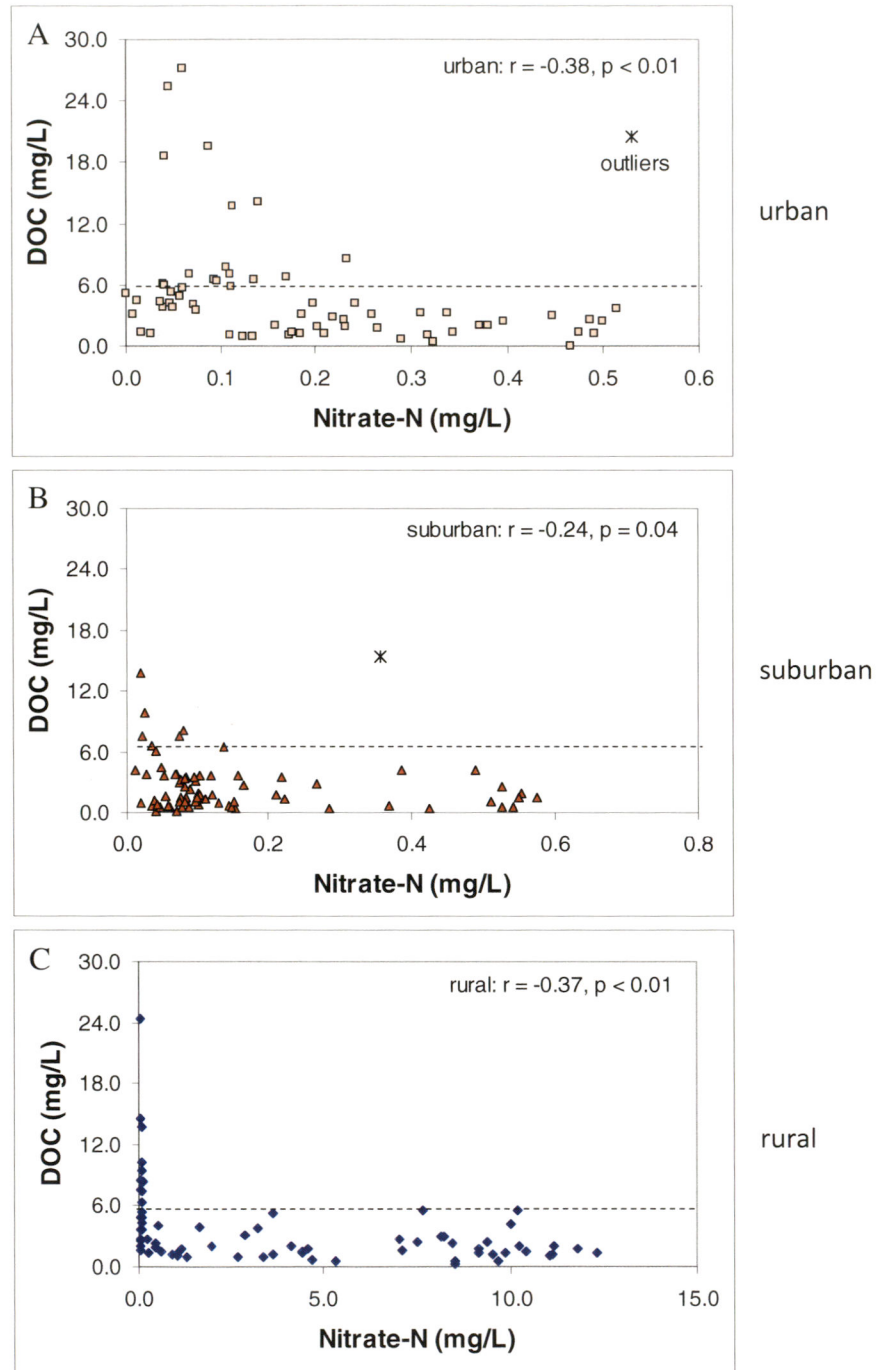


Figure 22. Correlations between nitrate-N and dissolved organic carbon (DOC) at the urban, suburban, and rural sites. Where DOC concentrations were greater than 6 mg/L (dashed line) nitrate-N concentrations were nearly always less than 1 mg/L. Outliers were excluded to highlight the general relationship.

Bivariate correlation of groundwater levels (m AMSL) and constituent concentrations in shallow floodplain wells (N1 and N2 locations) showed significant variation across the three study sites (Table 4). Groundwater levels showed significant positive correlation with ammonium-N (NH_4^+ -N) and dissolved oxygen (DO) at the urban site (when the water table was closest to the surface NH_4^+ -N and DO were elevated). Significant inverse correlation was observed between groundwater levels and both NO_3^- -N and NH_4^+ -N at the suburban site (when the water table was shallow, NO_3^- -N and NH_4^+ -N were diminished). Finally, at the rural site a significant inverse correlation was observed between NH_4^+ -N and groundwater levels (when the water table was shallow, NH_4^+ -N was diminished) as well as a significant positive correlation between DO and groundwater levels (when the water table was shallow, DO was elevated) (Table 4).

Table 4. Pearson correlation coefficients for bivariate correlation of monthly groundwater (gw) levels (m AMSL) and monthly groundwater concentrations (mg/L) from shallow floodplain wells (N1 and N2 locations) of each site. Bold-faced values represent significant relationships.

Site	Variable	NO_3^- -N	DOC	NH_4^+ -N	DO
urban	gw level	-0.21 (23)	0.41 (20) ^{\$}	0.53 (22)*	0.70 (20)**
suburban	gw level	-0.65 (24)**	0.28 (24)	-0.57 (24)*	-0.16 (22)
rural	gw level	0.36 (24) ^{\$}	-0.23 (23)	-0.52 (24)*	0.49 (20)*

** P < 0.005

* P < 0.05

^{\$} P < 0.1

Floodplain NO_3^- -attenuation and loading to incised stream channels

Monthly differences in NO_3^- -N concentrations (calculated as a percent) from up-gradient wells to near-stream wells at each study site were less across the urban and suburban floodplains than the differences that occurred across the rural floodplain (Figure 23). Relatively high monthly concentration differences at the rural site occurred in coordination with a shallow near-stream groundwater level (median depth = 0.82 m; N = 16680 measurements). Monthly percent differences at the urban site were significantly lower than differences at the suburban ($p = 0.02$) and rural ($p < 0.01$) sites, respectively. Percent differences at the suburban site were also significantly less than differences at the rural site ($p < 0.01$). On an annual basis, NO_3^- concentrations decreased laterally from up-gradient to near-stream wells (Figure 11) with significant attenuation along: 1) lateral groundwater flow at the urban site, where annual median NO_3^- concentrations were attenuated 46.4% ($p < 0.01$), 2) lateral groundwater flow at the suburban site, where median NO_3^- concentrations were attenuated 58.3% ($p < 0.01$), and 3) lateral groundwater flow at the rural site where median NO_3^- concentrations were attenuated approximately 99.2% ($p < 0.01$).

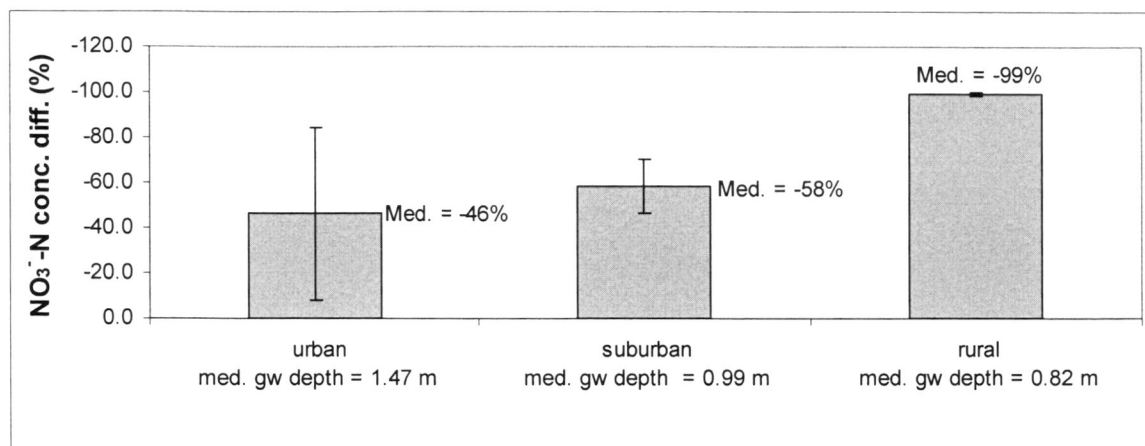


Figure 23. Monthly percent difference in $\text{NO}_3\text{-N}$ concentrations (%) over twelve months of chemical data at the urban, suburban and rural sites. Median groundwater (gw) depths at each site are median of 14631, 18269, 16680 measurements recorded at $\frac{1}{2}$ hour intervals by water level loggers in the near-stream shallow wells (N1 locations) of the urban, suburban and rural sites.

Median shallow and deep near-stream nitrate concentrations of the urban, suburban and rural floodplains were < 1 mg/L (Figure 11). Average near-stream nitrate concentrations at the urban and suburban sites were significantly greater than near-stream nitrate concentrations at the rural site ($p < 0.005$ in both cases). Nitrate loading (average near-stream groundwater concentration * groundwater discharge from each floodplain) to streams at the three sites showed considerable variation across sites (Figure 24-A). The combined effect of discharge and average near-stream nitrate concentration on loading caused monthly loading from the suburban floodplain to be significantly greater than loading from both the urban floodplain ($p < 0.0005$) and the rural floodplain ($p < 0.005$) respectively (Figure 24).

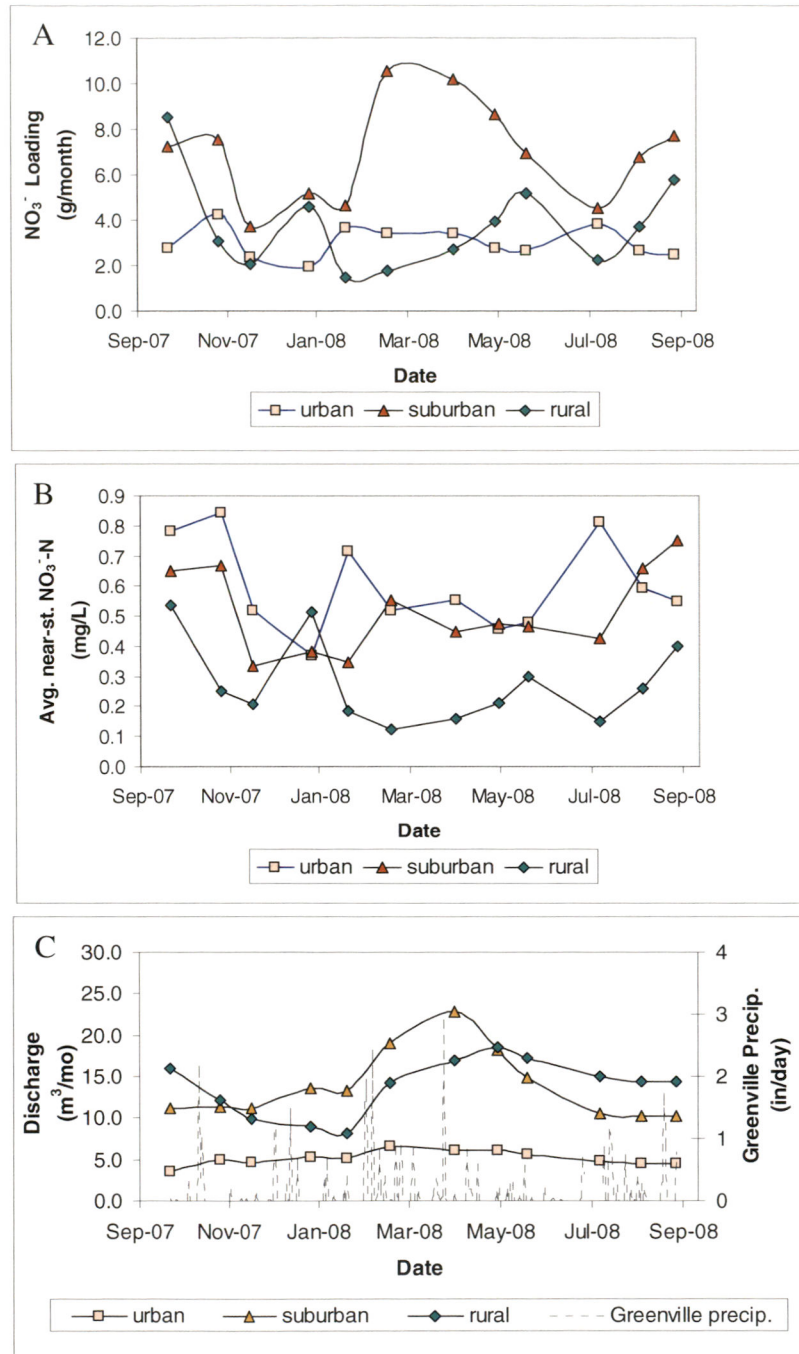


Figure 24. Seasonality graphs showing variability in A) NO₃⁻ loading (g/mo), B) average near-stream NO₃⁻-N concentrations (mg/L), and C) discharge (m³/mo) across the three floodplains. Dashed black line (C) shows daily precipitation for the Greenville area (in/day).

Discussion

Changes in organic matter with depth

The notable variation in % OM with depth and proximity to streams disproved the hypothesis that OM would be concentrated in the shallowest (0-30 cm) portion of the riparian sediment profiles of Greenville's low-order streams. The deep and laterally extensive peats found at the urban and suburban sites of this study were similar to peats and organic-rich sediments found at depths greater than 50 cm in a recent study conducted near Ontario, Canada by Hill et al. (2004). Peats of their study had % OM of 30-62 % which is consistent with the 6-49 % OM determined for peats of this study. They demonstrated that buried, laterally extensive, organic-rich soils and "hotspots" of buried OM in floodplain sediments have considerable potential to denitrify discharging groundwater. Advancements in the prediction and quantification of the spatial distribution of subsurface organic matter are needed to improve the accuracy at which riparian zone denitrification can be estimated (Groffman et al. 2009).

Effects of decline on OM contact

Deeper groundwater tables adjacent to heavily incised streams have been reported in both agricultural (Schilling et al. 2004, 2006; Burt et al. 2002; and Hupp, 2000) and urban settings (Groffman et al. 2002; Groffman et al. 2003; Hardison, 2008). The decline of water tables adjacent to incised stream channels was also observed during this study. Deeper water tables adjacent to incised channels are likely due to a combination of: 1) decreased recharge to the surficial aquifer in urban settings caused by impervious surface

cover and 2) rapid drainage of near-stream groundwater to enlarged urban channels. Floodplain groundwater recharge may also be limited by reduced overbank flow to the riparian areas of the incised channels, which was documented at two of three incised study sites of the Greenville area (Hardison et al., 2009, in press). Undisturbed Coastal Plain streams have frequent overbank events and interact with adjacent floodplains an average of five times per year (Sweet and Geratz, 2003). When channels are heavily incised, floodplains may become inactive (relict).

Incision and water table decline at the urban and suburban sites caused a significant reduction in contact between floodplain groundwater and shallow O- and A-horizon soils. Though groundwater levels at all sites showed no contact with surface soil during baseflow conditions, stormflow groundwater tables at the least incised, rural site made frequent and prolonged contact with surface soil (Figure 7). Aside from the 0.5 hours of contact observed at the suburban site following a storm on 4/5/2008 (Figure 7), no contact of floodplain groundwater with surface O- and A-horizon soils was observed at the heavily incised urban and suburban sites. Because of the occurrence of thick and extensive peat layers at the heavily incised sites, stormflow contact of floodplain groundwater and peat at the two sites occurred regularly (Figure 7). Assuming that near-saturated conditions observed in floodplains of the headwaters of the rural watershed are representative of the pre-developed state of the streams of this study, groundwater had reduced contact with buried peat at the urban and suburban sites (Figure 5). When groundwater levels were seasonally low, the greatest loss of contact with peat occurred (Figure 5).

DOC concentrations along shallow flowpaths at the urban and suburban sites were elevated relative to concentrations along deep flowpaths (Figure 17). At these sites, the shallow well screens were close to overlying peat. In the NC Coastal Plain, Boettger (2002) observed elevated riparian groundwater DOC concentrations associated with surface and buried OM (Baldwin Swamp, NC). Devito et al. (2000) and Hill et al. (2000) report DOC concentrations of 10 to 18 mg C/L in the pore water of saturated peats of their studies. Shallow median DOC concentrations of 4.2 to 14.2 mg/L at the urban site and 2.1 to 5.1 mg/L in wells near peat at the suburban site suggest that peat at both sites contributed considerable DOC to shallow groundwater.

In addition to elevated DOC concentrations, median groundwater temperature (N = 72 measurements) was higher at the urban site than it was at the suburban site ($p = 0.00$) as well as the rural site ($p < 0.01$) respectively. This pattern was significant across seasons (Appendix A8) with median groundwater temperature at the urban site being >1 °C greater than median groundwater temperatures at the rural and suburban sites. The suite of factors that could increase groundwater temperature in urban watersheds include: leakage from water supply or sewage infrastructure, increased air temperature due to the “urban heat island effect” (Pickett et al., 2001), changes in soil evaporation, increased direct solar radiation due to the removal of riparian vegetation, and advection from paved asphalt radiated by the sun.

Despite high spatial variability in the hydraulic conductivity of floodplain sediments, localized highs in hydraulic conductivities at depth in the urban and suburban floodplains

suggest the presence of fast groundwater flowpaths. Stratigraphic analyses revealed the occurrence of coarse- to pebble-sized gravel and sand along the base of the unconfined aquifer where high sediment hydraulic conductivities were found. This coarse basal layer is overlain by a distinct horizon where sediment becomes finer and less permeable. Hill et al. (2004), Boettger (2002), and Hill et al. (2000) have observed that sediments with high hydraulic conductivity promote fast groundwater velocities and short groundwater residence times in floodplain aquifers that often reduce the capacity of plant uptake and denitrification to remove NO_3^- from the floodplain groundwater system. The general conclusion by Hill et al. (2000; 2004) was that coarse- to gravel-sized sediment at depth may cause nitrate-laden groundwater to flow preferentially along deep groundwater flowpaths. Evidence that this may occur in the current study is provided by elevated nitrate concentrations in deep wells relative to shallow wells at the urban and suburban sites.

Effects of water table decline on NO_3^- -attenuation

Results indicate that urban channel incision and corresponding water table decline reduce the ability of the floodplain to process NO_3^- . However, geological variability of floodplain hydraulic properties also influences groundwater discharge and floodplain N-processing. On an annual basis nitrate concentrations decreased across each floodplain, suggesting a net attenuation of NO_3^- at all three sites. The greatest attenuation of nitrate occurred across the rural floodplain (99 %) where the median, near-stream water table was the shallowest (0.82 m; Figure 23). These data suggest that deeper water tables adjacent to incised urban streams may cause a net inhibition of processes that attenuate

NO_3^- in floodplain aquifers. For the single May 30, 2008 sampling date that DON concentrations were collected and assessed, five of six groundwater samples from near-stream wells had DON concentrations that were greater than corresponding NO_3^- concentrations (Figures 14-16). This suggests that DON may also play an important role in N transport to Coastal Plain streams.

Water table decline may act to inhibit NO_3^- -attenuation in the floodplain aquifers of this study by: 1) shifting groundwater out of contact with the root zones of riparian vegetation where nitrate is often assimilated by plants, 2) shifting groundwater out of contact with organic matter that can promote denitrification, and 3) accelerating the decomposition of subaerially exposed organic matter, and thus accelerating the leaching of inorganic-N to floodplain groundwater. Variation in the effects of other NO_3^- -attenuation processes and mechanisms, such as dilution, and DNRA across the sites of this study may also affect net NO_3^- -attenuation.

The concentrations of measured nutrients in shallow groundwater of the respective floodplains represent the net effect of N-cycle processes in shallow soil and groundwater. The data of this study provides limited insight to the priority, timing, or importance of each N-cycle process. The remaining discussion will focus on mechanisms of NO_3^- attenuation, how incision and water table decline affect specific N-cycle processes, and how results compare to other studies throughout the midwestern and eastern U.S. and Canada.

Plant uptake via assimilation of nitrate by the roots of riparian vegetation likely has a limited influence on groundwater nitrate decline observed during this study. Analyses of sediment cores showed surficial sand aquifers to be completely free of any root, stem, or other evidence of deep root systems at each site (Figure 11, Appendix C). Sod root systems were based at about 6 cm below the land surface at the urban and rural sites. Evidence for the active root systems of trees and sparse shrubs in cores from the suburban site suggests that active roots did not extend beyond 30 cm depth (Appendix C).

