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THE INFLUENCE OF URBAN CHANNEL INCISION AND WATER TABLE DECLINE ON FLOODPLAIN GROUNDWATER NITROGEN DYNAMICS; GREENVILLE, NC

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The contact between groundwater and organic matter (OM) across floodplains of low-order streams has important implications for groundwater and stream nitrogen (N)-dynamics. Stormwater-induced channel incision along low-order urban streams has been linked to the decline of riparian groundwater levels (water table decline). Water table decline adjacent to incised urban streams has the potential to diminish contact between floodplain groundwater and OM concentrated in surface soils that may alter the nitrate-removal capacity of floodplain riparian zones. The objectives of this study were to determine if water table decline across riparian, floodplain areas of incised streams in Greenville, NC: i) diminishes contact between floodplain groundwater and surface soil horizons, ii) diminishes the NO_3^- attenuation (loss, removal, and/or retention) capacity of incised floodplain riparian zones and iii) drives an increase in the loading of NO_3^- from floodplain groundwater to surface water. Three floodplain study sites with similar catchment size were selected adjacent to low-order streams with varying degrees of stream channel incision. These sites were classified as urban, suburban, and rural, based on the extent of watershed total impervious area (TIA; 36.7, 22, 3.8% respectively). Piezometer nests were installed across floodplains to measure groundwater levels and concentrations of groundwater nitrate-N (NO_3^--N), ammonium-N (NH_4^+-N), dissolved organic carbon (DOC), dissolved oxygen (DO), and chloride (Cl^-). Though water table decline resulted in diminished contact with organic surface soils at the urban and suburban sites, buried peats contributed to locally elevated DOC concentrations (> 4 mg/L) in shallow wells at both sites. The positive relationship observed between median annual near-stream groundwater levels and floodplain NO_3^- attenuation across the three study sites suggests that water table decline may cause a net decrease in the NO_3^- attenuation capacity of incised urban floodplains. Despite notably reduced NO_3^- attenuation across floodplain riparian areas, NO_3^- loading from groundwater to surface water was not consistently greater at the more incised sites. Differences in loading were influenced by variability in groundwater flux at each site due to differences in the median hydraulic permeability (K) of floodplain sediments at each site. This indicates that although land-use may influence floodplain groundwater NO_3^- attenuation, variability in the hydraulic properties of floodplain sediments both along individual streams, and from one stream to the next, also plays an important role in the loading of NO_3^- to low-order streams.

INTRODUCTION

Anthropogenic activity in coastal watersheds has greatly altered the nitrogen (N) cycle and significantly accelerated the delivery of N to coastal water bodies (Anderson et al., 2002; Boyer et al., 2002; and Howarth et al., 2002). Eutrophication leads to fish kills, increased abundance of toxic algal species, and more frequent anoxic conditions in coastal water bodies (Anderson et al., 2002; Burkholder, 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 N to coastal waters (Denver et al., 2004; 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, streams draining catchments with a substantial portion of land in urban land use showed notably higher N inputs than their rural counterparts, indicating the importance of urbanization, in addition to agriculture, as a source of N to coastal watersheds.

In-stream inorganic-N are often elevated in urban watersheds due to excess N contributions from surface runoff (Boyer et al., 2002), groundwater (Walsh et al., 2005), and from direct dissolution of atmospheric N (Howarth et al., 2002). Important to this study, dissolved inorganic-N in groundwater may be elevated in urban catchments due to: 1) N-based fertilizer application to residential yard space, 2) the persistence of legacy pollutants from past agricultural land use (Walsh et al., 2005), and 3) discharge, leakage, and overflow from sewer infrastructure (Walsh et al., 2005; Hatt et al., 2004).

Because NO_3^--N is often mobile and easily transported (Duff and Triska, 2000; Jones et al, 1995) attempts to better understand sources and sinks of nitrogen in coastal watersheds have focused on NO_3^--N as the form of inorganic-N most problematic in the eutrophication of coastal water bodies (Angier and McCarty, 2008; Harden and Spruill, 2008; Böhlke et al., 2007; Spruill et al., 2005, Tesoriero et al., 2005). Across floodplains of low-order streams, denitrification, the process whereby electrons are transferred from organic matter to $NO_3^-$to form N_2or N_2gas, is often effective at removing NO_3^--Nfrom floodplain groundwater. studies have shown higher riparian zone denitrification potential (DNP) for samples from surface soil horizons than for samples from sandy sediments of the unconfined aquifers they overlay (Groffman et al. 2003a, 2002; Burt et al. 1999). Stormwater induced incision of low-order, urban streams has been linked to the decline of water tables across floodplain, riparian zones in developed, urban watersheds (Hardison et al., 2009; Groffman et al., 2003b; Groffman et al., 2002). The occurrence and duration of contact between groundwater and surface soil layers with high DNP across urban floodplains may be diminished. This diminished contact may, in turn, lessen the N-removal capacity of urban riparian zones (Kaushal et al., 2008; Böhlke et al. 2007; Groffman et al., 2003a; Groffman et al., 2002; Gold et al. 2001). The primary objectives of this study were to determine if water table decline across riparian zones of incised urban streams: i) notably alters the contact of floodplain groundwater and riparian surface soil horizons, ii) notably affects the attenuation of groundwater NO_3^-, and iii) notably increases the mass of NO_3^-(g/month) loaded to low-order streams. Finally, the results are used to recommend restoration that could improve surface water quality in these and similar urban, low-order Coastal Plain streams.

STUDY DESIGN

Study area and hydrogeologic setting

This study focused on floodplains at locations selected for accessibility and similar sub-catchment size in the watersheds of three low-order streams of the Tar River Basin. Fornes Branch (FB), Meeting House Branch (MHB), and Phillippi Branch (PB) (Figure 1) were classified as urban, suburban, and rural respectively based on the total impervious area (TIA(%) = impervious surface area/total land surface area * 100%) in each sub-catchment. TIA percentages were calculated for each sub-catchment during a previous study using impervious cover data from the City of Greenville and the National Land Cover Database (Hardison, 2008) to be 36.7% (urban), 22.1% (suburban), and 3.8% (rural), respectively. A recent study in the Greenville area revealed that channel incision along FB and MHB was the result of excess urban stormwater runoff (Hardison et al. 2009). Wastewater in catchments of the urban and suburban sites is piped to a central treatment facility, whereas wastewater in the rural catchment is discharged directly to shallow groundwater as septic discharge.

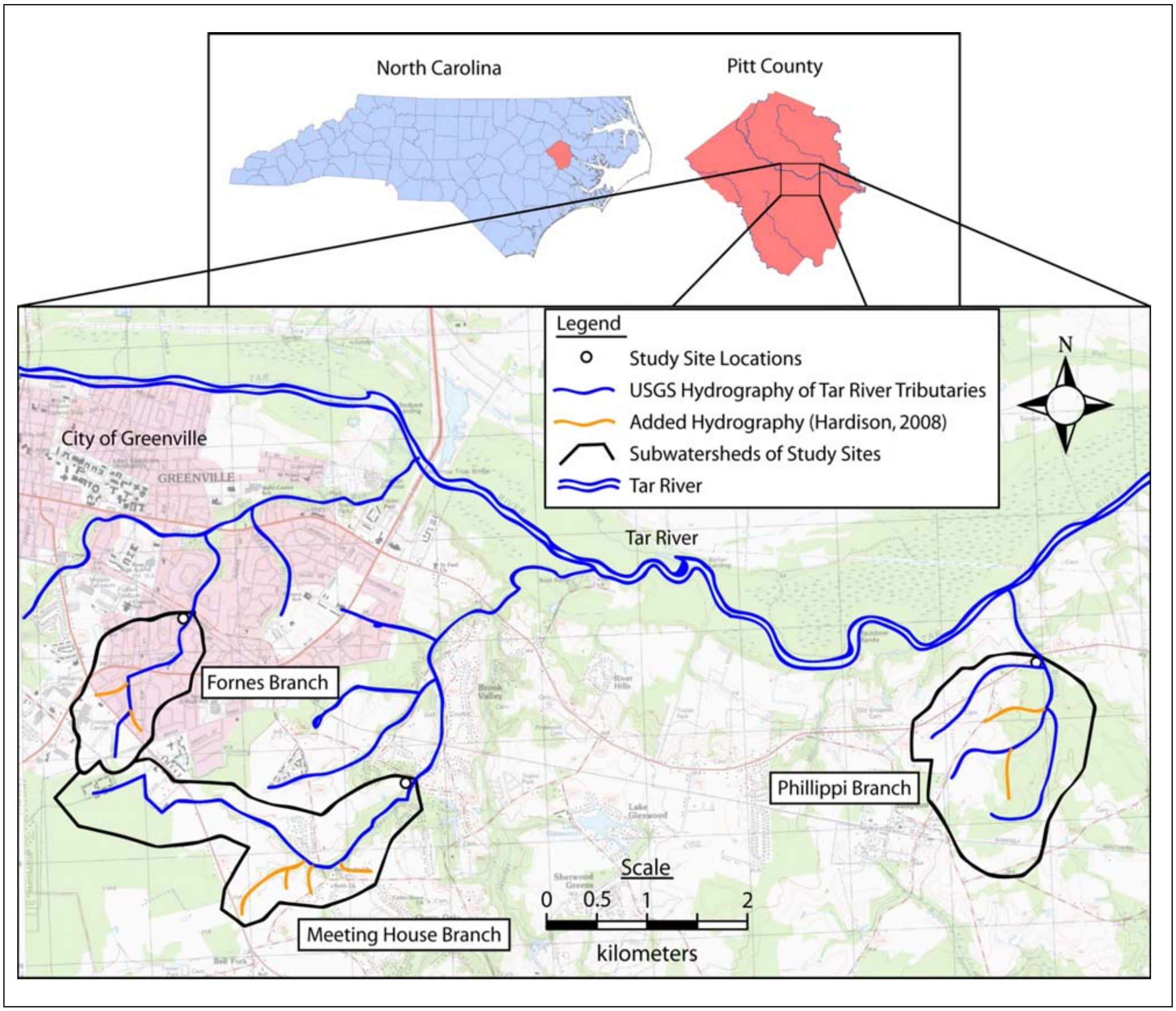

Figure 1. Study site location map showing well transect locations and site catchment boundaries. Background image is a cropped portion of the Greenville SE, 7.5" USGS Topographic Quadrangle, obtained using Terrain Navigator Pro 7.5 (Maptech Inc., Amesbury, MA).

The study area 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 terrace sediment is underlain by a vast, thick, and laterally extensive wedge of 5 distinct hydrogeologic units (Maddry, 1979), the uppermost being the Yorktown formation that includes both surficial aquifer sediments (~ 10 m; Winner and Coble, 1996), and the confining unit that limits the hydrology of groundwater and surface water examined in this work. In the Greenville area, 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 lower confining clay sediments of the Yorktown are likely marine in origin, and that the thin section of coarse, clastic sediment that overlays the confining unit were deposited by both marine and fluvial processes.

Recharge to the Coastal Plain of eastern North Carolina 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 rainfall 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) in the Greenville area was below average likely due to drought conditions into the late summer and fall of 2007. The combined annual discharge of groundwater from deep, confined aquifers to surficial aquifers has been estimated at 1.3 cm per year (Heath, 1975).

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). Generally speaking, at least 40% of the water flowing in Coastal Plain streams of eastern North Carolina is derived from groundwater (Harden and Spruill, 2008; Harden et al., 2003; Spruill et al., 1998; Winner and Simmons, 1977), but may be as great as 90% is some low-order catchments (Hutchinson, 2007; Williams and Pinder, 1990). Several studies in agricultural settings of the Coastal Plain have shown that surface water quality is strongly influenced by groundwater quality (Harden and Spruill, 2008; Spruill, 2004; Tesoriero et al. 2005; Denver et al. 2004).

Site design and geologic characterization

Well transects were installed along distinct hydrologic flowpaths (standard 3-point solution; Heath, 2004) at each site. Nested well groups consisting of a shallow well screened just below the water table and a deep well screened just above the confining unit at each site were installed approximately 6, 20, and 34 m from the streambank at the urban (Figure 2) and rural sites and 5, 15, and 25 m from the streambank at the suburban site. Wells were constructed using 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. Nested wells closest to each stream (labeled N1) are referred to hereafter as "near-stream" wells; nested wells near the edge of the floodplain away from the stream (labeled N2) are referred to as "floodplain" wells; and nested wells at floodplain edge/upland locations (labeled N3) are "up-gradient".