Boettger (2002) has suggested that the ability of riparian buffers to denitrify shallow groundwater moving from agricultural fields to channelized streams of Eastern North Carolina is strongly associated with the saturation of surface, organic-rich soil horizons. Because thick, laterally extensive peat layers occurred at the heavily incised urban and suburban sites, high DOC concentrations persisted in shallow wells despite significant water table decline. Patterns of elevated DOC concentrations along shallow flowpaths where NO_3^- concentrations were relatively low (Figures 11 and 17) suggest that NO_3^- was depleted by denitrification along shallow hydrologic flowpaths. These patterns are consistent with studies conducted by Devito et al. (2000) in Ontario who reported elevated DOC in the presence of decreasing NO_3^- and DO concentrations along zones bordering organic matter in two floodplain aquifers where $\delta^{15}\text{N-NO}_3^-$ isotopes in groundwater became enriched. Devito et al. (2000) goes on to suggest that the concurrent occurrence of decreasing NO_3^- with enrichment of $\delta^{15}\text{N-NO}_3^-$ provides strong evidence for the depletion of NO_3^- via denitrification for the floodplain aquifers of his study. The combination of strong positive correlations between DO and NO_3^- (Figure 21) at all three

sites in the presence of significant inverse relationships between NO_3^- and DOC (Figure 22) provide additional evidence that NO_3^- was depleted by denitrification in the three floodplain aquifers of this study (Harden and Spruill, 2008; Korom, 1992). Hill et al. (2000) and Devito et al. (2000) have shown that denitrification is limited by organic carbon in zones where DOC concentrations are low ($< 6 \text{ mg/L}$) and may become nitrate limited where DOC concentrations rise above 6 mg/L . Thus, denitrification may be NO_3^- limited along the shallow flowpath at the urban site and DOC limited along shallow and deep flowpaths at the suburban and rural sites.

Bivariate correlation of riparian groundwater levels with constituent concentrations in the shallow wells of the urban and suburban sites are presumably influenced by leaching of constituents from exposed peats during recharge of the floodplain aquifer. Correlation of groundwater levels with NH_4^+ -N concentrations showed a positive relationship at the urban site which contrasted directly with inverse correlations at the suburban and rural sites (Table 4).

The occurrence of relatively high NH_4^+ -N concentrations in the shallow wells of the urban site (Figures 13 and 14) is likely the result of mineralization and leaching of NH_4^+ from the shallow peat layer. Storage and release of NO_3^- from subaerially exposed, organic-rich layers has been observed in other studies (Angier and McCarthy, 2008; Schilling, 2006; Groffman, 2002). Because the mineralization of N from actively decomposing, organic-rich soil typically begins with the release of NH_4^+ by heterotrophic microbes (Schlesinger, 1997), elevated NH_4^+ -N and DON concentrations in shallow wells

at the urban study site may also be caused by storage and release from shallow organic matter. The marked decrease in NH_4^+ -N from the shallow N2 well to the shallow N1 well of the urban site is likely affected by a variety of N-cycle processes and mechanisms including: assimilation by microbes, adsorption to fine-grained sediments of the unconfined aquifer, and nitrification of NH_4^+ to form NO_3^- that may be subsequently denitrified as groundwater travels across the urban floodplain.

Dilution of NO_3^- along lateral groundwater flowpaths can occur due to the mixing of groundwater with other water with relatively low NO_3^- concentrations. The notable decrease in median chloride concentrations (-17%; Table 3) across the urban floodplain suggests that floodplain groundwater may be diluted by groundwater upwelling from the clay confining unit, since a median ($N = 12$), upward vertical hydraulic head gradient (-0.01 m/m) was measured at the near-stream wells of the urban floodplain. Chloride concentrations at the suburban site were consistently higher at the near-stream wells than at the up-gradient wells (Table 3). This may be due to evaporation of groundwater from the floodplain aquifer, since the residence time of groundwater in floodplain aquifers of the NC Coastal Plain may range from months to years (Spruill et al., 2005). The notable decrease in median chloride concentration from the up-gradient wells at the rural site (28.5 mg/L) to the shallow near-stream wells (19.9 mg/L) suggests dilution may decrease nitrate concentrations across the rural floodplain by a factor of 30% (Table 3). The average dilution effect at all three sites was a 24% decline in NO_3^- concentration across the floodplain. The average floodplain attenuation or decline in NO_3^- concentration was

68% (Figure 23). Overall, the results suggest that dilution contributed to NO_3^- concentration declines across the floodplains but was not the primary control.

As with plant uptake, the reduction of NO_3^- to NH_4^+ (DNRA) also likely had a limited influence on the observed water table decline, NO_3^- -attenuation relationship. Because the occurrence of notable DNRA along short groundwater flowpaths should cause concurrent NH_4^+ production and NO_3^- consumption, constant and decreasing NH_4^+ concentrations observed in parallel with significant NO_3^- -attenuation along lateral flowpaths between wells (Figures 14-16; Appendix A12 and A13) suggest that DNRA had little influence on observed values of NO_3^- -attenuation. Significant increase in NH_4^+ concentrations observed between the floodplain and near-stream wells of the rural site ($p < 0.001$; Figure 16B) may be caused by DNRA, since exceptionally high nitrate concentrations measured at floodplain wells of the rural site were more than sufficient to sustain microbial DNRA (An and Gardner, 2002). NH_4^+ concentration increases may also be related to mineralization of organic matter.

Comparison to previous studies

Near-stream groundwater NO_3^- -N concentrations at the incised sites of this study were below average with respect to near-stream (2-45 m depending on scale) NO_3^- concentrations measured in agricultural settings of the central and eastern US, and Canada (Table 5). Floodplain groundwater NO_3^- data of this study is compared to data measured in various agricultural settings because very little work has been conducted investigating N-dynamics in groundwater discharging to streams in predominantly urban

watersheds. Comparison of near-stream groundwater nitrate concentrations at sites listed in Table 5 to percentage NO_3^- -attenuation across each respective floodplain suggests that near-stream groundwater NO_3^- concentrations > 0.5 mg/L are indicative of buffer settings where NO_3^- -attenuation is often impaired ($< 85\%$). In all cases where near-stream groundwater NO_3^- concentrations were < 0.5 mg/L, percentage NO_3^- -attenuation was $> 95\%$. The pattern of high percentage NO_3^- -attenuation at riparian study sites with high concentrations of NO_3^- entering the floodplain groundwater system (incoming NO_3^- concentrations) at each site (e.g. sites 5B, 1, A-A' (ENC), B-B' (ENC) and A-A' Transect; Table 5) suggests that high incoming NO_3^- concentrations may enhance NO_3^- -attenuation. Low percentage NO_3^- -attenuation observed at the urban and suburban sites of this study may be at least partially due to low NO_3^- concentrations in groundwater entering floodplains of the incised study sites.

Table 5. Median NO₃⁻ concentrations and percentage attenuation (- = loss, + = gain) in floodplain, riparian groundwater estimated from studies conducted in agricultural catchments of the central United States, eastern United States, and Canada.

Study Location	Land use context	Site label	Flowpath Length (m)	NO ₃ ⁻ -N concentrations (mg/L)		% NO ₃ ⁻ -N Attenuated	Reference
				Up-gradient	Near-stream		
Eastern North Carolina	agriculture	Site 5A ^a	65	6.4	< 0.05	> -99	Harden & Spruill, 2008
		Site 5B	380	41.3	0.1	> -99	
		Site 5PT1 ^a	21	20.2	4.2	-79.2	
Eastern North Carolina	agriculture	Site 1	80	12.5	0.3	-97.6	Spruill, 2004
		Site 2	350	8.0	4.0	-50.0	
		Site 3	90	5.3	0.9	-84.0	
		Site 4	100	5.6	0.0	-99.6	
Eastern North Carolina (ENC)	agriculture	A-A'	200	12.0	0.1	-99.2	Tesoriero et al. 2005
		B-B'	80	15.0	0.1	-99.3	
Eastern North Carolina	agriculture w/ vegetated riparian zone	Baldwin Swamp	12-14	3.1	2.6	-16.1	Boettger, 2002
		Fork Swamp	12-14	3.3	4.1	+24.2	
		Pea Branch	12-14	0.7	0.3	-57.1	
	agriculture w/ cultivated riparian zone	Baldwin Swamp	12-14	2.9	2.8	-3.4	
		Fork Swamp	12-14	6.2	8.2	+32.3	
		Pea Branch	12-14	1.7	2.4	+41.2	
Lower Wisconsin River	agriculture	A-A' Transect	800	12.0	0.1	-99.2	Pfeiffer et al. 2006
Union County, Illinois	agriculture	forest ^b	6.6	6.3	1.2	-81.7	Schoonover & Williard, 2003
		cane ^b	10	7.5	0.1	-99.3	
NE Connecticut	agriculture	control ^b	20	7.2	1.6	-78.5	Clausen et al. 2000
		treatment ^b	20	4.8	1.4	-69.8	
NE Virginia	agriculture	main x-section ^b	120	7.1	3.3	-52.9	Snyder et al. 1998

Table 5. (Continued)

Ontario, Canada	agriculture	transect A	180	26.0	1.1	-95.9	Hill et al. 2000
		transect B	150	35.7	0.1	-99.7	
NE Maryland	agriculture	transect A	420	14.0	0.1	-99.2	Bohlke and Denver, 1995
		transect B	780	16.0	13.0	-18.8	
Fairmount Co., Delaware	agriculture	B-B'	4300	20.0	9.4	-53.0	Shedlock et al. 1993
Caroline Co., Virginia	agriculture	A-A' (rt. side)	125	3.5	0.1	-97.2	Speiran, 2003a
		A-A' (left side)	120	7.4	2.5	-66.8	
Rockingham Co., Virginia	agriculture	A-A'	180	6.2	2.5	-59.7	Speiran, 2003b
Average:			374 m	15 mg/L	4 mg/L	-62%	

^aNO₃⁻ conc. values are mean ± standard error

^bNO₃⁻ conc. values are reported in-text by the referred author(s).

Sites listed in Table 5 that had near-stream groundwater NO_3^- -N concentrations comparable to or higher than concentrations observed in this study possessed buffer conditions and/or hydrogeologic characteristics that inhibited NO_3^- processing across each riparian zone. The deep surficial aquifer at Site 2 (Spruill, 2004) for instance, likely allowed nitrate-laden groundwater to bypass the roots of buffer vegetation at the site. In the absence of a buried, organic-rich soil horizon, percentage NO_3^- -attenuation across the deep hydrologic flowpath at Site 2 was approximately 50%. Boettger (2002) suggested that an environment of markedly high hydraulic conductivity and corresponding fast groundwater flow velocity at his Baldwin Swamp study site may have prevented adequate groundwater residence time in the riparian zone of the site to sustain vigorous NO_3^- removal via denitrification and plant uptake. Though riparian areas of the sites of this study had almost no deep-rooted riparian vegetation, sites listed in Table 5 with deep and laterally extensive peats similar to the peats found at the urban and suburban sites of this study such as Site 1 (Spruill, 2004) and transects A and B (Hill et al. 2000) recorded nearly complete NO_3^- -attenuation (> -95%) across riparian, floodplain aquifers. Inhibited NO_3^- -attenuation values observed at the urban and suburban sites of this study relative to values observed at those sites are likely related to increased production and decreased consumption of NO_3^- provoked by declining water tables across the urban and suburban floodplain study sites.

Conclusions and Management Recommendations

Subsurface organic matter in riparian areas adjacent to low-order Coastal Plain streams was not always confined to the upper few centimeters of the riparian sediment profile. Subsurface organic matter occurred as shallow O- and A-horizon soils, buried peat layers, and as “hotspots” of concentrated plant debris in sand of the unconfined aquifers at each site.

Groundwater levels declined adjacent to incised streams up to 22 m from the edge of the stream channel. This decline had a notable effect in reducing contact between floodplain groundwater and buried organic matter at the urban and suburban sites. Despite this reduction in contact, groundwater DOC concentrations were often elevated, especially along shallow flowpaths near peat layers. Groundwater DOC concentrations greater than 6 mg/L and DO concentrations < 1 mg/L in shallow wells were common, suggesting conditions were suitable for denitrification in aquifers adjacent to all three low-order streams.

Monthly NO_3^- concentrations declined across all three floodplains on an annual basis. Floodplain groundwater NO_3^- -attenuation across the floodplain was greatest at the rural site where the shallowest water table occurred. Less attenuation occurred at the urban and suburban sites where the water table was deeper. This suggests that channel incision and associated water table decline may cause a net decrease in NO_3^- -attenuation across floodplain aquifers of low-gradient Coastal Plain streams. Though the contribution of DOC from buried peat may help to maintain conditions suitable for denitrification, fast

groundwater flowpaths along coarse-grained, basal sediments at the urban and suburban sites may allow nitrate-laden groundwater to bypass shallow reducing zones. Elevated concentrations of NH_4^+ in shallow wells at the urban site in combination with a positive correlation between floodplain groundwater levels and NH_4^+ concentrations at the urban site suggest that the subaerial exposure of peat by declining water tables may contribute inorganic-N (mineralization) to unconfined groundwater. Although near-stream NO_3^- concentrations at the urban and suburban sites were elevated relative to the rural site, the loading of NO_3^- to low-order stream channels is also influenced by groundwater discharge. Because groundwater discharge is controlled by the hydraulic properties of floodplain sediments and hydraulic gradients, discharge of groundwater from the floodplains of the sites of this study, and thus the loading NO_3^- to streams of this study, was variable across sites. These results suggest that for locations in the catchments of low-order streams where elevated groundwater discharge occurs in tandem with impaired attenuation of NO_3^- motivated by declining water tables, focused “hotspots” of NO_3^- loading may occur.

Floodplain N-removal is affected by declining water tables

Restoration of water tables adjacent to incised streams could improve NO_3^- -attenuation in floodplain aquifers and could be achieved by: 1) reconstructing and stabilizing the stream channels in a manner that elevates in-stream water levels to promote contact between groundwater and organic-rich soil horizons, and 2) capturing and re-directing stormwater from urban stormwater management networks to detention ponds up-gradient of floodplain aquifers. The effect would be to both recharge

floodplain groundwater levels and to cause nitrate in captured stormwater to be attenuated in floodplain aquifers prior to being discharged to impacted low-order streams.

In a study of the quantitative effects of two different types of geomorphic stream restoration techniques on rates of in situ N-removal via denitrification, Kaushal et al. (2008) concluded that geomorphic restoration whereby stream banks are armored and lowered to promote hydrologic “connection” of surface-water with shallow soils of riparian areas, promotes high rates of denitrification in riparian groundwater. Because the low-order tributaries of this study are often bordered directly by residential property, restoration that promotes hydrologic connectivity with floodplain areas may not always be practical. Based on this current study, it is recommended that geomorphic restoration be considered where hydrologic reconnection with riparian areas can occur without flooding residential property.

References

- Altman, S. J., and Parizek, R.R. 1995. Dilution of nonpoint-source nitrate in groundwater. *Journal of Environmental Quality* 24: 707– 718.
- American Public Health Association (APHA). 2005. Standard Methods for the Examination of Water and Wastewater, 21st edition. APHA- American Water Works Association (AWWA)-Water Pollution Control Federation (WEF): Washington, D.C.
- American Public Health Association. 1998. Standard Methods for the Examination of Water and Wastewater, 20th edition. APHA-AWWA-WEF: Washington, D.C.
- An, S., and Gardner, W. S. 2002. Dissimilatory nitrate reduction to ammonium (DNRA) as a nitrogen link, versus denitrification as a sink in a shallow estuary (Laguna Madre/Baffin Bay, Texas). *Marine Ecology – Progress Series*. 237: 41-50.
- Anderson, D.M., Glibert, P.M. and Burkholder, J.M. 2002. Harmful algal blooms and eutrophication: nutrient sources, composition, and consequences. *Estuaries*. 25(4): 704-726.
- Angier, J. T., McCarty, G.W. 2008. Variations in base-flow nitrate flux in a first-order stream and riparian zone. *Journal of the American Water Resources Association*. 44(2): 367-380.
- Baker, M.A., Valett, H.M., and Dahm, C.N. 2000. Organic carbon supply and metabolism in a shallow groundwater ecosystem. *Ecology*. 81 (11): 3133.
- Boettger, P. C. 2002. A comparison of shallow groundwater nitrate concentrations in vegetated vs. cultivated riparian zones adjacent to streams channelized for agricultural drainage. M.S. Thesis, East Carolina University, Greenville, NC.
- Bohlke, J.K., O'Connell, M.E. and Prestegard, K.L. 2007. Ground water stratification and delivery of nitrate to an incised stream under varying flow conditions. *J. of Environ. Qual.*, 36(3): 664-680.
- Bohlke, J.K., Wanty, R., Tuttle, M., Delin, G., and Landon, M. 2002. Denitrification in the recharge area and discharge area of a transient agricultural nitrate plume in a glacial outwash sand aquifer, Minnesota. *Water Resources Research*. 38, 7: 10.1-10.26.
- Bohlke, J.K., and Denver, J.M. 1995. Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two

- agricultural watersheds, Atlantic coastal plain, Maryland (Paper 95WR01584). *Water Resources Research*, 31 (9): 2319.
- Bouwer, H., and Rice, R.C. 1976. A slug test for determining hydraulic conductivity of unconfined aquifers with completely or partially penetrating wells. *Water Resources Research*, 12: 423-428.
- Boyer, E.W., Goodale, C.L., Jaworski, N.A. and Howarth, R.W. 2002. Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern U.S.A. *Biogeochemistry*, 57-58(1): 137-169.
- Burkholder, J.M. 2000. Eutrophication and Oligotrophication. In: Encyclopedia of Biodiversity. Academic Press: New York, NY, pp. 649-70.
- Burt, T.P., Matchett, L.S., Goulding, K.W.T., Webster, C.P., and Haycock, N.E. 1999. Denitrification in riparian buffer zones: the role of floodplain hydrology. *Hydrological Processes*, 13 (10): 1451-1463.
- Burt, T.P., Pinay, G., Matheson, F.E., Haycock, N.E., Butturini, A., Clement, J.C., Danielescu, S., Hefting, M.M., Hillbricht-Ilkowska, A., Maitre, V. 2002. Water table fluctuations in the riparian zone: comparative results from a pan-European experiment. *Journal of Hydrology*, 265 (1-4): 129-148.
- Clausen, J.C., Guillard, K., Sigmund, C.M., and Dors, K.M. 2000. Technical Reports - Ecosystem Restoration - Water Quality Changes from Riparian Buffer Restoration in Connecticut. *Journal of Environmental Quality*, 29 (6): 1751.
- Denver, J.M., Ator, S.W., DeBrewer, L.M., Ferrari, M.J., Barbaro, J.R., Hancock, T.C., Brayton, M.J., and Nardi, M.R. 2004. Water quality in the Delmarva Peninsula, Delaware, Maryland, and Virginia, 1999–2001. Reston, Va., U.S. Geological Survey Circular 1228, 32 pp.
- Devito, K.J., D. Fitzgerald, A.R. Hill, and R. Aravena. 2000. Nitrate dynamics in relation to lithology and hydrologic flow path in a river riparian zone. *Journal of Environmental Quality*, 29: 1075–1084.
- Dosskey, M.G., and Bertsch, P.M. 1994. Forest sources and pathways of organic matter transport to a blackwater stream: a hydrologic approach. *Biogeochemistry*, 24 (1): 1.
- Duff, J.H. and Triska, F.J. 2000. Nitrogen Biogeochemistry and Surface-Subsurface Exchange in Streams. In: Jones, J.B. and Mulholland, P.J. Streams and Ground Waters. San Diego, CA: Academic Press. 200.
- Fetter, C. W. 1994. Applied Hydrogeology. Prentice-Hall, Inc.: Englewood Cliffs, NJ.

251-256.

- Gold, A.J., Groffman, P.M., Addy, K., Kellogg, D. Q., Stolt, M., Rosenblatt, A.E. 2001. Landscape attributes as controls on ground water nitrate removal capacity of riparian zones. *Journal of the American Water Resources Association*, 37(6): 1457-1464.
- Groffman, P.M., Butterbach-Bahl, K., Fulweiler, R.W., Gold, A.J., Morse, J.L., Stander, E.K., Tague, C., Tonitto, C., Vidon, P. 2009. Challenges to incorporating spatially and temporally explicit phenomena (hotspots and hot moments) in denitrification models. *Biogeochemistry*. 93 (1-2): 49-77.
- Groffman, P.M., Bain, D.J., Band, L.E., Belt, K.T., Brush, G.S., Grove, J.M., Pouyat, R.V., Yesilonis, I.C., and Zipperer, W.C. 2003. Down by the Riverside: Urban Riparian Ecology. *Frontiers in Ecology and the Environment*, 1(6): 315-321.
- Groffman, P.M., Boulware, N.J., Zipperer, W.C., Pouyat, R.V., Band, L.E., and Colosimo, M.F. 2002. Soil nitrogen cycle processes in urban riparian zones. *Environ. and Sci. Technol.*, 36: 4547-4552.
- Groffman, P.M., Howard, G., Gold, A.J. and Nelson, W.M. 1996. Microbial Nitrate Processing in Shallow Groundwater in a Riparian Forest. *Journal of Environmental Quality*, 25 (6): 1309-1316.
- Gurwick, N.P., Yavitt, J.B., Groffman, P.M., Gold, A.J., Blazejewski, G., and Stolt, M. 2008. Microbially available carbon in buried riparian soils in a glaciated landscape. *Soil Biology and Biochemistry*. 40 (1): 85-96.
- Harden, S.L., and Spruill, T.B. 2008. Factors affecting nitrate delivery to streams from shallow ground water in the North Carolina Coastal Plain. U.S. Geological Survey Scientific Investigations Report 2008-5021. 39 pp. (online only at <http://pubs.water.usgs.gov/sir2008-5021>)
- Harden, S.L., Fine, J.M., and Spruill, T.B. 2003. Hydrogeology and ground-water quality of Brunswick County, North Carolina. U.S. Geological Survey Water-Resources Investigations Report 03-4051. 90 pp.
- Hardison, E.C. 2008. Effects of Urbanization on the Ecological Condition of Small Streams in the Inner Coastal Plain of North Carolina. M.S. Thesis, East Carolina University, Greenville, NC.
- Hardison, E.C. , O'Driscoll, M.A., DeLoatch, J.P., Howard, R.J., and Brinson, M.M. 2009. Urban land use, channel incision, and riparian water table decline along low-

- order Coastal Plain streams, North Carolina. In Press: *Journal of American Water Resources*.
- Heath, R. 2004. Basic Ground-Water Hydrology: U.S. Geological Survey Water Supply Paper 2220, 86 pp.
- Heath, R. 1975. Hydrology of the Albemarle-Pamlico Region of North Carolina: USGS Water Resources Investigation 9-75, 98 pp.
- Hefting, M., Clement, J.C., Dowrick, D., Cosandey, A.C., Bernal, S., Cimpian, C., Tatur, A., Burt, T.P., Pinay, G., 2004. Water table elevation controls on soil nitrogen cycling in riparian wetlands along a European climatic gradient. *Biogeochemistry*, 67(1): 113-134.
- Henshaw, P. C., and Booth, D. B. 2000. Re-equilibration of stream channels in urban watersheds. *Journal of the American Water Resources Association*, 36:1219–1236.
- Hill, A.R. 2000. Stream Chemistry and Riparian Zones. In: Jones, J.B. and Mulholland, P.J. *Streams and Ground Waters*. San Diego, CA: Academic Press. 87-94.
- Hill, A.R., Devito K.J., Campagnolo, S. and Sanmugadas, K. 2000. Subsurface denitrification in a forest riparian zone: Interactions between hydrology and supplies of nitrate and organic carbon. *Biogeochemistry* 51: 193–223
- Hill, A.R., Vidon, P.G.F., and Langat, J. 2004. Denitrification potential in relation to lithology in five headwater riparian zones. *Journal of Environmental Quality*, 33 (3): 911-919.
- Holmes, R.M., Fisher, S.G. and Grimm, N.B. 1994. "Parafluvial nitrogen dynamics in a desert stream ecosystem". *Journal of the North American Benthological Society*. 13 (4): 468.
- Howarth, R., Sharpley, A., and Walker, D. 2002. Sources of nutrient pollution to coastal waters in the United States: Implications for achieving coastal water quality goals. *Estuaries and Coasts*, 25(4): 656-676.
- Hupp, C.R. 2000. Hydrology, geomorphology and vegetation of Coastal Plain rivers in the south-eastern USA. *Hydrological Processes*, 14(16-17): 2991-3010.
- Hutchinson, H.W. 2007. Hydrologic and isotopic response of low-order coastal plain streams to urban land use. M.S. Thesis, East Carolina University, Greenville, NC: 126 pp.
- INTCAL04 calibration database. 2004. INTCAL04 Radiocarbon Age Calibration.

Intcal04: Calibration Issue of *Radiocarbon*. 46 (3).

- Jones, J.B., Fisher, S.G., and Grimm, N.B. 1995. Nitrification in the hyporheic zone of a desert stream ecosystem. *Journal of the North American Benthological Society*. 14 (2): 249.
- Karnowski, E.H. and the United States. 1974. Soil survey of Pitt County, North Carolina: Washington, NC, Soil Conservation Service: for sale by the Supt. of Docs., U.S. Govt. Print. Off.
- Kaushal, S.S., Groffman, P.M., Mayer, P.M., Striz, E. and Gold, A.J., 2008. Effects of stream restoration on denitrification in an urbanizing watershed. *Ecological Applications*. 18(3): 789-804.
- Korom, S.F. 1992. Natural denitrification in the saturated zone: a review. *Water Resources Research*. 41: 1657-1668.
- Lautier, J.C. 2001. Hydrogeologic framework and groundwater conditions in the North Carolina Central Coastal Plain. NC Dept. of Environment and Natural Resources, Div. of Water Resources, 38 pp.
- Madison, R.J. and Burnett, J.O. 1985. Overview of the occurrence of nitrate in ground water of the United States. U.S. Geological Survey Water Supply Paper 2275.
- Maddy, J. 1979. Geologic history of Coastal Plain streams eastern Pitt County, NC. M.S. Thesis, East Carolina University, Greenville, NC. 102 pp.
- McClain, M.E., Richey, J.E., and Pimentel, T.P. 1994. Groundwater nitrogen dynamics at the terrestrial-lotic interface of a small catchment in the Central Amazon Basin. *Biogeochemistry*. 27 (2): 113.
- McDowell, W.H., Bowden, W.B., and Asbury, C.E. 1992. Riparian nitrogen dynamics in two geomorphologically distinct tropical rain forest watersheds: subsurface solute patterns. *Biogeochemistry*. 18 (2): 53.
- National Research Council. 2000. Clean coastal waters: Understanding and reducing the effects of nutrient pollution. National Academy Press: Washington, D.C. 300 pp.
- O'Brien, A.K., Eshleman, K.N., and Pollard, J.S. 1994. Interactions Between Groundwater and Surface Water in a Virginia Coastal Plain Watershed. 2. Acid-Base Chemistry. *Hydrological Processes*. 8 (5): 411.
- Patrick Jr., W.H. and Tusneem, M.E. 1972. Nitrogen Loss from Flooded Soil. *Ecology*. 53 (4): 735-737.

- Paul, M.J. and Meyer, J.L., 2001. Streams in the urban landscape. *Annual Review of Ecology and Systematics*, 32(1): 333.
- Pfeiffer, S.M., Bahr, J.M., and Beilfuss, R.D. 2006. Identification of groundwater flowpaths and denitrification zones in a dynamic floodplain aquifer. *Journal of Hydrology*, 325 (1), 262.
- Pickett, S.T.A., Cadenasso, M.L., Grove, J.M., Nilon, C.H., Pouyat, R.V., Zipperer, W.C., and Costanza, R. 2001. Urban Ecological Systems: Linking Terrestrial Ecological, Physical, and Socioeconomic Components of Metropolitan Areas. *Annual Review of Ecology and Systematics*, 32: 127-57.
- Ponnamperuma, F.N. The Chemistry of Submerged Soils. New York: Academic Press, 1972.
- Schilling, K.E., Li, Z. and Zhang, Y.-K., 2006. Groundwater-surface water interaction in the riparian zone of an incised channel, Walnut Creek, Iowa. *Journal of Hydrology*, 327(1-2): 140-150.
- Schilling, K.E., Zhang, Y.K. and Drobney, P. 2004. Water table fluctuations near an incised stream, Walnut Creek, Iowa. *Journal of Hydrology*, 286(1-4): 236-248.
- Schlesinger, W.H. 1997. Biogeochemistry. Academic Press: San Diego, CA. 588 pp.
- Schoonover, J.E., and Williard, K.W.J. 2003. Ground water nitrate reduction in giant cane and forest riparian buffer zones. *Journal of the American Water Resources Association*, 39 (2): 347-354.
- Shedlock, R.J, Hamilton, P.A., Denver, J.M, Phillips, P.J. 1993. Multiscale approach to regional ground-water quality assessment of the Delmarva Peninsula. In: Alley, W.M. (ed.) *Regional Ground-Water Quality*. Van Nostrand Reinhold, New York, NY, USA.
- Shideler, G.L., and Swift, D.J.P. 1972. Seismic reconnaissance of post-Miocene deposits, Middle Atlantic continental shelf - Cape Henry, Virginia, to Cape Hatteras, North Carolina. *Marine Geology*, 12(3): 165-185.
- Snyder, N. J., Mostaghimi, S., Berry, D. F., Reneau, R. B., Hong, S., McClellan, P. W., and Smith, E.P. 1998. Impact of Riparian Forest Buffers on Agricultural Nonpoint Source Pollution. *Water Resources Bulletin*: 34 (2), 385.
- Soban, J. R. 2007. Stream channel response to urban land use in the inner coastal plain of North Carolina. M.S. Thesis, East Carolina University, Greenville, NC: 154 pp.

- Soil and Plant Analysis Council, Inc. 1999. Soil Analysis: Handbook of Reference Methods. CRC Press LLC: Boca Raton, FL. 245 pp.
- Southeast Regional Climate Center. 2007. Historical Climate Summaries for North Carolina, Dept. of Natural Resources. South Carolina. <http://radar.meas.ncsu.edu/>
- Shedlock, R.J., Hamilton, P.A., Denver, J.M., Phillips, P.J. 1993. Multiscale approach to regional ground-water quality assessment of the Delmarva Peninsula. In: Alley, W.M. (ed.) Regional Ground-Water Quality. Van Nostrand Reinhold, New York, NY, USA.
- Spalding, R.F., and Exner, M.E. 1993. Occurrence of Nitrate in Groundwater. *Journal of Environmental Quality*. 22 (3): 392.
- Speiran, G.K. 2003a. Polecat Creek Watershed, Virginia. In: Lindsey, B. D. Residence times and nitrate transport in ground water discharging to streams in the Chesapeake Bay Watershed. Water-resources investigations report, 03-4035. New Cumberland, Pa: U.S. Dept. of the Interior, U.S. Geological Survey. pp. 71-86.
- Speiran, G.K. 2003b. Muddy Creek Watershed, Virginia. In: Lindsey, B. D. Residence times and nitrate transport in ground water discharging to streams in the Chesapeake Bay Watershed. Water-resources investigations report, 03-4035. New Cumberland, Pa: U.S. Dept. of the Interior, U.S. Geological Survey. pp. 87-107.
- Spruill, T.B. 2005. Geochemistry and characteristics of nitrogen transport at a confined animal feeding operation in a coastal plain agricultural watershed, and implications for nutrient loading in the Neuse River Basin, North Carolina, 1999-2002. Scientific investigations report, 2004-5283. Reston, VA: U.S. Dept. of the Interior, U.S. Geological Survey. <http://purl.access.gpo.gov/GPO/LPS102347>.
- Spruill, T. B. 2004. Effectiveness of riparian buffers in controlling ground-water discharge of nitrate to streams in selected hydrogeologic settings of the North Carolina Coastal Plain. *Water Science and Technology*. 49: 63-70.
- Spruill, T.B., Harned, D.A., Ruhl, P.M., Eimers, J.L., McMahon, G., Smith, K.E., Galeone, D.R., Woodside, M.D. 1998. Water Quality in the Albemarle-Pamlico Drainage Basin, North Carolina and Virginia, 1992-95: U.S. Geological Survey Circular 1157. 41 pp.
- Stoddard, J. L. 1994. Long-term changes in watershed retention of nitrogen. In L.A. Baker (ed.) Environmental chemistry of lakes and reservoirs. Advances in Chemistry Series. Washington, DC: American Chemical Society. Volume 237. pp. 223-284.

- Sweet, W.V., and Geratz, J.W. 2003. Bankfull Hydraulic Geometry Relationships and Recurrence Intervals for North Carolina's Coastal Plain. *Journal of the American Water Resources Association*. 39: 861-872.
- Talma, A.S., and Vogel, J.C. 1993. A Simplified Approach to Calibrating ^{14}C Dates. *Radiocarbon*. 35 (2): 317-322.
- Tesoriero, A.J., Spruill, T.B., and Eimers, J.L. 2004. Geochemistry of shallow ground water in coastal plain environments in the southeastern United States: implications for aquifer susceptibility. *Applied Geochemistry*, 19(9): 1471-1482.
- Tesoriero, A.J., Spruill, T.B., Mew, H.E., Farrell, K.M., and Harden, S.L. 2005. Nitrogen transport and transformations in a coastal plain watershed: Influence of geomorphology on flow paths and residence times. *Water Resources Research*, 41 (2): W02008.
- U.S. Environmental Protection Agency (USEPA). 2003. List of Contaminants & their Maximum Contaminant Levels (MCLs), EPA 816-F-03-016; accessed online in March, 2009 at <http://www.epa.gov/safewater/contaminants/index.html>.
- U.S. Environmental Protection Agency. 1990. National survey of pesticides in drinking water wells phase I report. USEPA Rep. 570/9-90-015. Office of Water, Office of Pesticides and Toxic Substances. Washington, D.C. 98 pp.
- Vepraskas, M.J. and Faulkner, S.P. 2001. Redox Chemistry of Hydric Soils. In: Richardson, J.L., and Vepraskas, M.J. Wetland Soils: Genesis, Hydrology, Landscapes, and Classification. Boca Raton, Fla. [u.a.]: Lewis Publ. 417 pp.
- Walsh, C. J., Roy, A. H., Feminella, J.W., Cottingham, P.D., Groffman, P.M., and Morgan, R.P. 2005. The urban stream syndrome: current knowledge and the search for a cure. *Journal of the North American Benthological Society*. 24: 706–723.
- Westco Scientific, 2006a. SmartChem Method 375-100E-2-Rev.A-02-0906: Nitrate-Nitrite in water, wastewater, soil extracts and other aqueous samples. Details available at www.WestcoScientific.com.
- Westco Scientific, 2006b. Modified SmartChem Method 390-200E-Rev.A-0906: Total Kjeldahl Nitrogen (TKN) in Water, Waste Water, Soil Extracts and other aqueous samples for use with a Colorimetric, Block Digestor. Modified by Cooper, B.C. 2006. Copies available on request. Details available at www.WestcoScientific.com.
- Wetzel, R.G. Limnology. Philadelphia: Saunders, 1975.

- Williams, J.B., and Pinder, J.E. III. 1990. Ground Water Flow and Runoff in a Coastal Plain Stream. *Journal of the American Water Resources Association*. 26(2): 343-352.
- Winner, M.D. JR., and Coble, R.W. 1996. Hydrogeologic framework of the North Carolina Coastal Plain. U.S. Geol. Surv. Prof. Pap. 1404-I. 106 pp.
- Winner, M.D. JR., and Simmons, C.E. 1977. Hydrology of the Creeping Swamp Watershed, North Carolina: with reference to potential effects of stream channelization. USGS Water-resources investigation 77-26. Raleigh, NC. 54 pp.
- Worrall, F., Burt, T., and Adamson, J. 2004. Can climate change explain increases in DOC flux from upland peat catchments? *The Science of the Total Environment*. 326 (1): 95.

Appendix A: Summary Statistics of Measured Variables

Table A1. Descriptive statistics for the vertical distribution of organic matter (processed from samples as a percent) at the three study sites. Median values for cores from well nest locations reflect thickness and extent of buried organic matter across each floodplain.

		Organic Matter (%)			
		Position			
		near-st.	floodplain	up-grad.	Site Total
<i>urban</i>	N	24	23	32	79
	Median	.7	1.3	2.6	1.2
	Min	.0	.3	.0	.0
	Max	10.1	27.7	48.6	48.6
<i>suburban</i>	N	29	32	33	94
	Median	1.9	.9	.6	.9
	Min	.0	.0	.1	.0
	Max	73.3	26.2	6.3	73.3
<i>rural</i>	N	21	23	37	81
	Median	.6	.4	.5	.4
	Min	.2	.0	.0	.0
	Max	12.4	1.6	4.5	12.4

Table A2. Descriptive statistics for hydraulic conductivity across the three floodplains.

	log K (m/s)		
	Site		
	<i>urban</i>	<i>suburban</i>	<i>rural</i>
N	6	6	6
Mean	-6.5	-5.3	-6.0
Median	-6.6	-6.2	-6.0
Min	-7.1	-6.8	-7.8
Max	-6.1	-4.7	-5.7
Range	-6.1	-4.7	-5.7

Table A3. Logarithm of hydraulic conductivity (m/s) in wells of the urban, suburban, and rural sites. Hydraulic conductivities were generally lower in the shallow wells of the urban and suburban sites and the deep wells of the rural site. Higher conductivities in deep wells of the urban and suburban sites suggest faster groundwater flow velocity along the deeper hydrologic flowpaths.

		log K (m/s)		
		position		
		near-st.	floodplain	up-grad.
<i>urban</i>	shallow	-6.8	-6.5	-7.0
	deep	-7.1	-6.5	-6.1
<i>suburban</i>	depth	-6.2	-6.1	-6.4
	shallow	-4.7	-5.2	-6.8
<i>rural</i>	deep	-6.7	-5.7	-6.3
	depth	-7.8	-5.8	-5.8

Table A4. Descriptive data summary for continuous near-stream water table depth measured in near-stream wells of the three study sites.

		Depth to water table (m)		
		Site		
		<i>urban</i>	<i>suburban</i>	<i>rural</i>
<i>annual</i>	N	14236	14236	14236
	Mean	1.44	.96	.81
	Median	1.47	.99	.82
	Minimum	.82	.20	.00
	Maximum	1.55	1.22	1.31
	Range	.74	1.02	1.31
	Standard Deviation	.08	.12	.25

Table A5. Descriptive statistics for monthly depth to groundwater data at the three study sites.

Site: <i>Urban</i>				
Statistic	Nest location			Site Total
	Near-st.	Floodplain	Up-grad.	
N (# of samples)	12	12	12	36
annual median	1.60	1.53	1.56	1.58
max	1.67	1.69	1.84	1.84
min	1.52	1.27	1.36	1.27
range	0.15	0.42	0.48	0.57

Site: <i>Suburban</i>				
Statistic	Nest location			Site Total
	Near-st.	Floodplain	Up-grad.	
N (# of samples)	12	12	12	36
annual median	1.18	1.06	1.58	1.17
max	1.25	1.17	1.73	1.73
min	0.94	0.71	0.96	0.71
range	0.32	0.47	0.77	1.02

Site: <i>Rural</i>				
Statistic	Nest location			Site Total
	Near-st.	Floodplain	Up-grad.	
N (# of samples)	12	12	12	36
annual median	1.05	0.88	3.90	1.04
max	1.68	1.01	4.02	4.02
min	0.71	0.42	3.45	0.42
range	0.97	0.59	0.58	3.60

Table A6. Seasonal groundwater discharge from the floodplain of each site.

			Discharge (m3/mo)		
			Site		
			<i>urban</i>	<i>suburban</i>	<i>rural</i>
Season	fall	Count	3	3	3
		Median	4.6	11.2	12.1
		Minimum	3.5	11.1	9.9
		Maximum	5.0	11.3	15.9
		Range	1.5	.2	6.0
	winter	Count	3	3	3
		Median	5.3	13.6	8.9
		Minimum	5.1	13.3	8.1
		Maximum	6.5	19.0	14.2
		Range	1.5	5.8	6.1
	spring	Count	3	3	3
		Median	6.0	18.3	17.3
		Minimum	5.6	14.9	17.0
		Maximum	6.1	22.8	18.6
		Range	.5	8.0	1.6
	summer	Count	3	3	3
		Median	4.5	10.2	14.4
		Minimum	4.5	10.2	14.4
		Maximum	4.7	10.6	15.0
		Range	.3	.3	.7

Table A7. Data summary for groundwater levels (m AMSL) in shallow, up-gradient and near-stream wells at the three study sites. Shallow groundwater levels at both the up-gradient and near-stream wells had the smallest annual range at the urban site.

			Groundwater level (m AMSL)		
			Site		
			urban	suburban	rural
Position	Up-gradient	N	12	12	12
		Median	11.6	10.0	5.1
		Minimum	11.3	9.9	4.9
		Maximum	11.8	10.6	5.5
		Range	.5	.8	.6
	Near-stream	N	12	12	12
		Median	10.7	9.4	4.5
		Minimum	10.7	9.3	4.3
		Maximum	10.8	9.6	4.9
		Range	.1	.3	.6

Table A8. Descriptive Statistics for seasonal groundwater temperatures across the range of urban land use based on hand-dipped monthly measurements in all 6 wells of each floodplain.

			Temp (C)		
			Site		
			<i>urban</i>	<i>suburban</i>	<i>rural</i>
Season	<i>annual</i>	N	72	72	72
		Med.	18.6	17.3	17.2
		Min.	15.3	13.5	11.7
		Max.	22.6	20.8	21.9
		Range	7.3	7.3	10.2
	<i>fall</i>	N	18	18	18
		Med.	20.0	18.5	19.0
		Min.	19.6	17.3	16.5
		Max.	22.6	20.5	20.9
		Range	3.0	3.2	4.4
	<i>winter</i>	N	18	18	18
		Med.	17.0	14.8	14.2
		Min.	15.3	13.5	11.7
		Max.	18.5	16.5	17.2
		Range	3.2	3.0	5.5
	<i>spring</i>	N	18	18	18
		Med.	17.1	15.3	15.5
		Min.	16.1	14.2	14.1
		Max.	18.6	17.1	17.7
		Range	2.5	2.9	3.6
	<i>summer</i>	N	18	18	18
		Med.	20.8	19.0	19.5
		Min.	18.1	18.0	17.1
		Max.	22.0	20.8	21.9
		Range	3.9	2.8	4.8

Table A9. Descriptive statistics based on hand-dipped monthly measurements for annual temperature (C) by position in shallow and deep wells of the three study sites.