Groundwater levels in shallow and deep transect wells were determined manually on a monthly basis using a Solinst Model 107 TLC water level meter (Solinst Canada Ltd.) One groundwater level logger in the shallow, N1 well at each site recorded near-stream groundwater levels on a 1/

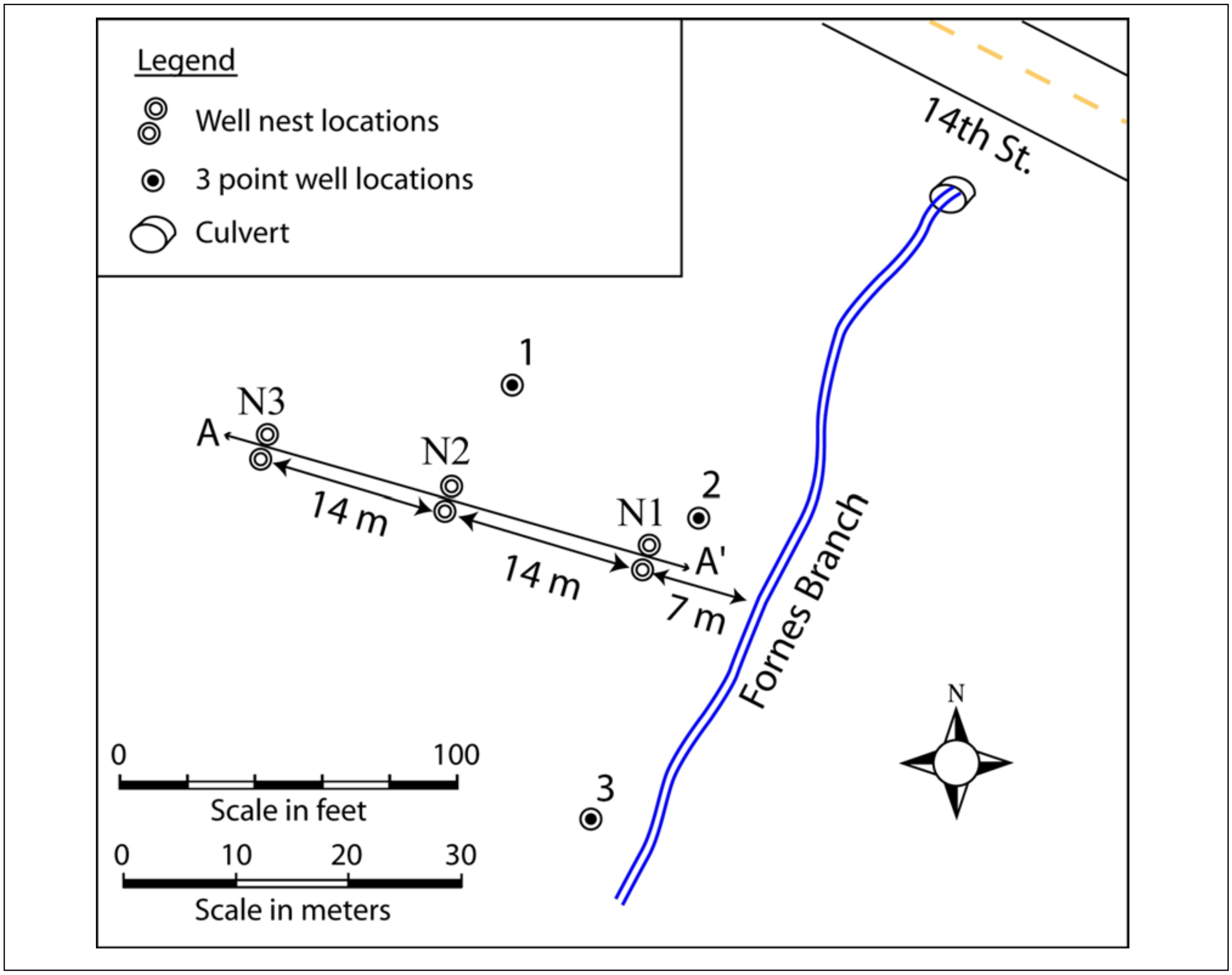

Figure 2. Sample layout diagram showing location, orientation, and spacing of wells at the urban study site. Three wells determined groundwater flow direction at each study site.

2 hourly basis. Monthly and continuous fluctuations in groundwater levels in shallow wells of each site were compared to depth of surface and subsurface organic matter (OM) to determine if contact between floodplain groundwater and OM has been altered by water table decline.

A single sediment core was taken at each well group (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 samples according to standard loss on ignition technique (Soil and Plant Analysis Council, 1999). Percent Organic Matter (% OM) results were paired with lithologic descriptions to establish 2D cross-sections of the floodplain stratigraphy.

Chemical analyses

Monthly (Oct. 2007-Sept. 2008) stream and groundwater samples for concentrations of dissolved nitrate-N (NO_3^--N), dissolved ammonium-N (NH_4^+N), dissolved organic carbon (DOC), and dissolved oxygen (DO) were collected at each of the three study sites (Harnsberger, 2009). Prior to collecting groundwater samples from transect wells, three well volumes were purged from each well and wells were left to sit 3-4 hours to allow time for water levels to recover. Groundwater samples were collected using PVC bailers and were transferred to 200 mL plastic

(NO_3^-N and NH_4^+N) and amber (DOC) glass bottles which were stored in a cooler for transport to the lab. Samples for NO_3^-N and NH_4^+N were filtered (0.45 µm) and processed for analysis within 24 hours. Samples for DOC were filtered (0.45 µm), preserved with phosphoric acid to a pH less than 2.0, and processed for analysis within14 days. Dissolved NO_3^-N and NH_4^+N were analyzed at the ECU Central Environment Laboratory (CEL). NO_3^-N was 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, 2006). $_4^+$N was analyzed according to Method 4500-NH3-F: "Phenate Method" (APHA, 1998). DOC concentrations were measured by Mr. Jesse Chadwick at the main drinking water treatment plant of Greenville Utilities Commission (GUC) using a Teckmar Dorhmann Phoenix 8000 TOC analyzer as described by the method: *UV Persulfate procedure Method 5310C* (APHA, 2005). DO was measured using a handheld YSI DO200 field meter. Chloride concentrations were analyzed in the lab within one day of sampling using a Nexsens WQ-Cl Smart USB ion-specific Cl^-electrode. The lower limits of detection for each analysis procedure were 0.02 mg/L N, 0.0014 mg/L N, 0.02 mg/L, 0.01 ppm, and 1.8 ppm for NO_3^-N, NH_4^+N, DOC, DO, and Cl^-respectively.

NO_3^- attenuation and loading calculations

Monthly percent difference in NO_3^-N and Cl^-concentrations from up-gradient to near-stream wells at each site were estimated using the following equation:

$$\frac{(UG - NS)}{UG} * 100\% \qquad (1)$$

where:

UG = up-gradient NO_3^-N or Cl^-concentration = average NO_3^-N or Cl^-concentration (mg/L) of up-gradient (N3) shallow and deep wells at a site for a given month, and

NS = near-stream NO_3^-N or Cl^-concentration = average NO_3^-N or Cl^-concentration (mg/L) of near-stream (N1) shallow and deep wells at a site for a given month.