				Temp (C)		
				Position		
				<i>up-gradient</i>	<i>floodplain</i>	<i>near-st.</i>
Site	<i>urban</i>	deep	N	12	12	12
			Median	19.0	19.1	19.3
			Minimum	15.8	15.4	16.0
			Maximum	21.0	21.9	22.6
		shallow	N	12	12	12
			Median	18.2	19.1	19.1
			Minimum	16.3	15.3	15.6
			Maximum	19.9	22.2	21.9
	<i>suburban</i>	deep	N	12	12	12
			Median	16.7	16.9	18.3
			Minimum	13.7	13.8	14.5
			Maximum	19.0	20.4	20.8
		shallow	N	12	12	12
			Median	16.6	16.7	17.3
			Minimum	13.7	13.5	14.1
			Maximum	18.9	19.6	20.3
	<i>rural</i>	deep	N	12	12	12
			Median	17.2	17.4	17.4
			Minimum	14.9	12.1	14.1
			Maximum	19.5	21.9	20.0
		shallow	N	12	12	12
			Median	17.3	16.8	17.1
			Minimum	15.0	11.7	12.5
			Maximum	19.7	21.9	20.9

Table A10. Descriptive data for NO₃⁻-N concentrations (mg/L) from floodplain wells of the three sites grouped by depth.

				Nitrate-N (mg/L)			
				position			
				<i>up-grad.</i>	<i>floodplain</i>	<i>near-st.</i>	<i>total</i>
Site	<i>urban</i>	shallow	Count	12	12	12	36
			Median	.1	.1	.1	.1
			Minimum	.0	.0	.0	.0
			Maximum	.2	.2	.3	.3
			Range	.2	.2	.2	.3
		deep	Count	12	12	12	36
			Median	.4	.3	.2	.3
			Minimum	.1	.0	.1	.0
			Maximum	.5	.5	.3	.5
			Range	.4	.5	.2	.5
	<i>suburban</i>	shallow	Count	12	12	12	36
			Median	.1	.0	.1	.1
			Minimum	.0	.0	.1	.0
			Maximum	.3	.2	.2	.3
			Range	.2	.2	.1	.3
		deep	Count	12	12	12	36
			Median	.5	.1	.1	.1
			Minimum	.4	.0	.1	.0
			Maximum	.6	.3	.2	.6
			Range	.2	.3	.2	.5
	<i>rural</i>	shallow	Count	12	12	12	36
			Median	9.3	9.6	.1	8.3
			Minimum	7.0	7.5	.0	.0
			Maximum	12.3	11.2	.2	12.3
			Range	5.3	3.7	.2	12.3
		deep	Count	12	12	12	36
			Median	3.9	1.0	.1	1.0
			Minimum	2.0	.3	.0	.0
			Maximum	5.3	3.7	.1	5.3
			Range	3.4	3.4	.1	5.3

Table A11. Descriptive data for in-stream nitrate concentrations compared to average near-stream nitrate concentrations from shallow and deep near-stream wells.

			Nitrate-N (mg/L)	
			Position	
			<i>near-st. avg.</i>	<i>stream</i>
Site	<i>urban</i>	N	12	12
		Median	.1	.2
		Minimum	.1	.0
		Maximum	.2	.5
		Range	.1	.5
	<i>suburban</i>	N	12	12
		Median	.1	1.6
		Minimum	.0	.9
		Maximum	.2	2.3
		Range	.1	1.4
	<i>rural</i>	N	12	12
		Median	.1	.3
		Minimum	.0	.0
		Maximum	.1	.8
		Range	.1	.8

Table A12. Comparative statistics for nitrate-N and ammonium-N (mg/L) from *shallow* wells along the three study transects.

		Nitrate-N (mg/L)				Ammonium-N (mg/L)			
		Position				Position			
		<i>up-grad.</i>	<i>floodplain</i>	<i>near-st.</i>	<i>stream</i>	<i>up-grad.</i>	<i>floodplain</i>	<i>near-st.</i>	<i>stream</i>
urban	Count	12	12	12	12	12	12	12	12
	Median	.1	.1	.1	.2	.4	2.6	1.1	.1
	Minimum	.0	.0	.0	.0	.0	.0	.8	.0
	Maximum	.2	.2	.3	.5	.6	5.3	1.3	.3
	Range	.2	.2	.2	.5	.6	5.3	.5	.3
suburban	Count	12	12	12	12	12	12	12	12
	Median	.1	.0	.1	1.6	.1	.1	.1	.1
	Minimum	.0	.0	.1	.9	.0	.0	.0	.0
	Maximum	.3	.2	.2	2.3	.1	.2	.1	.3
	Range	.2	.2	.1	1.4	.1	.1	.1	.2
rural	Count	12	12	12	12	12	12	12	12
	Median	9.3	9.6	.1	.3	.1	.1	.7	.0
	Minimum	7.0	7.5	.0	.0	.0	.0	.5	.0
	Maximum	12.3	11.2	.2	.8	.1	.2	1.1	.1
	Range	5.3	3.7	.2	.8	.1	.2	.6	.1

Table A13. Comparative statistics for nitrate-N and ammonium-N (mg/L) from *deep* wells along the three study transects.

			Nitrate-N (mg/L)				Ammonium-N (mg/L)			
			Position				Position			
			<i>up-grad.</i>	<i>floodplain</i>	<i>near-st.</i>	<i>stream</i>	<i>up-grad.</i>	<i>floodplain</i>	<i>near-st.</i>	<i>stream</i>
Site	urban	Count	12	12	12	12	12	12	12	12
		Median	.4	.3	.2	.2	.2	.1	.2	.1
		Minimum	.1	.0	.1	.0	.1	.0	.1	.0
		Maximum	.5	.5	.3	.5	.4	.3	.2	.3
		Range	.4	.5	.2	.5	.3	.3	.1	.3
	suburban	Count	12	12	12	12	12	12	12	12
		Median	.5	.1	.1	1.6	.1	.1	.1	.1
		Minimum	.4	.0	.1	.9	.0	.0	.0	.0
		Maximum	.6	.3	.2	2.3	.1	.1	.1	.3
		Range	.2	.3	.2	1.4	.0	.1	.1	.2
	rural	Count	12	12	12	12	12	12	12	12
		Median	3.9	1.0	.1	.3	.1	.1	.5	.0
		Minimum	2.0	.3	.0	.0	.1	.0	.1	.0
		Maximum	5.3	3.7	.1	.8	.4	.2	1.8	.1
		Range	3.4	3.4	.1	.8	.3	.2	1.7	.1

Table A14. Comparative statistics for nitrate-N and DON (mg/L) by position and depth across the three study transects.

			Nitrate-N (mg/L)				DON from 5/30/2008 (mg/L)			
			position				position			
			<i>up-gradient</i>	<i>floodplain</i>	<i>near-st.</i>	<i>stream</i>	<i>up-gradient</i>	<i>floodplain</i>	<i>near-st.</i>	<i>stream</i>
urban	<i>shallow</i>	N	12	12	12	12	1	1	1	1
		Median	.1	.1	.1	.9	.2	.7	.3	.3
	<i>deep</i>	N	12	12	12	12	1	1	1	1
		Median	.4	.3	.2	.9	.1	.5	.6	.3
suburban	<i>shallow</i>	N	12	12	12	12	1	1	1	1
		Median	.1	.0	.1	7.0	.2	.6	.3	.2
	<i>deep</i>	N	12	12	12	12	1	1	1	1
		Median	.5	.1	.1	7.0	.2	.8	.4	.2
rural	<i>shallow</i>	N	12	12	12	12	1	1	1	1
		Median	9.3	9.6	.1	1.5	.3	.7	.5	.7
	<i>deep</i>	N	12	12	12	12	1	1	1	1
		Median	3.9	1.0	.1	1.5	.7	.3	.7	.7

Table A15. Seasonal statistics for nitrate-N and ammonium-N (mg/L) from shallow and deep wells along the three transects.

			Nitrate-N (mg/L)				Ammonium-N (mg/L)			
			Season				Season			
			<i>fall</i>	<i>winter</i>	<i>spring</i>	<i>summer</i>	<i>fall</i>	<i>winter</i>	<i>spring</i>	<i>summer</i>
urban	<i>shallow</i>	N	9	9	9	9	9	9	9	9
		Median	.1	.0	.0	.1	1.1	.3	1.0	.9
		Range	.2	.2	.1	.2	2.2	2.2	5.1	4.0
	<i>deep</i>	N	9	9	9	9	9	9	9	9
		Median	.2	.3	.4	.3	.2	.1	.2	.3
		Range	.3	.4	.4	.3	.2	.1	.3	.2
suburban	<i>shallow</i>	N	9	9	9	9	9	9	9	9
		Median	.2	.1	.0	.1	.1	.1	.1	.1
		Range	.2	.1	.1	.1	.1	.1	.1	.1
	<i>deep</i>	N	9	9	9	9	9	9	9	9
		Median	.1	.1	.1	.2	.1	.0	.1	.1
		Range	.5	.5	.4	.5	.1	.1	.0	.1
rural	<i>shallow</i>	N	9	9	9	9	9	9	9	9
		Median	11.1	8.2	7.5	8.4	.1	.1	.1	.1
		Range	12.3	10.4	9.5	10.2	1.1	.7	.7	.7
	<i>deep</i>	N	9	9	9	9	9	9	9	9
		Median	1.0	.5	.5	1.6	.1	.1	.2	.2
		Range	2.8	5.3	4.4	4.6	.6	.2	.9	1.7

Table A16. Descriptive statistics for DOC concentrations across study sites by floodplain (f.p.) position. Concentrations are grouped by depth to show variation with depth and distance from organic rich sediment layers.

				DOC (mg/L)			
				Position			
				<i>up-gradient</i>	<i>floodplain</i>	<i>near-st</i>	<i>f.p. total</i>
Site	urban	<i>shallow</i>	N	12	12	12	36
			Median	6.2	14.2	4.2	5.7
			Minimum	1.3	.0	3.1	.0
			Maximum	7.7	27.2	6.1	27.2
			Range	6.4	27.2	2.9	27.2
		<i>deep</i>	N	12	12	12	36
			Median	2.6	1.9	1.3	2.0
			Minimum	.0	.4	1.0	.0
			Maximum	20.5	3.6	6.5	20.5
			Range	20.5	3.2	5.5	20.5
	suburban	<i>shallow</i>	N	12	12	12	36
			Median	1.4	5.1	2.1	2.8
			Minimum	.5	1.0	.6	.5
			Maximum	4.5	13.8	8.2	13.8
			Range	4.0	12.9	7.5	13.3
		<i>deep</i>	N	12	12	12	36
			Median	1.5	1.2	1.1	1.3
			Minimum	.4	.2	.1	.1
			Maximum	15.4	3.8	3.7	15.4
			Range	14.9	3.6	3.6	15.2
	rural	<i>shallow</i>	N	12	12	12	36
			Median	1.5	2.2	3.6	2.3
			Minimum	.3	.5	1.6	.3
			Maximum	5.5	5.5	7.5	7.5
			Range	5.2	5.0	5.9	7.2
		<i>deep</i>	N	12	12	12	36
			Median	1.5	1.6	9.0	2.2
			Minimum	.5	.9	4.9	.5
			Maximum	3.7	5.2	33.3	33.3
			Range	3.2	4.4	28.5	32.8

Table A17. Descriptive statistics for dissolved oxygen (DO) concentrations across the floodplains of the three study sites. Data has been grouped by depth and floodplain position for consideration of spatial relationships.

				DO (mg/L)			
				Position			
				<i>up- gradient</i>	<i>floodplain</i>	<i>near-st</i>	<i>f.p. total</i>
Site	urban	shallow	N	11	11	11	33
			Median	1.0	1.0	.8	.8
			Minimum	.5	.4	.3	.3
			Maximum	3.8	5.6	1.3	5.6
			Range	3.3	5.2	.9	5.3
		deep	N	11	11	11	33
			Median	1.9	1.5	.8	1.5
			Minimum	.4	.3	.0	.0
			Maximum	3.7	2.7	1.9	3.7
			Range	3.3	2.4	1.9	3.7
	suburban	shallow	N	11	11	11	33
			Median	.7	.3	.4	.5
			Minimum	.5	.2	.2	.2
			Maximum	3.7	1.4	1.2	3.7
			Range	3.2	1.2	1.0	3.5
		deep	N	11	11	11	33
			Median	1.2	.4	.6	.7
			Minimum	.6	.2	.1	.1
			Maximum	1.7	.9	1.5	1.7
			Range	1.1	.7	1.3	1.6
	rural	shallow	N	11	11	11	33
			Median	.8	.5	.4	.5
			Minimum	.3	.1	.2	.1
			Maximum	1.7	1.3	1.7	1.7
			Range	1.4	1.2	1.5	1.6
		deep	N	11	11	11	33
			Median	.6	.4	.3	.4
			Minimum	.2	.2	.1	.1
			Maximum	1.9	2.4	1.1	2.4
			Range	1.7	2.2	1.0	2.3

Table A18. Chloride concentrations from floodplain well samples at the three sites grouped by depth. Chloride concentrations were determined for samples from five monthly sampling events from 2/29/2008 to 8/13/2008.

				Chloride conc. (mg/L)			
				Position			
				<i>up-grad</i>	<i>floodplain</i>	<i>near-st</i>	<i>in-stream</i>
Site	urban	<i>shallow</i>	N	5	5	5	5
			Median	12.6	7.2	10.9	21.8
			Minimum	10.1	5.1	7.1	6.7
			Maximum	15.1	8.0	11.8	22.6
			Range	5.0	2.9	4.7	15.9
		<i>deep</i>	N	5	5	5	
			Median	10.2	7.8	9.4	
			Minimum	9.6	5.7	7.4	
			Maximum	13.2	10.5	10.9	
			Range	3.7	4.9	3.5	
	suburban	<i>shallow</i>	N	5	5	5	5
			Median	15.1	16.8	17.3	24.2
			Minimum	12.0	11.8	15.6	15.1
			Maximum	16.9	30.1	28.0	43.0
			Range	4.9	18.3	12.4	27.9
		<i>deep</i>	N	5	5	5	
			Median	20.0	21.0	23.5	
			Minimum	14.2	14.0	17.8	
			Maximum	38.4	31.1	29.3	
			Range	24.2	17.1	11.5	
	rural	<i>shallow</i>	N	5	5	5	5
			Median	28.1	40.0	25.6	15.7
			Minimum	23.0	30.5	17.3	12.2
			Maximum	31.5	44.4	44.0	18.7
			Range	8.4	13.9	26.7	6.5
		<i>deep</i>	N	5	5	5	
			Median	28.4	31.1	19.0	
			Minimum	21.1	23.7	10.2	
			Maximum	32.0	35.5	48.2	
			Range	10.9	11.8	38.0	

Appendix B: Electroconductivity Response Logs

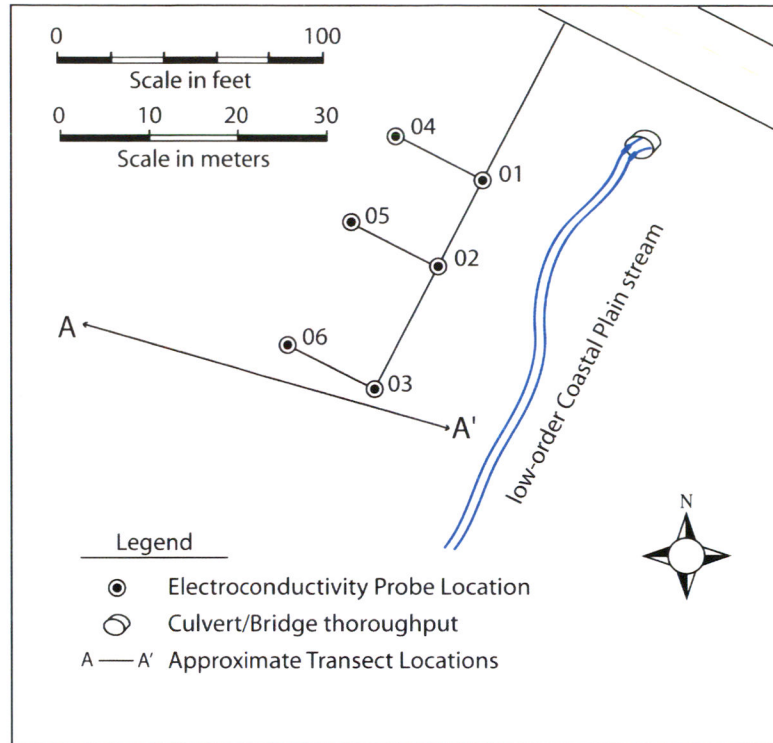
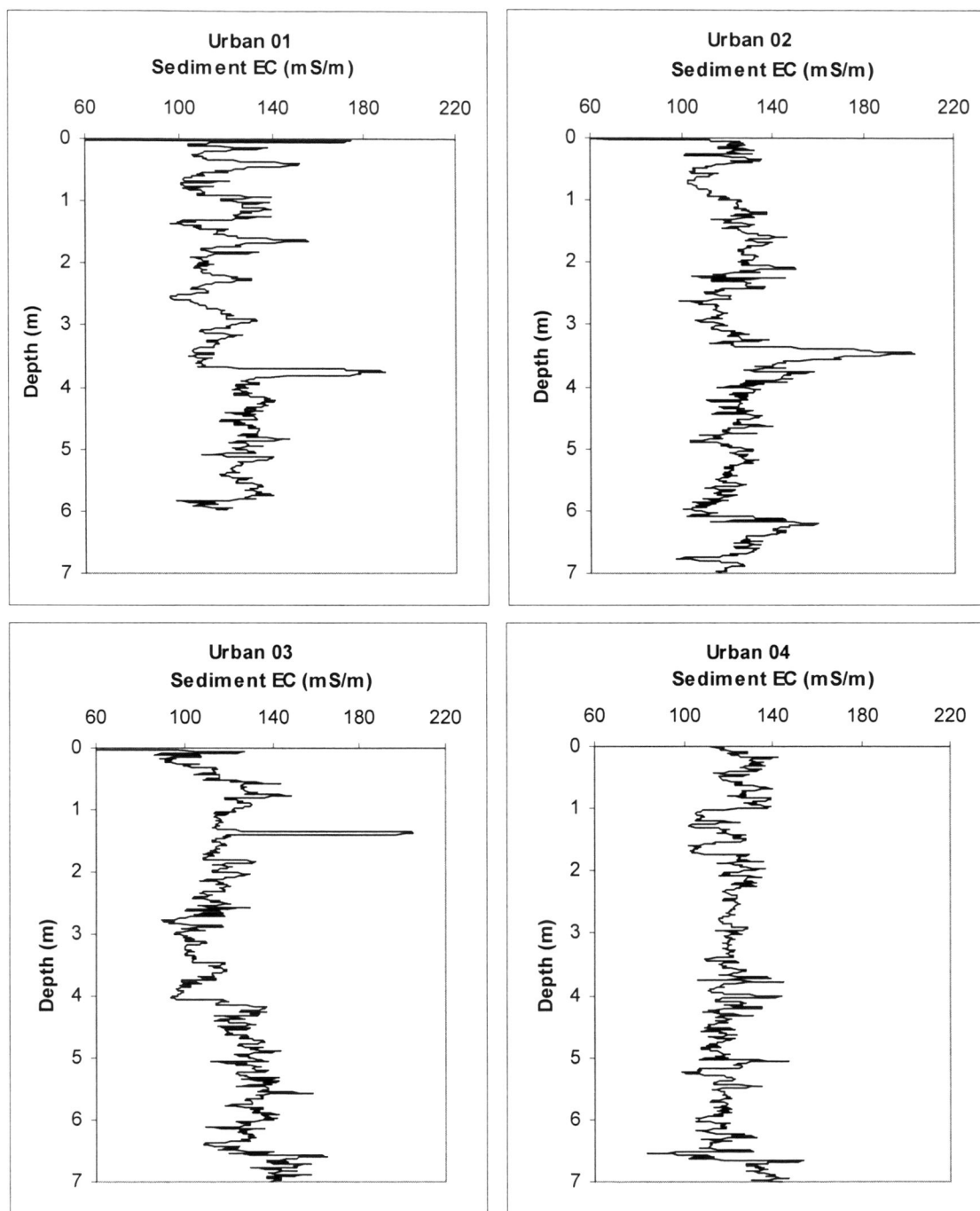
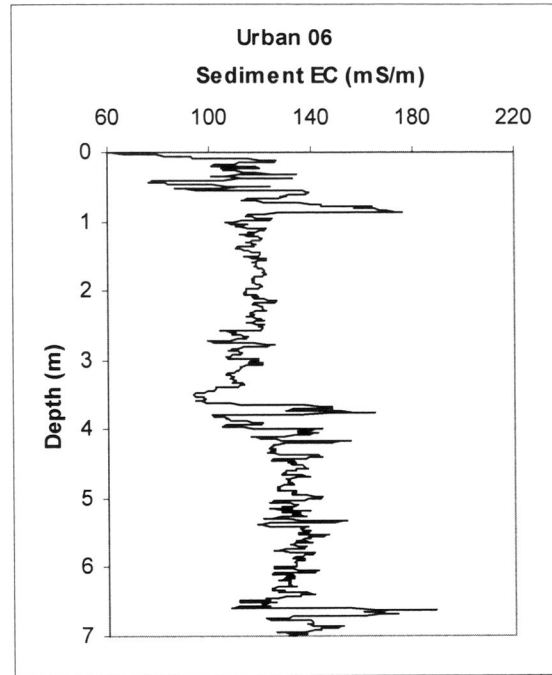
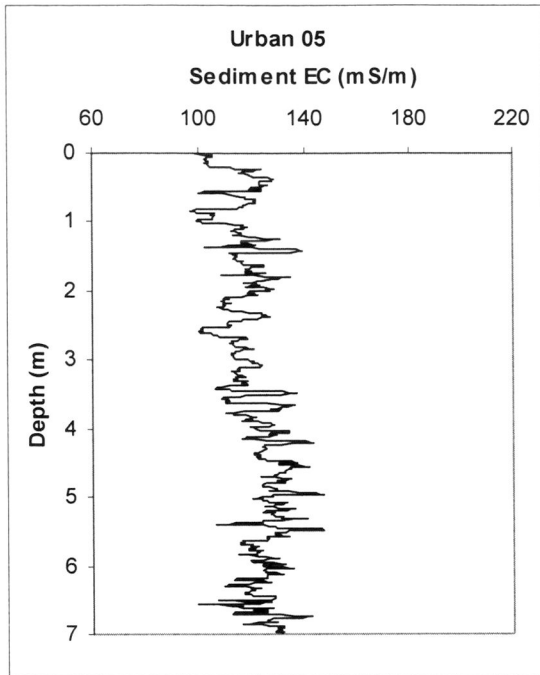


Figure B1. Generalized location map showing approximate layout of the 5-6 point electroconductivity grids used to estimate floodplain stratigraphy in preparation for well transect installation at each study site.

Appendix B1

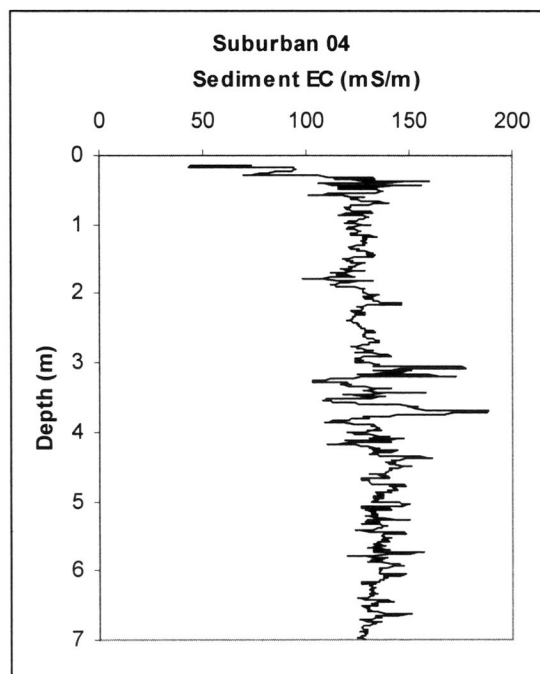
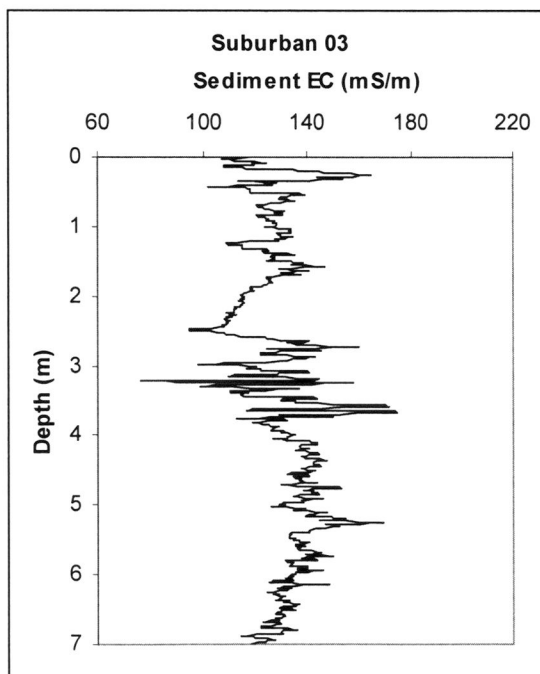
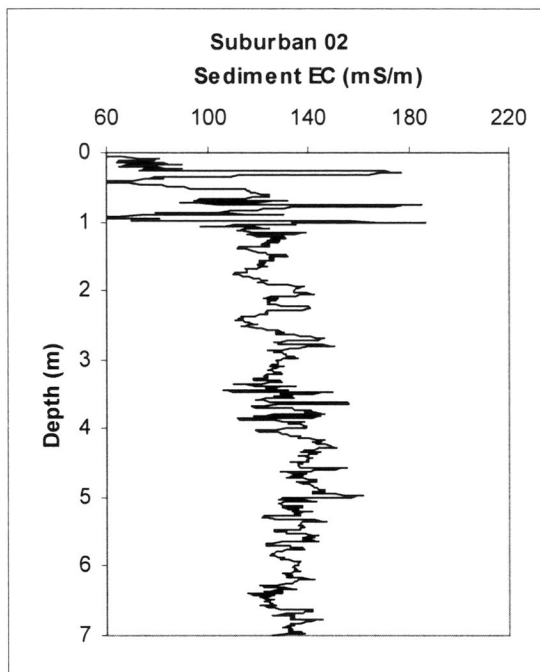
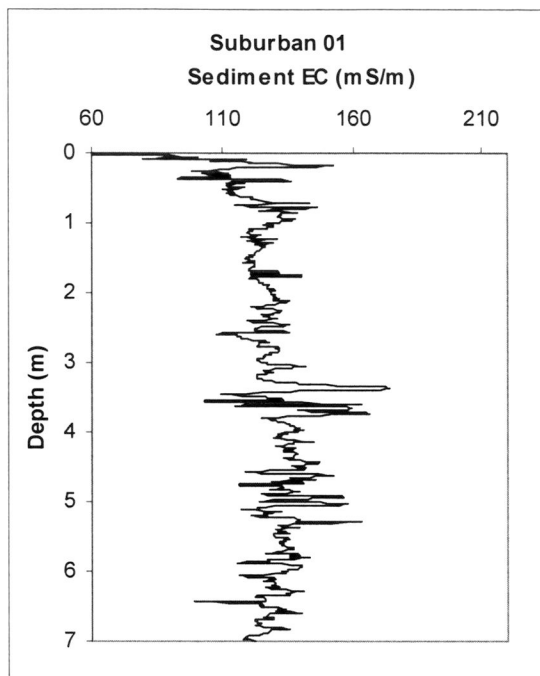
Urban Electroconductivity Logs

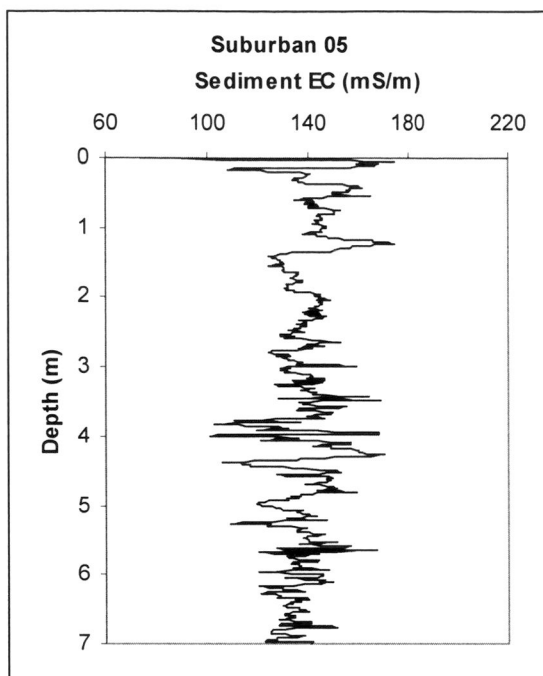




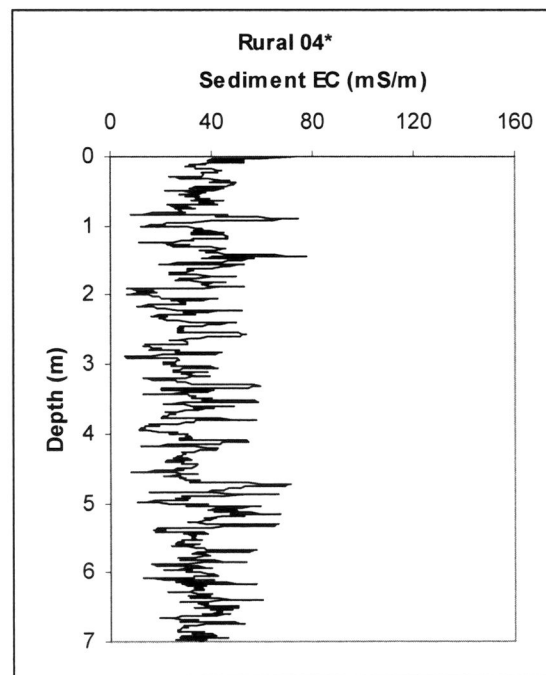
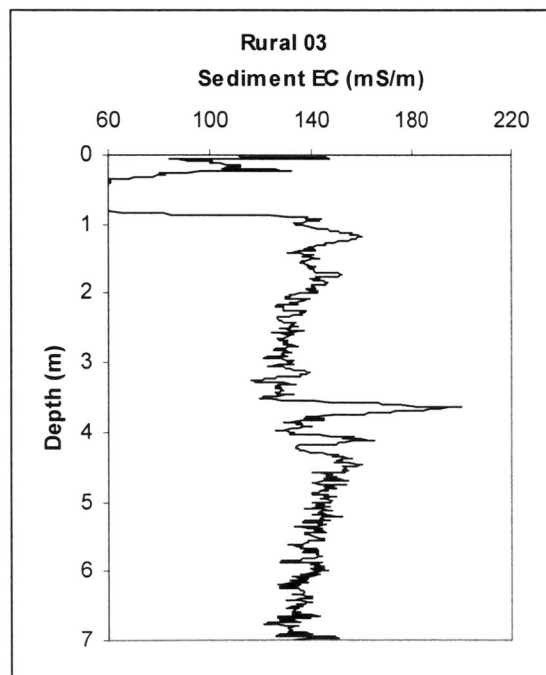
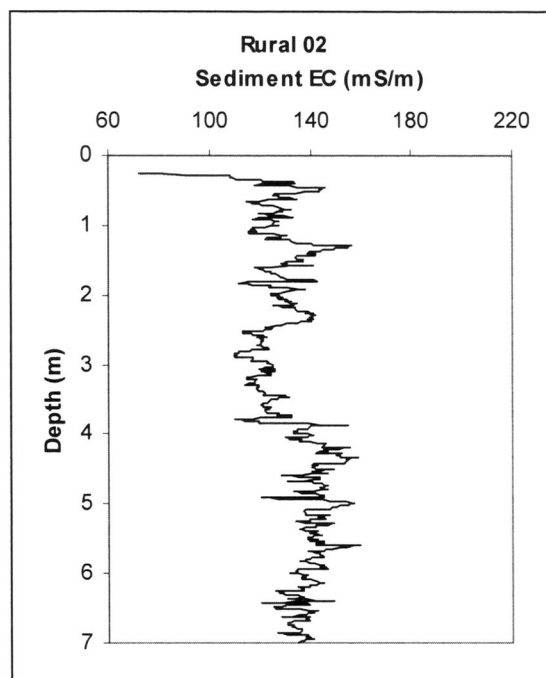
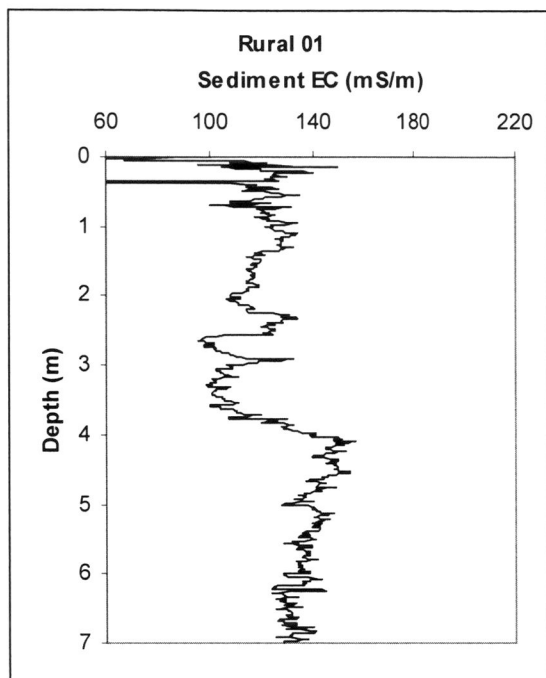
Appendix B2

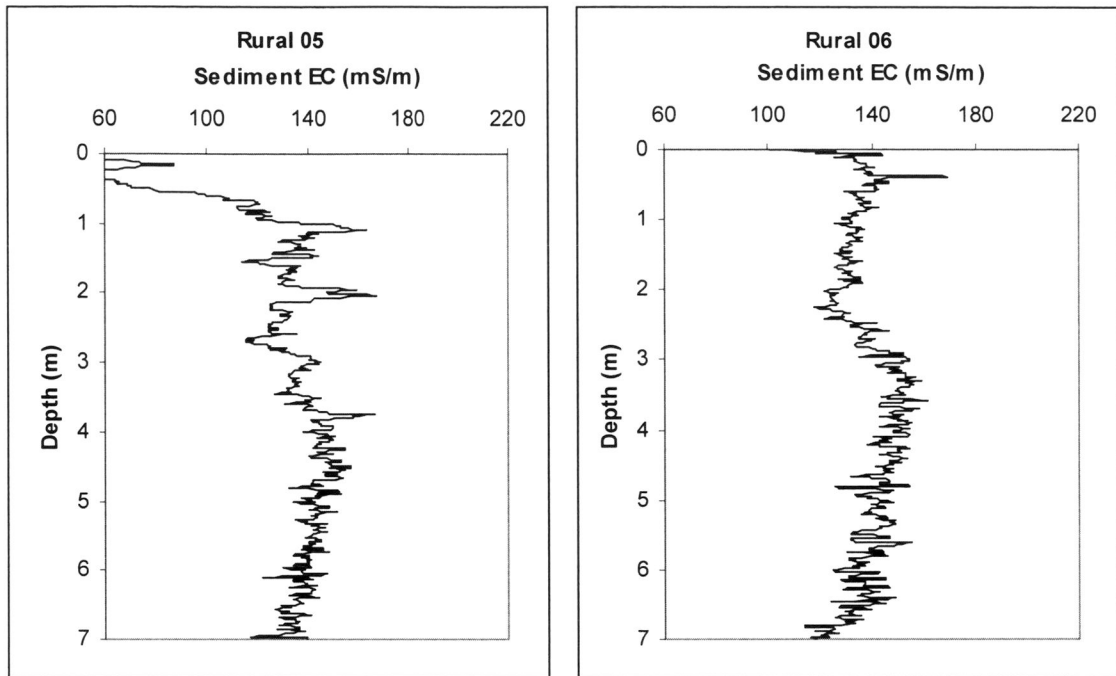
Suburban Electroconductivity Logs





Appendix B3 Rural Electroconductivity Logs





* Electroconductivity log Rural 04 likely experienced considerable interference from an overlying electric dog fence.

Appendix C: Sediment Core Logs

Figure C1. Symbol key for lithologic symbols used on the core logs to delineate distinct stratigraphic units and their characteristics.

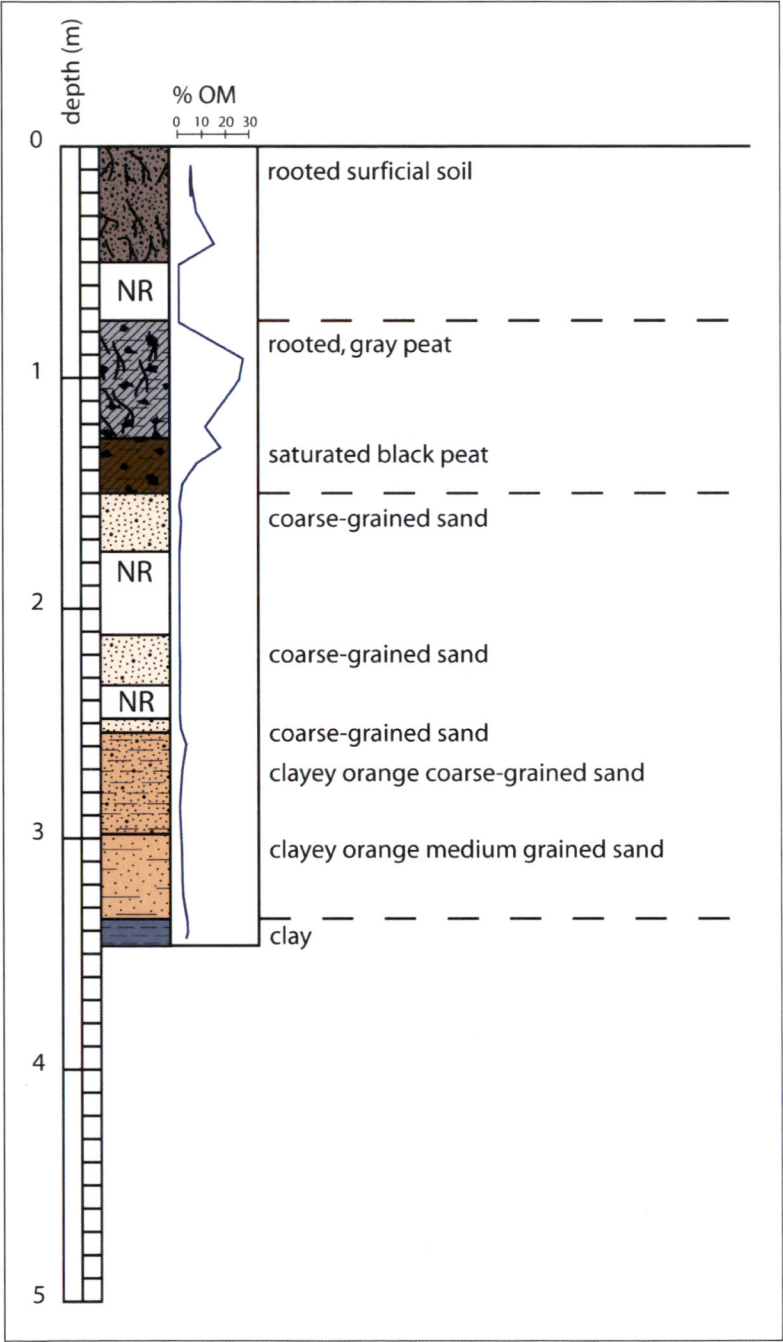
Lithologic symbols used for core logs

 rooted surface soil	 loamy sand
 sand with clay lenses	 clay
 plant debris and wood chips	 shell material lenses
 peat	 gravel driveway
 fine-grained sand	 very coarse sand and gravel
 medium-grained sand	 roots and plant debris
 coarse-grained sand	- - - major facies change
 sandy loam	

Note i: Core labels correspond with well nest locations shown on floodplain transects throughout this manuscript. i.e. Urban Floodplain Core N1 corresponds with the near-stream N1 wells shown in Figures 4, 12, and 15.