To summarize, medians of 12 monthly percent difference calculations at each site were used to assess median annual "NO_3^-attenuation" (NO_3^-production + NO_3^-loss, removal and/or retention) and net Cl- concentration change across each floodplain. Positive percent difference values represent a decrease in NO_3^-N or Cl^- , where negative values represent an increase. The distance between up-gradient and near-stream wells was 28 m at the urban and rural sites and was 20 m at the suburban site.

The loading of NO_3^-N from floodplain groundwater to surface water (NO_3^- loading) at each site was calculated on a monthly basis as the product of near-stream NO_3^--N concentrations and monthly groundwater discharge (Q) from each floodplain:

$$\text{near-stream } [NO_3^-N] * Q \qquad (2)$$

where:

near-stream [NO_3^-N] = average NO_3^-N concentration (mg/L) of near-stream (N1) shallow and deep groundwater at a site for a given month, and

Q = groundwater flux across a 100m reach of floodplain = KA dh/dl (m^3/month).

To calculate Q, Darcy's law (Q=KA dh/dl) was applied across the complete width of each floodplain. Hydraulic conductivity (K) values were determined using slug-tests (see Harnsberger, 2009) performed in wells (N = 6/site) at each site and the median K (N = 6) at each site was used to calculate Q. Cross-area (A) was the product of: a) a 100 m length of stream reach over which floodplain hydraulics were assumed to be roughly constant, and b) monthly manual measurements of the thickness of the floodplain aquifer at mid-floodplain wells of each site. Hydraulic gradient (dh/dl) was the difference in measured hydraulic head between up-gradient and near-stream wells at each floodplain.

Statistical analyses

Mann-Whitney-U comparisons were completed using Minitab v.15.1. 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 standard Anderson-Darling normality test. Of the 22 sets tested, 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 medians for hydrological and chemical data sets were significantly different from one site to the next. Only comparisons that returned p-values ? 0.05 were considered statistically significant.

RESULTS

Floodplain OM distribution

The occurrence of thick (1 – 1.5 m), buried peat layers at the urban and suburban sites resulted in high percent organic matter (% OM) values (> 20%) at depths of 1 m or greater (Figure 3). Due to the absence of peat at the rural site, floodplain sediments showed significantly less % OM (median % OM = 0.4) than sediments at the urban (median % OM = 1.2, $p < 0.01$) and suburban sites (median % OM = 0.9, $p < 0.01$) respectively (Table 1). Very shallow soil layers (0-20 cm) showed % OM > 1% at all three sites (Figure 3). This pattern was less obvious at the urban site, where shallow organic-rich soil grades directly into underlying peat. Peaks of % OM were observed from 2-2.5 m at the suburban site (Fig. 3B, MHB-N1) and from 1.7 to 2 m at the rural site (Fig. 3C, PB-N1) that represented isolated "hot-spots" of concentrated organic matter where woody debris and organic litter were sampled directly. Peat thickness varied across the sites (Figure 3).

Groundwater – OM contact

Median, near-stream groundwater level (9/14/2007 to 9/4/2008) as measured by continuous water level loggers was 0.48 m deeper at the urban (U) site than at the suburban (S) site ($p < 0.01$), and was 0.65 m deeper at the urban site than at the rural site ($p < 0.01$) (Figure 4A, Table 2). This is related to channel incision at the sites; the deeper channels had floodplains with deeper water tables (Figure 4B). Comparison of these groundwater levels to average surface soil thickness at the three sites determined during stratigraphic analysis of each floodplain cross-section suggests that water table decline at the urban and suburban sites has diminished contact between near-stream groundwater and organic-rich surface soil (Figure 4A). With a conservative estimate of 30 cm as the base of O- and A-horizon soils (Karnowski et al., 1974, Harnsberger, 2009), near-stream groundwater at the urban site made zero hours of 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 study period. Despite notably diminished contact between groundwater and surface soil at the

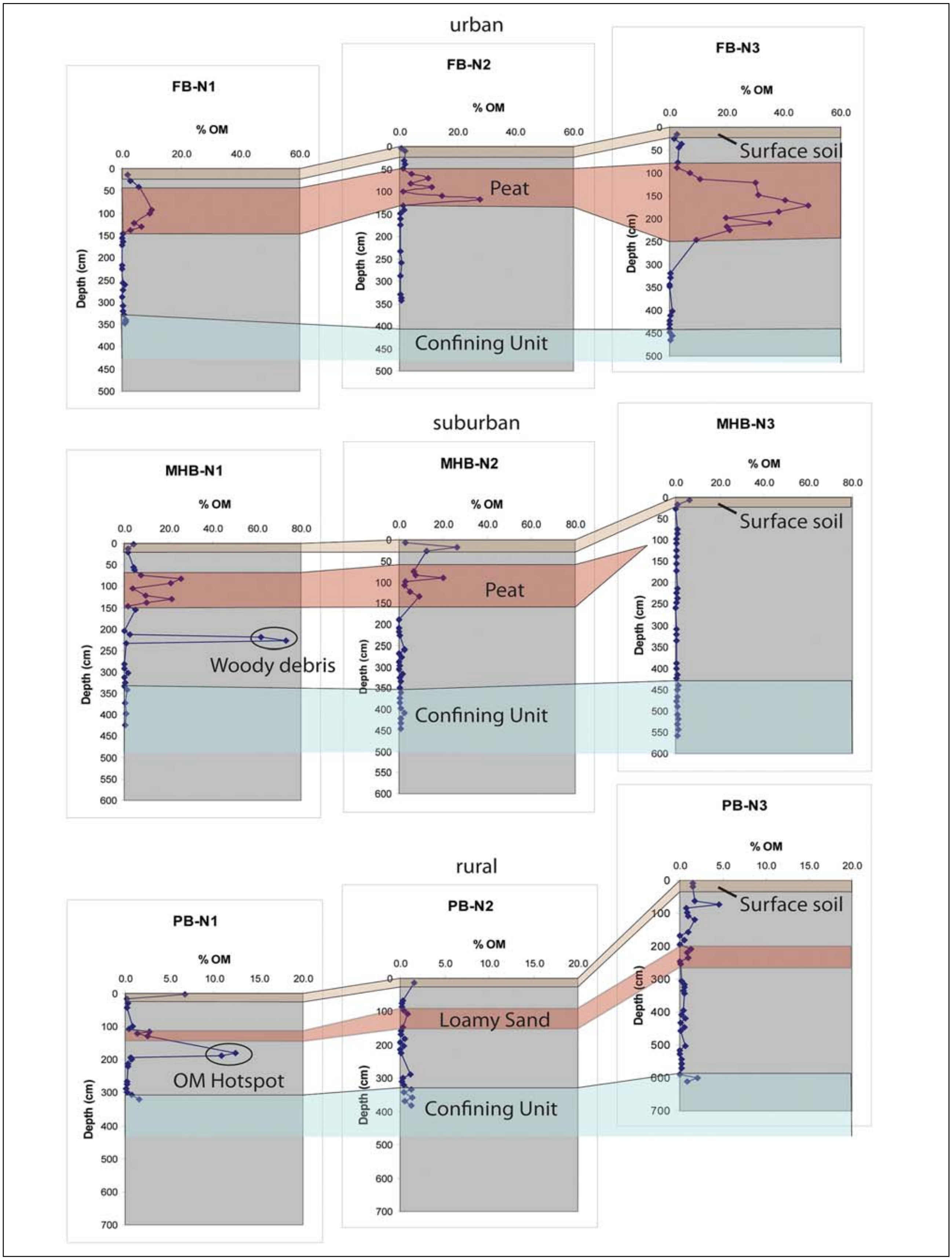

Figure 3. Vertical distribution of % OM from floodplain sediment cores of each study site. Cores were spaced 14 m apart at the urban and rural sites and 10 m apart at the suburban site. X-axis showing % OM for sediment samples at each site are scaled to highlight depths where elevated % OM occurred.

Table 1. Descriptive statistics for the vertical distribution of organic matter at well nest locations of the three study sites. Median values for cores from well nest locations reflect thickness of buried peat at the urban and suburban sites.

		Organic Matter (%)			
		Position			
		near-st.	floodplain	up-grad.	Site Total
urban	Count	24	23	32	79
	Mean	2.1	3.8	10.4	5.9
	Median	.7	1.3	2.6	1.2
	Minimum	.0	.3	.0	.0
	Maximum	10.1	27.7	48.6	48.6
	Coeff. of var.(%)	141.8	172.9	141.0	179.8
suburban	Count	29	32	33	94
	Mean	9.2	3.5	.8	4.3
	Median	1.9	.9	.6	.9
	Minimum	.0	.0	.1	.0
	Maximum	73.3	26.2	6.3	73.3
	Coeff. of var.(%)	192.2	171.1	133.0	252.5
rural	Count	21	23	37	81
	Mean	2.1	.5	.7	1.0
	Median	.6	.4	.5	.4
	Minimum	.2	.0	.0	.0
	Maximum	12.4	1.6	4.5	12.4
	Coeff. of var.(%)	168.4	89.6	117.8	193.4

incised study sites, near-stream groundwater contacted buried peat at the urban site frequently (Figure 4A; approximately 1 event/month) and nearly constantly at the suburban site (Figure 4A).

DOC, DO and Cl^- concentrations

Floodplain DOC concentrations were highest near peat layers at the urban and suburban site and lowest along deep groundwater flowpaths where hot-spots of organic matter were not encountered (Figure 5). The highest median DOC concentration of 14.2 mg/L occurred at the shallow, mid-gradient well of the urban site (Figure 5). DOC concentrations were significantly greater in shallow wells than in deep wells at the urban site ($p < 0.01$) and at the suburban site ($p < 0.01$).

Table 2. Descriptive data summary for groundwater depths measured by continuous water level indicators in near-stream, shallow wells of the three study sites.

		Depth to water table (m)		
		Site		
		urban	*suburban*	*rural*
annual	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

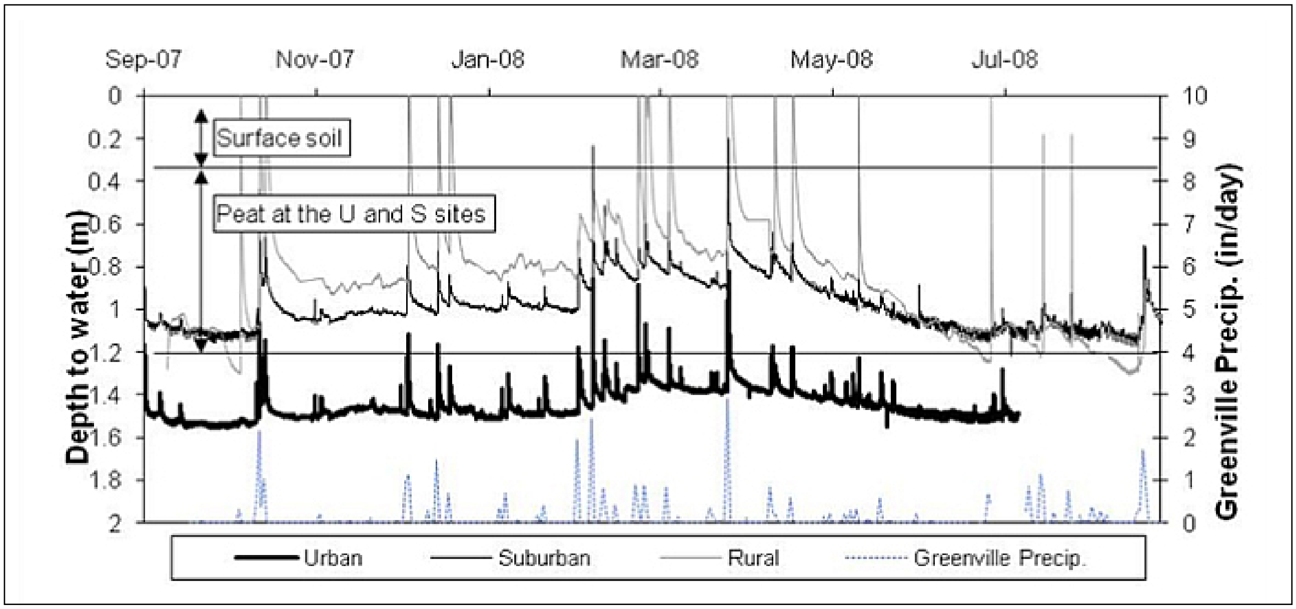

Figure 4A. Near-stream water table depths measured in deep, near-stream wells of each of the study sites from 9/14/2007 to 9/4/2008. Urban data from 7/15/2008 to 9/4/2008 is missing due to a logger failure. Both seasonal and storm-induced changes in depth are consistent across the three sites.