Urban Floodplain Core N1

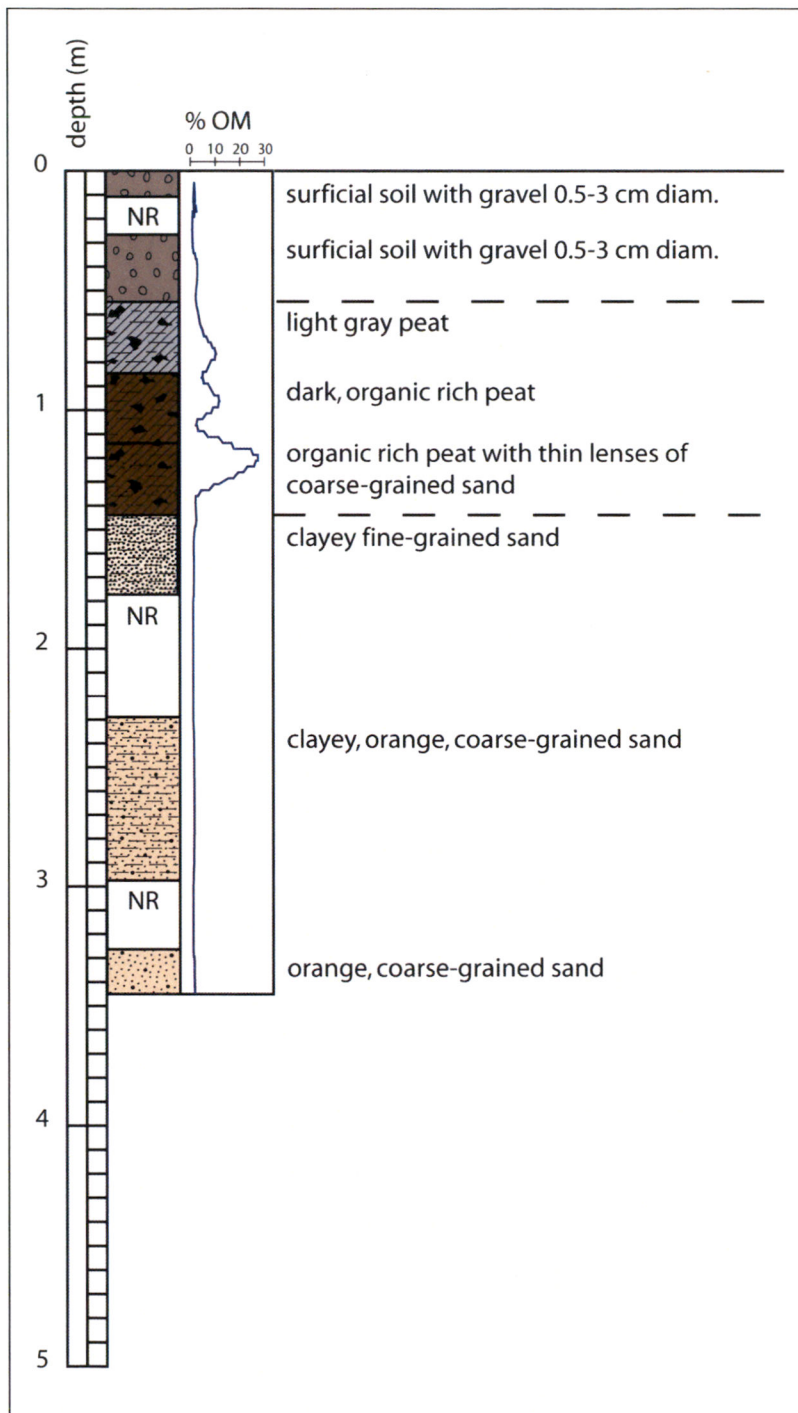
Lat. 35°35'41.8" N
Long. 77°21'23.77" W



Urban Floodplain Core N2

Lat. 35°35'41.9" N

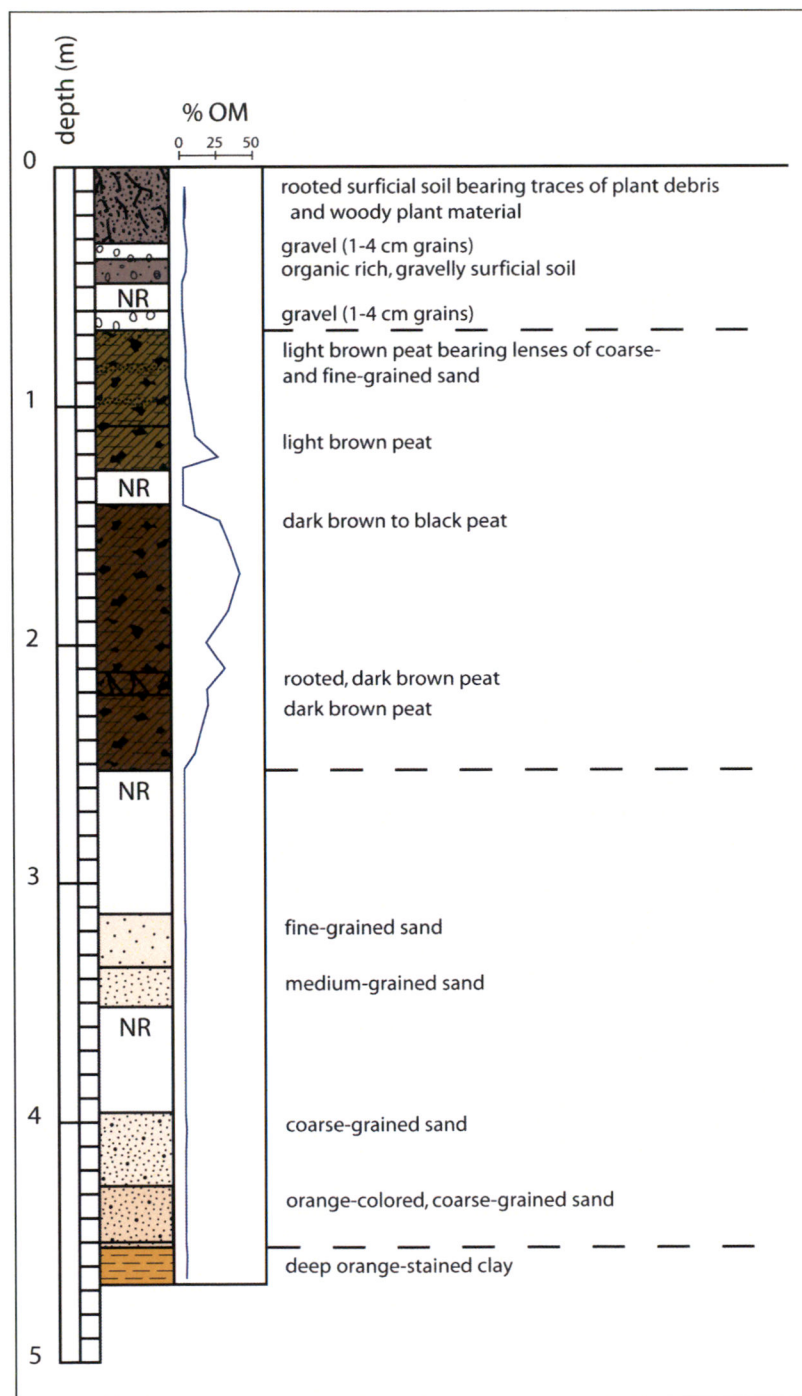
Long. 77°21'24.1" W



Urban Floodplain Core N3

Lat. 35°35'41.9" N

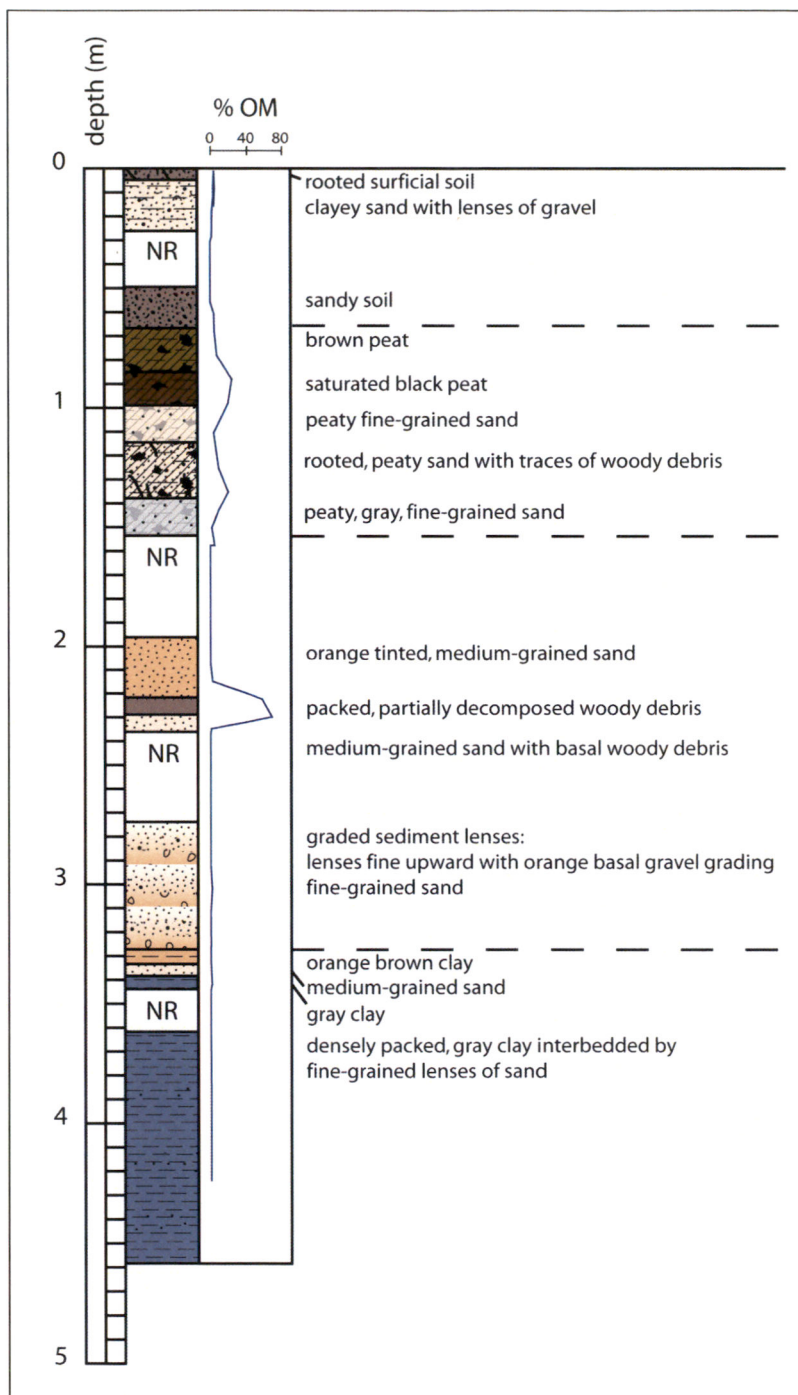
Long. 77°21'24.1" W



Suburban Floodplain Core N1

Lat. 35°34'47.8" N

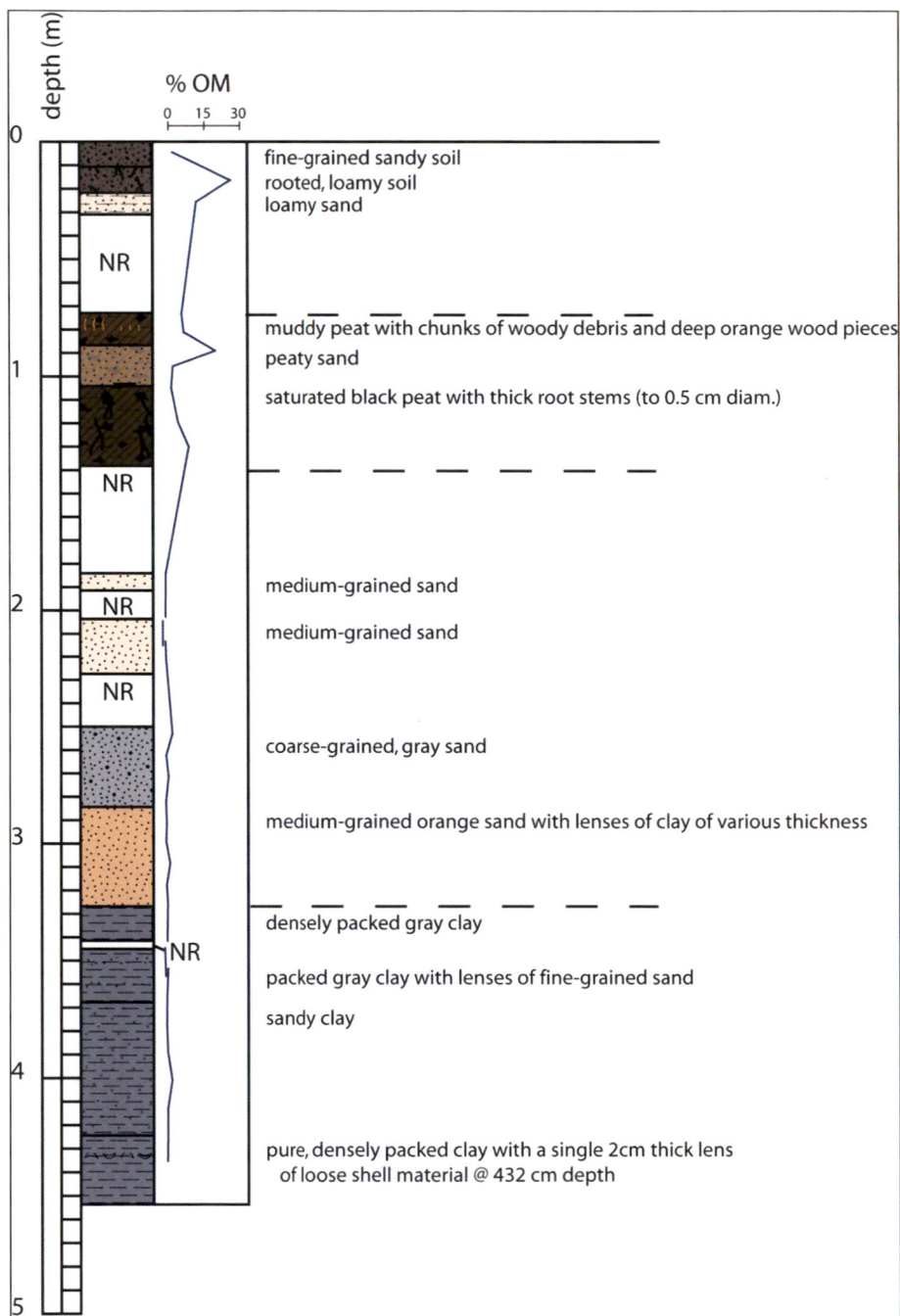
Long. 77°19'56.7" W



Suburban Floodplain Core N2

Lat. 35°34'48.1" N

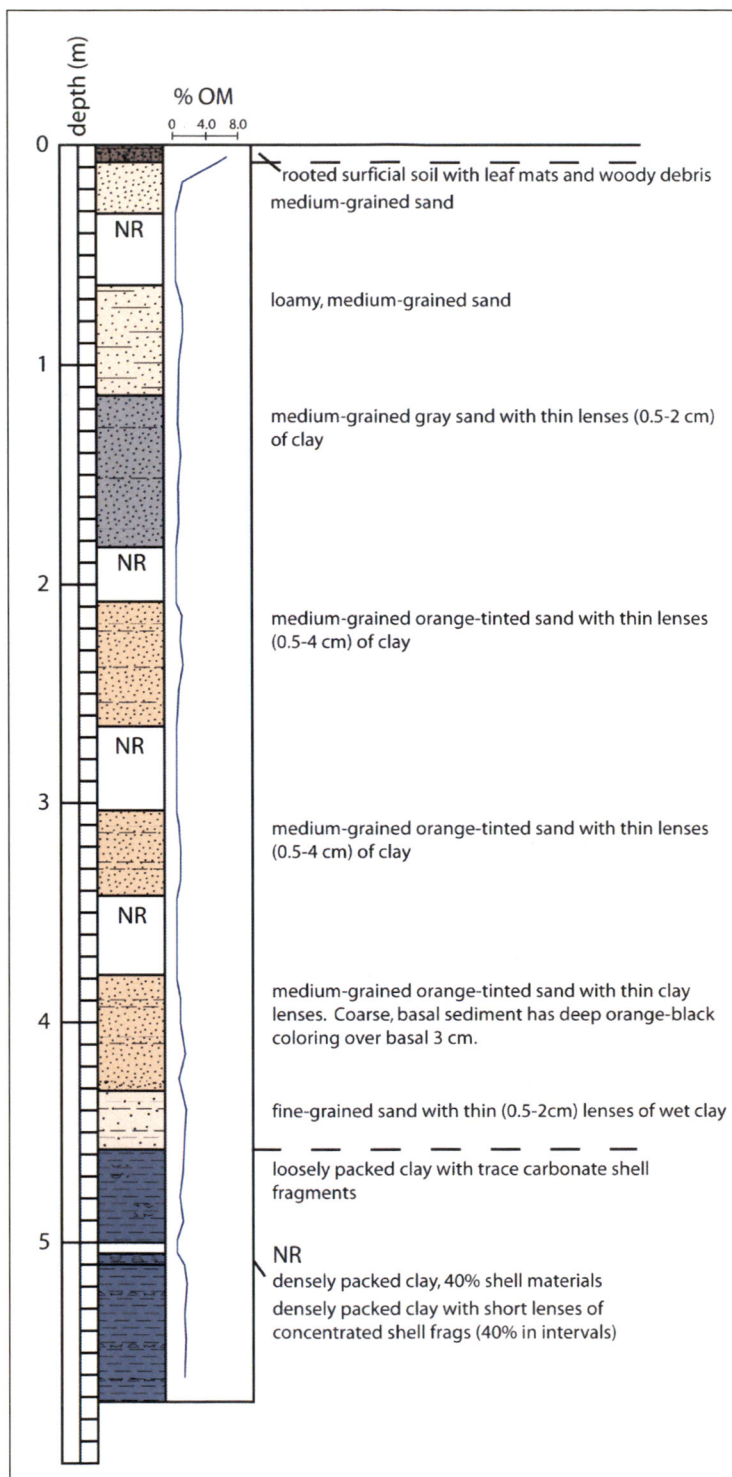
Long. 77°19'57.2" W



Suburban Floodplain Core N3

Lat. 35°34'48.6" N

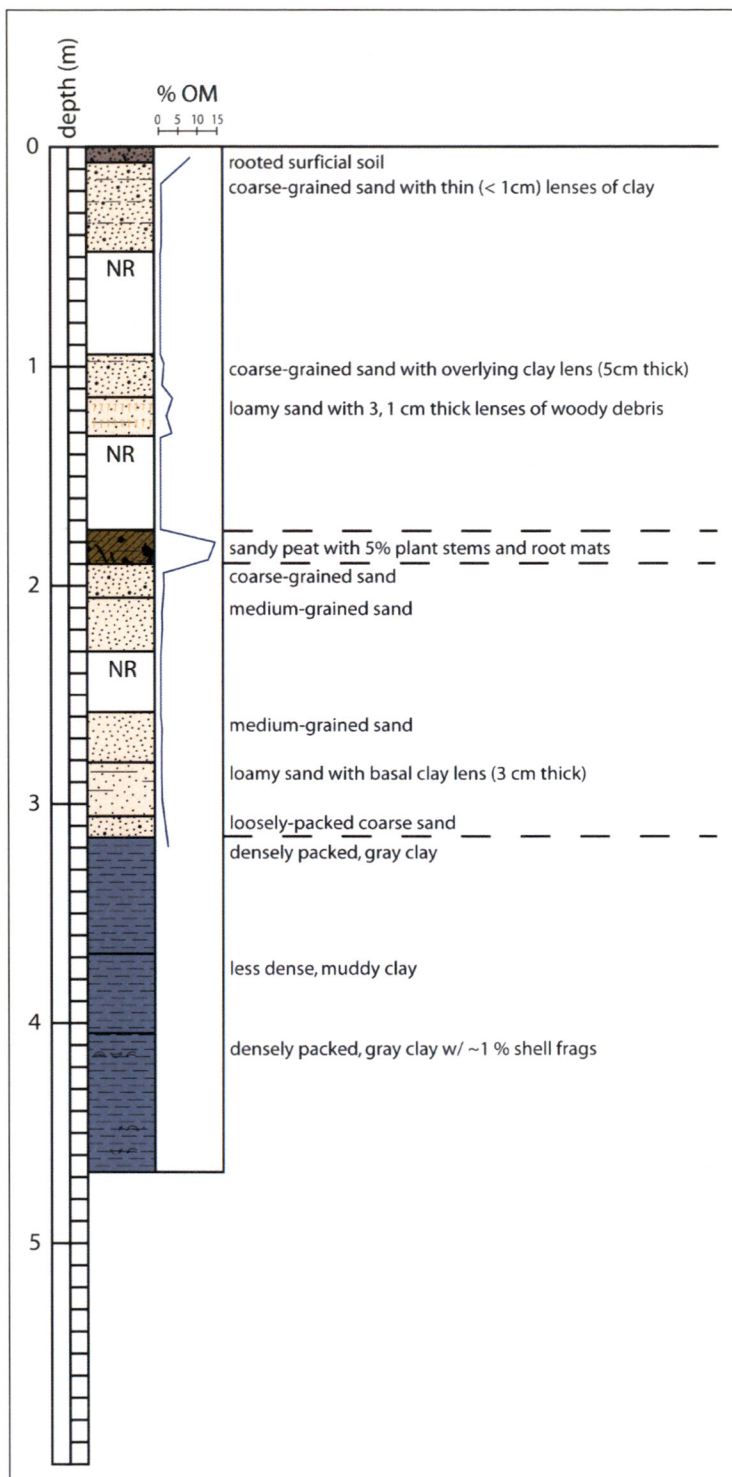
Long. 77°19'57.6" W



Rural Floodplain Core N1

Lat. 35°35'23.0" N

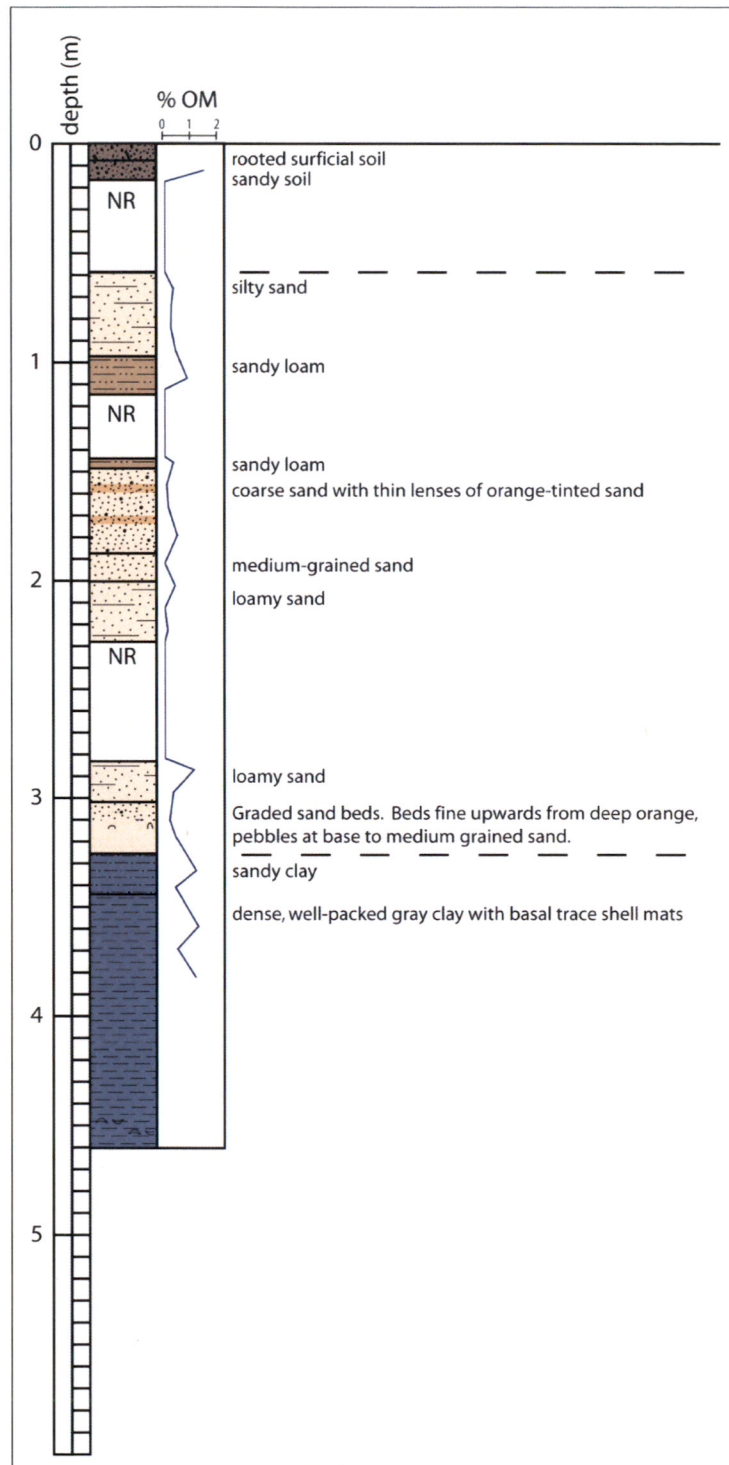
Long. 77°15'45.5" W



Rural Floodplain Core N2

Lat. 35°35'22.9" N

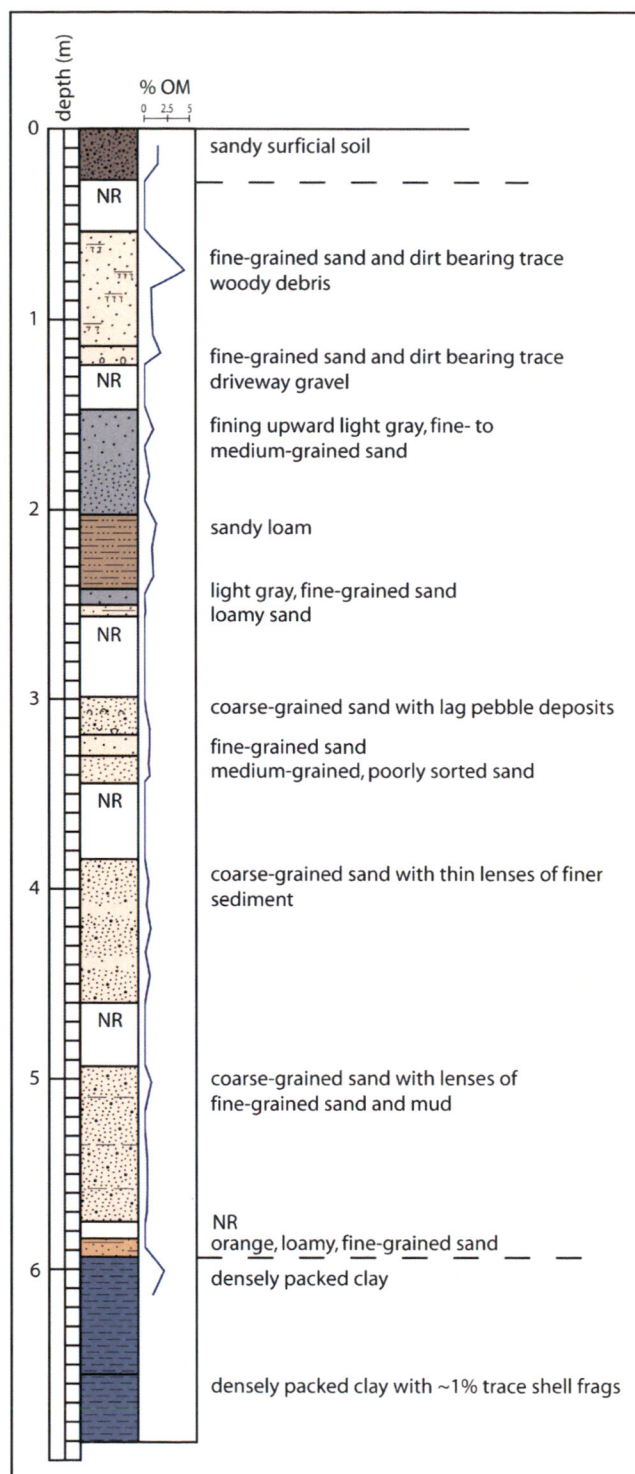
Long. 77°15'46.0" W



Rural Floodplain Core N3

Lat. 35°35'22.8" N

Long. 77°15'46.5" W



Appendix D: Percent Organic Matter Data

Table D1. Sediment sample depths and LOI results for the urban site.

Core					
Urban N1		Urban N2		Urban N3	
Depth (m)	% OM	Depth (m)	% OM	Depth (m)	% OM
14	1.9	4	0.6	16	2.5
28	2.7	9	1.8	25	1.7
42	5.5	31	1.7	36	4.2
92	10.1	39	2.0	44	3.1
100	9.4	49	1.3	78	2.8
122	4.1	60	4.2	89	2.7
130	6.5	71	9.8	101	7.2
139	2.7	82	3.9	114	10.7
147	0.4	90	11.2	122	30.2
157	0.0	100	1.3	148	31.3
164	0.3	110	14.6	160	40.5
172	0.1	117	27.7	171	48.6
218	0.0	131	1.2	185	38.3
226	0.1	141	1.5	198	19.7
256	0.2	149	0.3	210	35.1
261	1.0	160	0.4	218	20.3
273	0.4	174	0.3	225	21.0
289	0.0	234	0.3	246	9.5
308	0.3	259	0.5	319	0.5
321	0.4	289	0.4	329	0.4
328	0.5	330	0.4	344	0.1
339	1.1	337	0.5	348	0.2
344	1.2	344	0.7	402	1.0
348	1.0			411	0.2
				432	0.1
				440	0.1
				455	0.9
				465	0.3
Median	0.7		1.3		3.0
Min	0.0		0.3		0.1
Max	10.1		27.7		48.6
Range	10.1		27.4		48.5

Table D2. Sediment sample depths and LOI results for the suburban site.

Core					
Suburban N1		Suburban N2		Suburban N3	
Depth (m)	% OM	Depth (m)	% OM	Depth (m)	% OM
2	4.2	48	2.9	6	6.3
13	1.9	59	26.2	18	0.9
22	1.7	69	12.4	27	0.2
55	4.1	77	6.6	75	0.8
63	4.7	86	7.4	86	0.8
74	7.5	93	20.2	98	0.4
83	25.5	100	3.0	108	0.3
94	21.0	110	2.4	126	0.2
106	3.9	123	5.1	140	0.6
122	9.6	134	9.4	156	0.3
130	21.3	189	0.1	172	0.3
138	10.0	226	0.2	213	0.7
146	1.8	259	2.7	225	0.5
154	4.9	269	0.2	237	0.8
204	0.1	278	1.2	248	0.3
212	2.5	289	0.1	260	0.1
220	61.8	298	0.4	310	0.3
228	73.3	307	0.2	323	0.5
233	0.9	316	1.7	337	0.5
282	0.1	325	0.4	389	0.4
291	0.1	334	0.9	401	0.4
302	1.6	349	0.6	415	1.0
312	0.1	361	0.9	425	0.2
324	0.2	373	0.5	440	1.1
342	1.5	385	0.5	451	1.0
372	0.3	397	0.8	468	0.7
398	0.7	409	2.5	478	0.3
425	0.5	421	0.9	490	0.8
		433	0.9	509	0.9
		445	0.7	520	1.2
				533	0.9
				544	1.1
				560	0.9
Median	2.2		0.9		0.6
Min	0.1		0.1		0.1
Max	73.3		26.2		6.3
Range	73.2		26.1		6.2

Table D3. Sediment sample depths and LOI results for the rural site.

Core					
Rural N1		Rural N2		Rural N3	
Depth (m)	% OM	Depth (m)	% OM	Depth (m)	% OM
4	6.8	14	1.6	9	1.5
16	0.2	66	0.3	20	1.5
29	0.3	75	0.3	61	1.8
43	0.2	85	0.2	74	4.5
99	0.8	96	0.4	85	0.8
107	0.4	107	0.9	97	0.8
115	2.7	147	0.3	108	0.9
121	1.4	158	0.1	118	1.7
130	2.6	168	0.1	157	1.0
180	12.4	181	0.5	182	0.6
188	10.9	204	0.4	209	1.3
195	0.6	224	0.1	219	0.8
201	0.8	288	1.2	236	1.0
212	0.3	299	0.3	253	0.1
221	0.3	310	0.2	306	0.2
267	0.3	320	0.4	315	0.5
275	0.2	333	1.3	325	0.5
287	0.2	341	0.4	334	0.4
298	0.3	359	1.3	342	0.5
306	0.7	370	0.5	395	0.4
320	1.6	382	1.2	409	0.2
				420	0.6
				433	0.1
				445	0.5
				458	0.1
				502	0.7
				543	0.2
				557	0.3
				570	0.2
				601	2.1
				612	0.9
Median	0.6	204.0	0.4	315.0	0.6
Min	0.2	14.0	0.1	9.0	0.1
Max	12.4	382.0	1.6	612.0	4.5
Range	12.3	368.0	1.5	603.0	4.4

Appendix E: Hydrologic Data

Table E1. Depth to water (m) values for shallow and deep wells at each site.

Well	10/5/2007	11/8/2007	11/29/2007	1/8/2008	2/1/2008	2/29/2008	4/12/2008	5/10/2008	5/30/2008	7/15/2008	8/13/2008	9/4/2008
Urban N1-S	1.66	1.61	1.60	1.59	1.57	1.58	1.52	1.58	1.62	1.67	1.61	1.66
Urban N1-D	1.64	1.66	1.62	1.59	1.57	1.55	1.58	1.57	1.61	1.65	1.66	1.64
Urban N2-S	1.69	1.55	1.58	1.51	1.50	1.37	1.27	1.41	1.50	1.64	1.55	1.62
Urban N2-D	1.58	1.55	1.56	1.50	1.50	1.40	1.33	1.43	1.49	1.59	1.58	1.61
Urban N3-S	1.84	1.58	1.63	1.52	1.54	1.36	1.39	1.42	1.50	1.65	1.67	1.69
Urban N3-D	1.69	1.66	1.67	1.63	1.62	1.52	1.42	1.51	1.57	1.69	1.68	1.72
Suburban N1-S	1.25	1.19	1.19	1.15	1.15	0.98	0.94	1.08	1.16	1.25	1.23	1.23
Suburban N1-D	1.22	1.16	1.16	1.11	1.12	0.94	0.90	1.04		1.25	1.23	1.22
Suburban N2-S	1.17	1.09	1.10	1.01	1.03	0.78	0.71	0.91	1.03	1.17	1.15	1.13