Median annual DOC concentrations were greater at the urban site than at the suburban site ($p < 0.01$) and rural site ($p = 0.05$) respectively. Significant decreases in median annual DOC concentrations occurred along lateral groundwater flowpaths between: 1) the shallow N2 to N1 wells at the urban site ($p < 0.01$), 2) the deep N3 to N1 wells at the urban site ($p = 0.02$), 3) and the shallow N2 to N1 wells of the suburban site ($p = 0.01$). Median annual DOC increased significantly from the N2 to the N1 wells of the rural site ($p < 0.01$).

DO concentrations were generally < 2.0 mg/L in all but the deep, up-gradient well of the urban site (Table 3). Median annual DO concentrations were greater in deep wells than in shallow wells at the urban site ($p = 0.10$) and were significantly greater in deep wells than in shallow wells at the

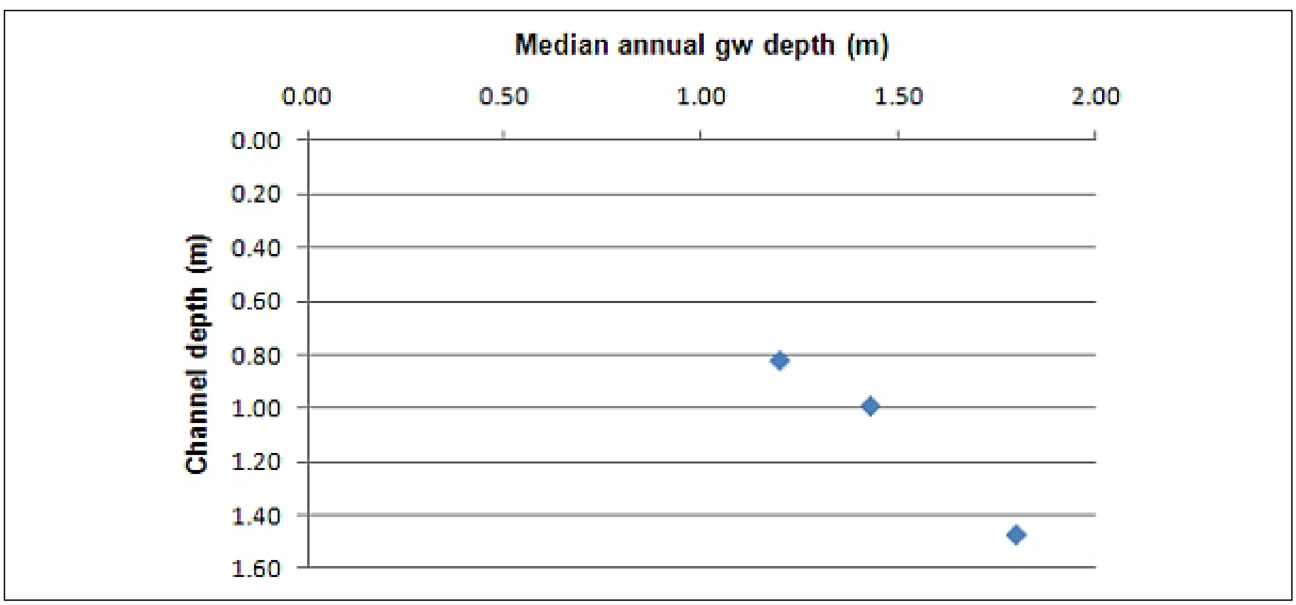

Figure 4B. Scatterplot showing channel depth (m) vs. median annual groundwater (gw) depth determined from 14,236 measurements recorded by continuous water level loggers in shallow, near-stream wells of each study site.