Suburban N2-D	1.10	1.01	1.01	0.94	0.96	0.72	0.63	0.80	0.95	1.11	1.09	1.06
Suburban N3-S	1.69	1.65	1.65	1.50	1.52	1.15	0.96	1.24	1.45	1.72	1.73	1.69
Suburban N3-D	1.76	1.63	1.73	1.54	1.57	1.20	1.01	1.30	1.51	1.78	1.77	1.73
Rural N1-S	1.30	1.07	1.10	0.92	0.90	0.90	0.71	0.90	1.00	1.18	1.26	1.16
Rural N1-D	1.41	1.10	1.05	0.94	1.05	0.84	0.81	0.92	1.05	1.25	1.33	1.21
Rural N2-S	1.01	0.88	0.95	0.88	0.89	0.66	0.42	0.53	0.65	0.87	0.96	1.01
Rural N2-D	0.91	0.82	0.94	0.87	0.90	0.66	0.41	0.53	0.64	0.84	0.94	1.00
Rural N3-S	3.92	3.90	4.02	3.90	3.92	3.69	3.45	3.55	3.67	3.89	3.97	4.02
Rural N3-D	3.96	3.92	4.02	3.81	3.92	3.69	3.45	3.54	3.65	3.88	3.97	4.01

Table E2. Calculated elevation head (m) values for shallow and deep wells at each site..

Well	10/5/2007	11/8/2007	11/29/2007	1/8/2008	2/1/2008	2/29/2008	4/12/2008	5/10/2008	5/30/2008	7/15/2008	8/13/2008	9/4/2008
Urban N1-S	10.7	10.7	10.7	10.8	10.8	10.8	10.8	10.8	10.7	10.7	10.7	10.7
Urban N1-D	10.7	10.7	10.7	10.8	10.8	10.8	10.8	10.8	10.7	10.7	10.7	10.7
Urban N2-S	11.2	11.3	11.3	11.3	11.4	11.5	11.6	11.4	11.4	11.2	11.3	11.2
Urban N2-D	11.3	11.3	11.3	11.3	11.4	11.5	11.5	11.4	11.4	11.3	11.3	11.2
Urban N3-S	11.3	11.6	11.6	11.7	11.7	11.8	11.8	11.8	11.7	11.5	11.5	11.5
Urban N3-D	11.5	11.5	11.5	11.6	11.6	11.7	11.8	11.7	11.6	11.5	11.5	11.5
Suburban N1-S	9.3	9.3	9.3	9.4	9.4	9.6	9.6	9.5	9.4	9.3	9.3	9.3
Suburban N1-D	9.3	9.4	9.4	9.4	9.4	9.6	9.6	9.5	10.5	9.3	9.3	9.3
Suburban N2-S	9.4	9.5	9.4	9.5	9.5	9.8	9.8	9.6	9.5	9.4	9.4	9.4
Suburban N2-D	9.5	9.5	9.5	9.6	9.6	9.8	9.9	9.7	9.6	9.4	9.5	9.5
Suburban N3-S	9.9	9.9	9.9	10.1	10.1	10.4	10.6	10.4	10.1	9.9	9.9	9.9
Suburban N3-D	9.8	10.0	9.9	10.1	10.0	10.4	10.6	10.3	10.1	9.8	9.8	9.9
Rural N1-S	4.3	4.5	4.5	4.7	4.7	4.7	4.9	4.7	4.6	4.4	4.3	4.4
Rural N1-D	4.2	4.5	4.5	4.6	4.5	4.7	4.8	4.7	4.5	4.3	4.2	4.4
Rural N2-S	4.9	5.1	5.0	5.1	5.0	5.3	5.5	5.4	5.3	5.1	5.0	4.9
Rural N2-D	5.0	5.1	5.0	5.1	5.0	5.3	5.5	5.4	5.3	5.1	5.0	4.9
Rural N3-S	5.0	5.1	4.9	5.1	5.1	5.3	5.5	5.4	5.3	5.1	5.0	4.9
Rural N3-D	5.0	5.0	4.9	5.2	5.0	5.3	5.5	5.4	5.3	5.1	5.0	5.0

Table E3. Monthly hydraulic gradient (m/m) and discharge (m³/month) data for the three floodplain aquifers.

	Site					
	Urban		Suburban		Rural	
Date	dh/dl (m/m)	Q (m ³ /mo)	dh/dl (m/m)	Q (m ³ /mo)	dh/dl (m/m)	Q (m ³ /mo)
10/5/2007	0.023	3.5	0.031	11.2	0.028	15.9
11/8/2007	0.031	5.0	0.030	11.3	0.020	12.1
11/29/2007	0.029	4.6	0.029	11.1	0.017	9.9
1/8/2008	0.033	5.3	0.035	13.6	0.015	8.9
2/1/2008	0.031	5.1	0.034	13.3	0.013	8.1
2/29/2008	0.038	6.5	0.044	19.0	0.021	14.2
4/12/2008	0.034	6.1	0.051	22.8	0.023	17.0
5/10/2008	0.036	6.0	0.044	18.3	0.027	18.6
5/30/2008	0.034	5.6	0.038	14.9	0.026	17.3
7/16/2008	0.031	4.7	0.029	10.6	0.025	15.0
8/13/2008	0.028	4.5	0.028	10.2	0.024	14.4
9/5/2008	0.028	4.5	0.028	10.2	0.024	14.4

Appendix F: Water Quality Data

Table F1. Monthly groundwater specific conductivity data (uS/m) measured in wells of the three study sites.

Well	Specific Conductivity (uS/m)											
	10/5/07	11/8/07	11/29/07	1/8/08	2/1/08	2/29/08	4/12/08	5/10/08	5/30/08	7/15/08	8/30/08	9/5/08
Urban N1-S	72.0	61.8	59.3	77.7	61.0	122.5	84.9	68.9	64.1	68.8	64.4	68.5
Urban N1-D	244.3	123.2	152.0	83.0	107.2	54.7	59.9	59	60.5	58.8	61.5	67.1
Urban N2-S	215.2	178.5	141.1	52.8	95.1	100.1	76.6	86	108.4	122.4	104.8	101.1
Urban N2-D	59.3	53.0	55.1	87.7	49.5	48.8	51.4	53.2	56.8	62.9	59.7	59.5
Urban N3-S	151.5	112.5	113.0	78.7	82.4	92.9	70.6	94.5	119.2	99.5	98.5	105.8
Urban N3-D	57.5	57.8	56.6	52.6	51.0	50.0	53.4	71.4	72.4	71.5	65.6	58.0
Suburban N1-S	73.6	65.6	111.6	71.5	80.9	75.6	73.4	76.8	88.4	81.2	75.2	72.6
Suburban N1-D	151.2	138.7	145.6	144.1	142.8	136.2	133.0	145.6		157.2	151.5	149.6
Suburban N2-S	76.9	144.3	101.0	150.8	127.4	111.6	73.0	78.2	150.2	82.4	87.7	155.4
Suburban N2-D	126.2	144.7	132.9	134.9	135.4	125.1	143.1	125.8	97.4	142.2	130.6	138.5
Suburban N3-S	75.8	73.1	84.0	74.5	74.8	76.6	78.6	80.3	68.6	81.8	79.5	81.1
Suburban N3-D	59.7	57.9	58.2	54.1	52.3	51.5	52.5	54.4	97.1	61.6	58.4	60.5
Rural N1-S	156.3	59.2	136.6	142.9	150.0	82.0	74.5	108.4	213.7	193.4	178.0	146.0
Rural N1-D	275.0	169.9	250.1	204.7	216.4	193.8	53.9	132.3	227.0	223.0	150.1	248.2
Rural N2-S	227.3	219.7	213.4	185.0	169.5	168.6	167.7	177.6	230.0	216.1	230.1	238.9
Rural N2-D	192.8	179.8	162.3	152.5	161.3	151.6	169.1	169.8	203.5	190.0	193.6	178.7
Rural N3-S	233.5	219.2	223.5	221.9	221.3	176.4	152.7	174.1	234.0	186.2	197.6	182.4
Rural N3-D	180.7	173.4	164.0	172.3	179.3	166.5	172.1	168.1	222.8	170.7	174.0	155.4

Table F2. Monthly groundwater temperature data (°C) measured in shallow and deep wells of the three study sites.