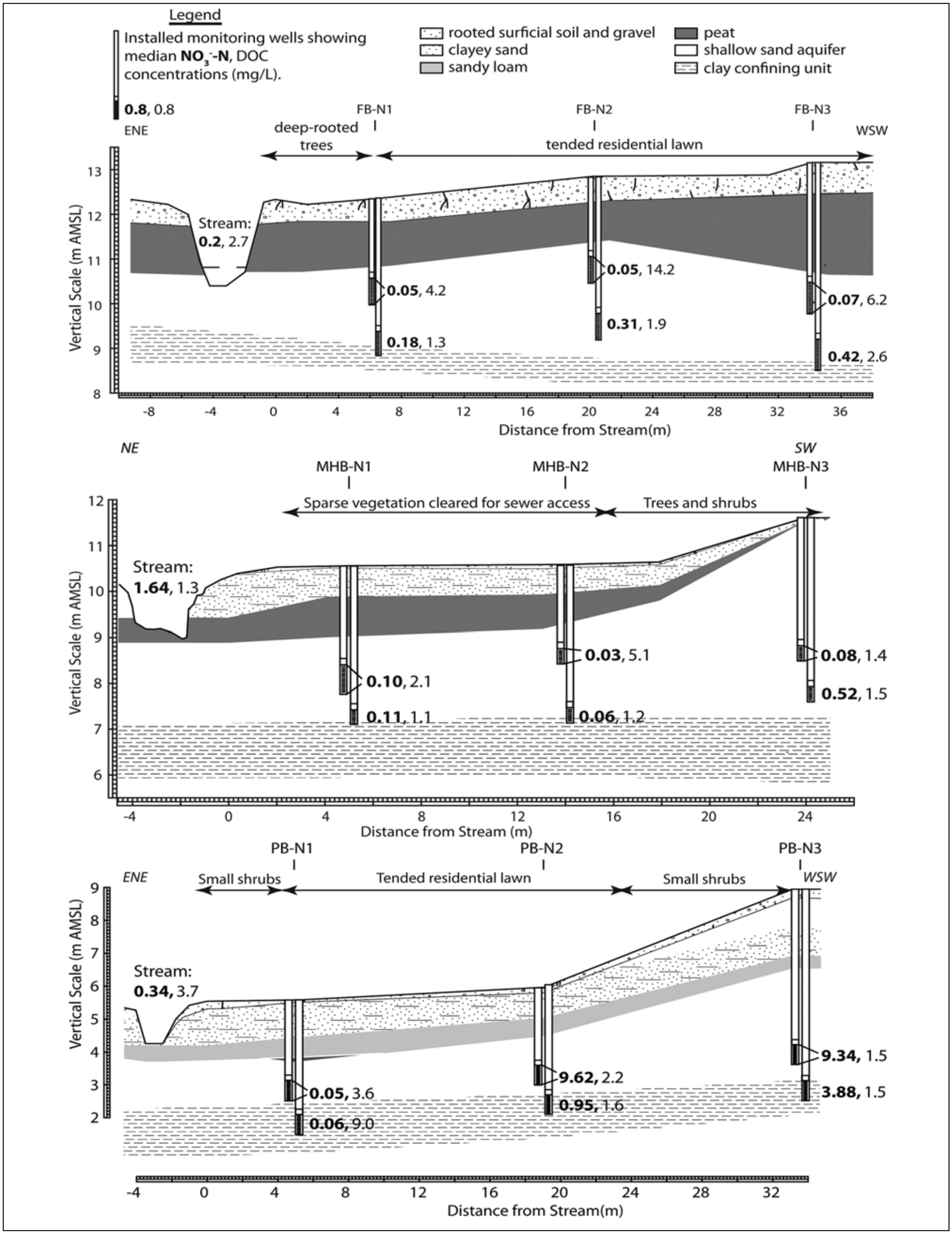

Figure 5. Geological cross-sections showing median NO_3^--N and DOC concentrations at shallow and deep wells of the: A) urban, B) suburban and C) rural sites respectively. Vertical scale is exaggerated by a factor of 2.9 at the urban site, 2.1

suburban site (p = 0.03). Median annual DO concentrations also decreased significantly between up-gradient and near-stream wells at all three sites ($p < 0.01$ for the urban and suburban sites; p = 0.03 for the rural site). Lastly, median annual floodplain DO concentration was significantly greater at the urban site (1.0 ppm) than at the suburban (0.7 ppm, $p < 0.01$) and the rural (0.5 ppm, $p < 0.01$) sites.

Median annual Cl^-concentrations ranged from 6.6-37.8 mg/L in floodplain groundwater of all 3 sites (Table 3). Median annual percent difference in Cl^-concentrations from the up-gradient to down-gradient locations across the three floodplains was significantly less than median annual percent difference in NO_3^-N concentrations ($p < 0.01$ for each site; Table 4). Cl^-concentrations decreased at the urban site (13.4%), increased at the suburban site (-32.9%) and decreased at the rural site (19.7%) (Table 4).

Floodplain NO_3^-attenuation and loading to incised stream channels

NO_3^-N concentrations were significantly greater in: 1) deep vs. shallow wells at the urban and suburban sites ($p < 0.01$ for both sites) and 2) up-gradient as compared to near-stream wells at all three sites (N = 12, $p < 0.01$ for each site). Mid- and up-gradient NO_3^-N concentrations greater than 9 mg/L at the rural site may have been related to discharge from a septic tank that occurred

Table 3. Summary of analytical data (Oct. 2007 – Sept. 2008) for water samples collected at the urban, suburban and rural sites.

			stream			near-st.			floodplain			up-grad.		
Site	**Constituent**	**Depth**	Median	Range	N	Median	Range	N	Median	Range	N	Median	Range	N
urban	NO3--N (mg/L as N)	shallow	.20	.51	12	.05	.22	12	.05	.23	12	.07	.23	12
		deep	.	.		.18	.22	12	.31	.50	12	.42	.42	12
	NH4+-N (mg/L as N)	shallow	.08	.31	12	1.06	.50	12	2.59	5.28	12	.44	.61	12
		deep	.	.		.17	.13	12	.15	.26	12	.19	.35	12
	DOC (mg/L)	shallow	2.7	7.3	12	4.2	2.9	12	14.2	27.2	9	6.2	6.4	10
		deep	.	.		1.3	5.5	12	1.9	3.2	12	2.6	20.5	11
	DO (ppm)	shallow	6.05	6.37	9	.78	.93	11	1.00	5.24	11	.96	3.25	11
		deep	.	.		.80	1.87	11	1.45	2.42	11	1.89	3.29	11
	Cl- (mg/L)	shallow	16.7	16.3	6	10.1	5.4	6	6.6	4.8	6	12.6	5.0	5
		deep	.	.		9.0	3.5	6	7.7	4.9	6	10.0	8.0	6
suburban	NO3--N (mg/L as N)	shallow	1.64	1.39	12	.10	.14	12	.03	.15	12	.08	.23	12
		deep	.	.		.11	.22	12	.06	.25	12	.52	.22	12
	NH4+-N (mg/L as N)	shallow	.07	.22	12	.07	.07	12	.09	.12	12	.05	.08	12
		deep	.	.		.07	.12	12	.06	.08	12	.05	.05	12
	DOC (mg/L)	shallow	1.3	3.2	12	2.1	7.5	12	5.1	12.9	12	1.4	4.0	12
		deep	.	.		1.1	3.6	11	1.2	3.6	12	1.5	14.9	12
	DO (ppm)	shallow	6.84	5.09	10	.42	1.00	11	.33	1.19	11	.74	3.23	11
		deep	.	.		.65	1.34	10	.40	.70	11	1.18	1.10	11
	Cl- (mg/L)	shallow	20.3	15.1	6	18.9	15.9	6	18.7	15.9	6	13.9	8.5	6
		deep	.	.		19.5	14.2	6	19.4	19.3	6	16.0	9.8	6
rural	NO3--N (mg/L as N)	shallow	.34	.75	12	.05	.19	12	9.62	3.66	12	9.34	5.28	12
		deep	.	.		.06	.10	12	.95	3.40	12	3.88	3.35	12
	NH4+-N (mg/L as N)	shallow	.04	.07	12	.74	.64	12	.10	.16	12	.06	.08	12
		deep	.	.		.46	1.68	12	.10	.19	12	.12	.33	12
	DOC (mg/L)	shallow	3.7	9.2	12	3.6	5.9	11	2.2	5.0	12	1.5	5.2	12
		deep	.	.		9.0	28.5	12	1.6	4.4	12	1.5	3.2	12
	DO (ppm)	shallow	6.36	9.35	9	.35	1.50	11	.48	1.20	11	.78	1.44	11
		deep	.	.		.28	.96	11	.40	2.22	11	.56	1.70	11
	Cl- (mg/L)	shallow	15.3	11.3	6	23.7	25.0	6	37.8	16.3	6	28.9	21.8	6
		deep	.	.		17.0	32.8	6	30.1	27.7	6	27.3	24.3	6

Table 4. Percent difference in groundwater Cl^- concentrations between up-gradient and near-stream locations at the urban, suburban and rural study sites.