	Date											
Well	10/5/07	11/8/07	11/29/07	1/8/08	2/1/08	2/29/08	4/12/08	5/10/08	5/30/08	7/15/08	8/13/08	9/4/08
Urban N1-S	21.9	20.9	20.0	18.0	16.9	15.6	16.8	17.6	18.2	20.5	21.1	21.8
Urban N1-D	22.6	21.1	20.0	18.5	17.6	16.0	16.7	17.3	17.7	20.1	20.6	21.2
Urban N2-S	22.2	21.4	19.6	18.0	16.2	15.3	16.1	17.2	18.6	20.7	21.4	22.0
Urban N2-D	21.2	21.1	19.9	17.7	16.9	15.4	16.2	17.2	18.3	20.8	21.4	21.9
Urban N3-S	19.6	19.9	19.7	18.2	17.2	16.3	16.3	16.6	17.1	18.1	18.8	19.6
Urban N3-D	19.8	20.0	19.6	18.4	17.1	15.8	16.2	17	17.1	20.2	21.0	19.6
Suburban N1-S	20.3	19.5	18.0	16.5	14.1	14.2	15.1	16.6	16.3	19.7	19.7	20.0
Suburban N1-D	20.5	19.4	18.3	16.2	14.8	14.5	15.0	17.1		20.8	19.3	20.0
Suburban N2-S	19.6	19.0	17.3	15.5	14.7	13.5	14.2	15.3	16.1	18.4	18.5	19.6
Suburban N2-D	18.8	18.3	17.9	15.8	14.8	13.8	14.3	15.3	15.9	19.0	18.7	20.4
Suburban N3-S	18.9	18.4	17.3	15.4	14.7	13.7	14.6	15.5	15.9	18.3	18.3	18.8
Suburban N3-D	18.6	18.0	17.5	15.7	15.3	13.7	14.5	15.2	15.9	18.0	18.3	19.0
Rural N1-S	20.9	19.1	17.8	13.8	14.0	12.5	15.0	15.6	16.4	20.1	20.1	20.8
Rural N1-D	20.0	18.8	18.4	17.2	14.1	14.2	15.0	16.1	15.9	17.5	18.6	18.9
Rural N2-S	20.3	19.1	16.5	13.3	12.7	11.7	14.4	15.4	17.1	20.5	21.9	21.3
Rural N2-D	20.1	18.6	17.1	14.3	12.5	12.1	14.1	15.2	17.7	20.5	21.9	21.4
Rural N3-S	19.7	19.2	18.8	17.2	16.4	15.0	15.0	15.3	15.9	17.4	18.5	18.5
Rural N3-D	19.5	18.7	18.7	17.2	16.1	14.9	15.5	15.4	16.2	17.1	18.0	18.6

Appendix G: Monthly Water Chemistry Data

Table G1. Groundwater chemistry data from the sampling date of 10/5/2007.

Well	NO ₃ ⁻ -N (mg/L)	NH ₄ ⁺ -N (mg/L)	DOC (mg/L)	DO (mg/L)	Cl ⁻ (mg/L)
Urban N1-S	0.3	1.3	3.1	6.4	
Urban N1-D	0.1	0.2	6.5	6.8	
Urban N2-S	0.1	2.4	13.7	6.9	
Urban N2-D	0.3	0.1	0.7	5.7	
Urban N3-S	0.1	0.6	6.4	7.2	
Urban N3-D	0.1	0.2	5.9	6.9	
Urban SW	0.1	0.1	2.0		
Suburban N1-S	0.2	0.1	3.5	6.4	
Suburban N1-D	0.1	0.1	1.5	6.5	
Suburban N2-S	0.2	0.1	2.7	5.8	
Suburban N2-D	0.1	0.1	1.8	6.5	
Suburban N3-S	0.2	0.1	1.8	5.8	
Suburban N3-D	0.5	0.1	2.6	6.1	
Suburban SW	2.3	0.1	0.5		
Rural N1-S	0.1	1.1		3.7	
Rural N1-D	0.1	0.4	8.3	3.7	
Rural N2-S	10.3	0.1	2.0	5.0	
Rural N2-D	1.2	0.1	1.8	4.7	
Rural N3-S	11.1	0.1	1.1	4.6	
Rural N3-D	2.9	0.1	3.2	3.9	
Rural SW	0.1	0.0	3.1		

Table G2. Groundwater chemistry data from the sampling date of 11/8/2007

Well	NO ₃ ⁻ -N (mg/L)	NH ₄ ⁺ -N (mg/L)	DOC (mg/L)	DO (mg/L)	Cl ⁻ (mg/L)
Urban N1-S	0.1	1.1	4.0	0.8	
Urban N1-D	0.3	0.2	3.3	1.9	
Urban N2-S	0.1	2.6	14.2	4.3	
Urban N2-D	0.3	0.2	1.8	1.6	
Urban N3-S	0.1	0.5	6.5	3.8	
Urban N3-D	0.2	0.2	2.9	1.9	
Urban SW	0.1	0.1	1.3		
Suburban N1-S	0.1	0.1	0.6	0.9	
Suburban N1-D	0.2	0.1	0.5	0.7	
Suburban N2-S	0.1	0.1	7.6	1.4	
Suburban N2-D	0.1	0.1	0.5	0.9	
Suburban N3-S	0.2	0.1	1.1	3.7	
Suburban N3-D	0.5	0.1	0.5	1.6	
Suburban SW	2.2	0.3	0.9		
Rural N1-S	0.1	0.7	4.3	1.7	
Rural N1-D	0.1	0.7	10.2	0.1	
Rural N2-S	11.2	0.1	2.0	0.7	
Rural N2-D	1.0	0.1	1.1	2.4	
Rural N3-S	11.8	0.1	1.8	1.4	
Rural N3-D	2.0	0.1	2.0	0.6	
Rural SW	0.3	0.1	2.8		

Table G3. Groundwater chemistry data from the sampling date of 11/29/2007

Well	NO ₃ ⁻ -N (mg/L)	NH ₄ ⁺ -N (mg/L)	DOC (mg/L)	DO (mg/L)	Cl ⁻ (mg/L)
Urban N1-S	0.0	0.8	4.2	0.5	
Urban N1-D	0.2	0.1	3.1	0.5	
Urban N2-S	0.2	2.6	8.6	0.5	
Urban N2-D	0.0	0.0	1.4	1.8	
Urban N3-S	0.0	0.5	6.0	0.7	
Urban N3-D	0.3	0.2	3.2	3.7	
Urban SW	0.0	0.0	2.2	3.5	
Suburban N1-S	0.1	0.0	8.2	0.7	
Suburban N1-D	0.1	0.1	1.1	0.7	
Suburban N2-S	0.0	0.0	6.7	0.5	
Suburban N2-D	0.1	0.0	0.6	0.4	
Suburban N3-S	0.3	0.0	2.8	0.7	
Suburban N3-D	0.5	0.0	1.1	0.6	
Suburban SW	1.6	0.1	1.5	4.2	
Rural N1-S	0.0	0.8	2.5	0.4	
Rural N1-D	0.1	0.2	4.9	0.3	
Rural N2-S	11.1	0.1	1.3	0.5	
Rural N2-D	0.9	0.0	1.2	0.3	
Rural N3-S	12.3	0.1	1.3	0.3	
Rural N3-D	2.7	0.2	0.9	0.6	
Rural SW	0.0	0.1	11.3	1.4	

Table G4. Groundwater chemistry data from the sampling date of 1/8/2008

Well	NO ₃ ⁻ -N (mg/L)	NH ₄ ⁺ -N (mg/L)	DOC (mg/L)	DO (mg/L)	Cl ⁻ (mg/L)
Urban N1-S	0.1	1.2	4.9	0.8	
Urban N1-D	0.1	0.1	1.1	0.6	
Urban N2-S	0.0	0.0		0.5	
Urban N2-D	0.1	0.1	0.9	0.8	
Urban N3-S	0.0	0.2	3.1	1.1	
Urban N3-D	0.5	0.1	1.4	2.5	
Urban SW	0.3	0.3	2.1	6.1	
Suburban N1-S	0.1	0.0	0.9	1.2	
Suburban N1-D	0.1	0.0	0.1	1.0	
Suburban N2-S	0.0	0.1	6.0	0.6	
Suburban N2-D	0.3	0.0	0.4	0.9	
Suburban N3-S	0.1	0.0	0.5	1.0	
Suburban N3-D	0.5	0.0	0.6	1.7	
Suburban SW	1.6	0.1	1.0	7.0	
Rural N1-S	0.2	0.7	2.7	1.0	
Rural N1-D	0.0	0.2	8.5	0.8	
Rural N2-S	9.9	0.1	1.4	1.3	
Rural N2-D	0.6	0.1	1.5	1.1	
Rural N3-S	10.4	0.0	1.4	1.7	
Rural N3-D	3.4	0.1	1.0	1.2	
Rural SW	0.3	0.0	3.7		

Table G5. Groundwater chemistry data from the sampling date of 2/1/2008

Well	NO ₃ ⁻ -N (mg/L)	NH ₄ ⁺ -N (mg/L)	DOC (mg/L)	DO (mg/L)	Cl ⁻ (mg/L)
Urban N1-S	0.2	1.1	4.2	0.6	
Urban N1-D	0.1	0.2	1.0	0.0	
Urban N2-S	0.0	0.0		3.5	
Urban N2-D	0.3	0.1	0.4	1.5	
Urban N3-S	0.0	0.0	5.1	0.5	
Urban N3-D	0.5	0.1	0.0	2.2	
Urban SW	0.2	0.0	4.7	8.7	
Suburban N1-S	0.1	0.1	1.1	0.4	
Suburban N1-D	0.1	0.1	0.6	0.4	
Suburban N2-S	0.0	0.1	4.1	0.4	
Suburban N2-D	0.0	0.1	0.2	0.3	
Suburban N3-S	0.1	0.0	1.1	0.7	
Suburban N3-D	0.4	0.0	0.4	1.6	
Suburban SW	1.5	0.0	1.1	8.1	
Rural N1-S	0.0	0.7	1.6	0.3	
Rural N1-D	0.1	0.1	13.7	0.3	
Rural N2-S	8.5	0.0	0.5	0.5	
Rural N2-D	0.3	0.1	1.4	0.4	
Rural N3-S	9.7	0.1	0.5	1.1	
Rural N3-D	5.3	0.1	0.5	0.4	
Rural SW	0.4	0.0	3.3	10.8	

Table G6. Groundwater chemistry data from the sampling date of 2/29/2008

Well	NO ₃ ⁻ -N (mg/L)	NH ₄ ⁺ -N (mg/L)	DOC (mg/L)	DO (mg/L)	Cl ⁻ (mg/L)
Urban N1-S	0.1	1.2	5.7	1.2	10.9
Urban N1-D	0.2	0.1	1.1	1.9	7.4
Urban N2-S	0.0	2.2		1.3	5.1
Urban N2-D	0.3	0.1	1.3	1.8	5.7
Urban N3-S	0.0	0.3	4.5	0.7	10.1
Urban N3-D	0.5	0.1	1.3	2.6	13.2
Urban SW	0.3	0.1	2.1	9.9	21.8
Suburban N1-S	0.1	0.1	1.8	0.3	28.0
Suburban N1-D	0.1	0.1	0.6	0.6	29.3
Suburban N2-S	0.0	0.1	9.8	0.2	30.1
Suburban N2-D	0.0	0.1	0.5	0.7	31.1
Suburban N3-S	0.0	0.1	1.2	0.6	16.9
Suburban N3-D	0.4	0.0	0.7	1.1	20.8
Suburban SW	1.8	0.1	1.2	9.3	26.6
Rural N1-S	0.0	0.5	7.5	0.3	17.3
Rural N1-D	0.0	0.3	4.9	0.3	19.0
Rural N2-S	8.2	0.1	2.9	1.0	44.4
Rural N2-D	0.5	0.1	2.3	1.4	31.1
Rural N3-S	7.1	0.1	1.6	0.8	31.5
Rural N3-D	4.6	0.1	1.8	1.9	29.6
Rural SW	0.8	0.0	5.3	10.5	18.6

Table G7. Groundwater chemistry data from the sampling date of 4/12/2008

Well	NO ₃ ⁻ -N (mg/L)	NH ₄ ⁺ -N (mg/L)	DOC (mg/L)	DO (mg/L)	Cl ⁻ (mg/L)
Urban N1-S	0.0	1.2	6.1	0.8	11.8
Urban N1-D	0.2	0.1	1.3	1.9	10.9
Urban N2-S	0.0	5.3		5.6	7.5
Urban N2-D	0.4	0.3	3.0	2.7	10.5
Urban N3-S	0.0	0.2	1.3	1.0	15.1
Urban N3-D	0.5	0.1	20.5	3.6	11.1
Urban SW	0.2	0.0	5.4		22.3
Suburban N1-S	0.1	0.0	1.4	0.4	21.1
Suburban N1-D	0.1	0.0	3.6	1.1	24.8
Suburban N2-S	0.0	0.1	1.0	0.5	17.1
Suburban N2-D	0.1	0.0	3.6	0.7	22.7
Suburban N3-S	0.0	0.0	0.8	0.7	15.7
Suburban N3-D	0.4	0.0	15.4	1.1	20.0
Suburban SW	1.6	0.0	1.4	7.6	24.2
Rural N1-S	0.1	0.6	3.6	0.8	28.8
Rural N1-D	0.0	0.3	14.5	0.2	10.2
Rural N2-S	7.5	0.1	2.5	0.3	40.0
Rural N2-D	0.5	0.1	1.9	0.7	31.9
Rural N3-S	7.0	0.1	2.7	0.8	29.8
Rural N3-D	4.4	0.1	1.5	0.4	32.0
Rural SW	0.6	0.0	7.9	3.4	18.7

Table G8. Groundwater chemistry data from the sampling date of 5/1/2008

Well	NO ₃ ⁻ -N (mg/L)	NH ₄ ⁺ -N (mg/L)	DOC (mg/L)	DO (mg/L)	Cl ⁻ (mg/L)
Urban N1-S	0.0	0.9	5.4	0.4	7.1
Urban N1-D	0.2	0.2	2.0	0.5	8.2
Urban N2-S	0.1	3.1	19.6	1.9	6.1
Urban N2-D	0.5	0.2	2.5	0.3	7.5
Urban N3-S	0.1	0.4	7.7	0.8	11.1
Urban N3-D	0.2	0.4	4.1	0.5	9.6
Urban SW	0.3	0.1	8.6	3.8	11.6
Suburban N1-S	0.1	0.0	3.5	0.2	15.6
Suburban N1-D	0.1	0.1	0.9	0.3	17.8
Suburban N2-S	0.0	0.1	13.8	0.2	14.2
Suburban N2-D	0.1	0.0	1.6	0.2	17.8
Suburban N3-S	0.1	0.1	3.8	0.7	12.0
Suburban N3-D	0.4	0.1	4.2	0.9	14.2
Suburban SW	1.5	0.1	2.2	6.3	16.4
Rural N1-S	0.1	0.5	4.8	0.7	21.8
Rural N1-D	0.0	0.9	33.3	1.1	19.1
Rural N2-S	8.2	0.1	2.9	0.4	30.5
Rural N2-D	0.5	0.1	4.0	0.8	23.7
Rural N3-S	9.2	0.0	1.8	0.6	23.9
Rural N3-D	4.4	0.4	1.4	0.2	21.1
Rural SW	0.5	0.1	6.5	6.6	15.7

Table G9. Groundwater chemistry data from the sampling date of 5/30/2008

Well	NO ₃ ⁻ -N (mg/L)	NH ₄ ⁺ -N (mg/L)	DOC (mg/L)	DO (mg/L)	Cl ⁻ (mg/L)
Urban N1-S	0.0	1.0	3.9	0.6	
Urban N1-D	0.2	0.2	1.4	1.2	
Urban N2-S	0.0	2.3	18.5	0.4	
Urban N2-D	0.5	0.2	3.6	1.4	
Urban N3-S	0.2	0.5	6.8	1.9	
Urban N3-D	0.4	0.3	2.1	0.4	
Urban SW	0.2	0.1	3.2	6.9	
Suburban N1-S	0.1	0.1	3.1	0.9	
Suburban N1-D	0.0	0.0			
Suburban N2-S	0.0	0.2	7.5	0.3	
Suburban N2-D	0.1	0.1	3.8	0.2	
Suburban N3-S	0.0	0.0	4.5	1.5	
Suburban N3-D	0.5	0.1	4.2	0.7	
Suburban SW	1.7	0.1	1.8	7.1	
Rural N1-S	0.1	0.7	5.3	0.2	
Rural N1-D	0.1	0.9	9.5	0.1	
Rural N2-S	9.4	0.1	2.4	0.1	
Rural N2-D	1.1	0.1	1.5	0.2	
Rural N3-S	9.5	0.1	1.2	0.4	
Rural N3-D	3.6	0.2	1.2	0.6	
Rural SW	0.4	0.1	5.3	8.3	

Table G10. Groundwater chemistry data from the sampling date of 7/16/2008

Well	NO ₃ ⁻ -N (mg/L)	NH ₄ ⁺ -N (mg/L)	DOC (mg/L)	DO (mg/L)	Cl ⁻ (mg/L)
Urban N1-S	0.0	1.0	3.8	0.8	11.5
Urban N1-D	0.3	0.2	1.0	0.8	9.4
Urban N2-S	0.0	4.0	25.4	0.7	8.0
Urban N2-D	0.4	0.3	2.0	0.9	7.8
Urban N3-S	0.2	0.6		2.4	12.6
Urban N3-D	0.4	0.3		1.3	10.2
Urban SW	0.2	0.1	4.7	3.9	23.0
Suburban N1-S	0.1	0.1	2.3	0.2	22.6
Suburban N1-D	0.1	0.1	3.7	1.5	17.3
Suburban N2-S	0.1	0.1	2.5	0.2	23.5
Suburban N2-D	0.1	0.1	3.0	0.4	11.8
Suburban N3-S	0.1	0.1	1.4	0.5	14.0
Suburban N3-D	0.6	0.1	1.9	1.5	15.1
Suburban SW	2.0	0.1	1.3	6.4	28.4
Rural N1-S	0.0	0.8	2.0	0.3	38.4
Rural N1-D	0.0	1.8	24.4	0.4	43.0
Rural N2-S	10.0	0.1	4.2	0.3	44.0
Rural N2-D	1.6	0.2	3.8	0.3	48.2
Rural N3-S	8.4	0.1	2.3	1.0	40.0
Rural N3-D	4.1	0.2	2.0	0.5	35.5
Rural SW	0.1	0.0	2.1	5.7	15.0

Table G11. Groundwater chemistry data from the sampling date of 8/13/2008

Well	NO ₃ ⁻ -N (mg/L)	NH ₄ ⁺ -N (mg/L)	DOC (mg/L)	DO (mg/L)	Cl ⁻ (mg/L)
Urban N1-S	0.0	0.9	4.3	0.3	9.2
Urban N1-D	0.2	0.2	1.9	0.5	10.2
Urban N2-S	0.1	3.4	27.2	0.4	7.2
Urban N2-D	0.2	0.1	2.6	0.5	8.3
Urban N3-S	0.1	0.5	7.0	0.7	12.7
Urban N3-D	0.4	0.3	2.5	1.0	9.7
Urban SW	0.5	0.1	7.4	6.1	6.7
Suburban N1-S	0.1	0.1	6.4	0.3	16.6
Suburban N1-D	0.2	0.1	3.7	0.1	21.1
Suburban N2-S	0.1	0.1	3.5	0.3	16.8
Suburban N2-D	0.1	0.0	3.2	0.4	21.0
Suburban N3-S	0.1	0.1	3.3	0.7	13.7
Suburban N3-D	0.6	0.0	1.5	1.3	17.0
Suburban SW	0.9	0.1	3.6	6.7	15.1
Rural N1-S	0.1	0.8	2.7	0.5	25.6
Rural N1-D	0.1	0.9	7.4	0.7	14.9
Rural N2-S	9.2	0.2	1.3	0.4	35.7
Rural N2-D	1.3	0.2	0.9	0.4	29.2
Rural N3-S	8.5	0.1	0.3	0.3	28.1
Rural N3-D	4.7	0.1	0.6	0.2	25.0
Rural SW	0.2	0.1	3.7	6.4	12.2

Table G12. Groundwater chemistry data from the sampling date of 9/5/2008

Well	NO ₃ ⁻ -N (mg/L)	NH ₄ ⁺ -N (mg/L)	DOC (mg/L)	DO (mg/L)	Cl ⁻ (mg/L)
Urban N1-S	0.1	0.9	3.5	1.3	6.4
Urban N1-D	0.2	0.2	1.2	1.5	8.6
Urban N2-S	0.1	3.8	7.1	1.0	3.3
Urban N2-D	0.2	0.3	2.0	1.5	5.8
Urban N3-S	0.0	0.0		2.1	
Urban N3-D	0.5	0.3	2.6	1.5	5.2
Urban SW	0.1	0.1	1.9	4.6	8.8
Suburban N1-S	0.1	0.1	1.8	0.3	12.1
Suburban N1-D	0.2	0.1	1.3	0.5	15.1
Suburban N2-S	0.0	0.1	3.8	0.2	20.4
Suburban N2-D	0.0	0.1	0.7	0.3	15.5
Suburban N3-S	0.1	0.1	1.4	0.8	8.3
Suburban N3-D	0.5	0.1	1.5	1.2	11.0
Suburban SW	1.8	0.1	1.1	4.6	13.4
Rural N1-S	0.1	0.7	3.7	0.2	13.4
Rural N1-D	0.1	0.5	6.4	0.3	11.3
Rural N2-S	10.2	0.1	5.5	0.7	28.1
Rural N2-D	3.7	0.1	5.2	0.4	20.5
Rural N3-S	7.7	0.1	5.5	0.8	18.2
Rural N3-D	3.2	0.1	3.7	0.8	11.2
Rural SW	0.1	0.0	3.0	6.3	7.5