	% Diff in [Cl-]			% Diff in [NO3-]		
	urban	suburban	rural	urban	suburban	rural
N	6	6	6	12	12	12
Median	13.4	-32.9	19.7	46.4	58.3	99.2
Minimum	8.5	-52.2	-7.8	-70.1	38.4	98.3
Maximum	26.5	-23.0	40.6	65.3	80.5	99.5
Range	17.9	29.2	48.4	135.4	42.1	1.3

20 m up-gradient of the transect at the rural site (pers. comm., landowner Christopher Graves, spring 2008). Despite large variability in monthly percent differences in NO_3^-N concentrations from up-gradient to near-stream wells at the urban site (Figure 6), percent difference values (N = 12/site) were significantly greater at the rural site than at the urban ($p < 0.01$), and suburban ($p < 0.01$) sites, respectively. Median annual percent difference in NO_3^-concentrations from twelve months of data at the urban (46.4%), suburban (58.3%) and rural (99.2%) sites increased in coordination with decreasing median near-stream groundwater depth (1.47 m, 0.99 m, 0.82 m; Figure 6) as compared across the three study sites.

Median annual near-stream NO_3^-N concentrations at the sites were significantly lower than 10 and 3 mg/L, the maximum contaminant level for NO_3^-N and reported mean natural background NO_3^-N concentrations in US waters, respectively)(USEPA, 2003; and Madison and Burnett, 1985). Though near-stream NO_3^-N concentrations (N = 24/site) at the urban and suburban sites were significantly greater than near-stream concentrations at the rural site ($p < 0.01$ for both tests), monthly NO_3^-loading (g/mo) was variable across sites (Table 5). Specifically, the product of average near-stream NO_3^-N concentrations and floodplain groundwater discharge caused NO_3^- loading to be significantly greater at the suburban site than loading at the urban site ($p < 0.01$) and rural site ($p < 0.01$), respectively. NO_3^- loading at the urban site was not significantly different from NO_3^- loading at the rural site at $p < 0.05$.

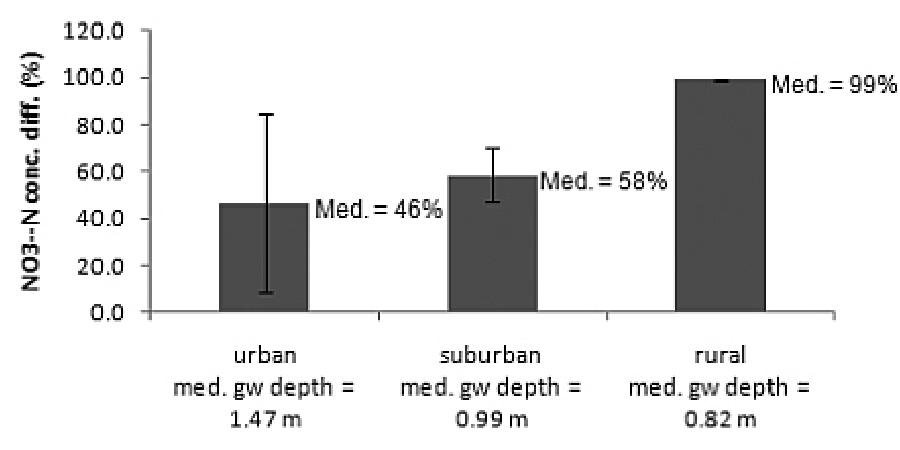

Figure 6. Monthly percent difference in NO_3^--N concentrations (%) between upgradient and near-stream wells at the urban, suburban and rural sites. Error bars show range in calculated percent difference values for the twelve months of NO_3^--N concentration data collected for this study. Median annual groundwater (gw) depths at each site are median of 14,236 measurements recorded by continuous water level loggers in near-stream, shallow wells at each site. Positive NO_3^--N concentration difference represents a decrease in NO_3^--N concentrations across the floodplain where negative difference represents an increase.

Table 5. Descriptive statistics for NO_3^-- loading (g/mo), average near-stream NO_3^--N concentrations (mg/L) and floodplain groundwater discharge Q (m3/mo) estimated for the urban, suburban and rural study sites.

		Site		
		urban	suburban	rural
NO_3^- loading (g/mo)	N	12	12	12
	Median	2.8	7.1	3.4
	Minimum	2.0	3.7	1.5
	Maximum	4.2	10.5	8.5
	Range	2.3	6.8	7.0
Avg. near-stream $[NO_3^-]$ (mg/L)	N	12	12	12
	Median	.55	.47	.23
	Minimum	.37	.34	.12
	Maximum	.85	.75	.54
	Range	.47	.41	.41
Q (m^3/mo)	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

DISCUSSION

In our efforts to determine if water table decline across riparian zones of incised urban streams: i) notably alters the contact of floodplain groundwater and riparian surface soils, and ii) notably affects the capacity of floodplain riparian zones to attenuate groundwater NO_3^-N, we discovered the vertical and horizontal distribution of organic matter across low-order floodplains substantially influences both potential relationships. Difference in the distribution of floodplain organic matter between the three study sites caused the contact of floodplain groundwater and both surface and buried organic-rich sediments to be much less diminished than it would have been had the three study transects been more geologically similar. Exposure of buried, organic-rich peat at the urban and suburban sites may have caused NO_3^-production to accelerate, but also improved conditions for DOC production, and likely increased the complexity of N-dynamics and chemical reaction of N-species in both soil pore water, and in unconfined groundwater at the incised urban and suburban sites. If NO_3^-produced in these exposed peats is transported to the underlying groundwater system during storm events, measured changes in NO_3^-concentrations between up-gradient and near-stream wells represent the net effect of reactions that both produce and consume NO_3^-in soil pore water and groundwater across the floodplain at each study site.

Vertical distribution of organic matter

The notable variation in % OM with depth and proximity to streams observed in this study is consistent with the results of recent work conducted by Gurwick et al. (2008a), and Hill et al. (2004) that demonstrated standard occurrence of thick and laterally extensive organic rich soil layers buried to depths greater than has been previously considered standard (~1 m; Schlesinger, 1997) for O- and A-horizon soils. The deep (> 1 m) and laterally extensive (> 20 m) peats found at the urban and suburban sites of this study were similar in OM content (2-49%), lateral extent, and depth to buried organic-rich soil layers encountered in the Hill et al. (2004) and Gurwick et al. (2008a) studies. Peat at the Maskinonge site (southern Ontario, Canada) of the Hill et al. (2004) study occurred at a depth of 45 to 200 cm, extended laterally for nearly 40 m, and had % OM of 30-62%. Gurwick et al. (2008a) demonstrated that buried organic-rich soil layers and hotspots of concentrated OM at depths of up to 2.6 m have the capacity to sustain C mineralization rates sufficient to affect landscape N budgets. Advancement in prediction and quantification of subsurface organic matter distribution across floodplain sediment profiles is needed to improve the accuracy at which riparian zone denitrification can be estimated (Groffman et al. 2009).

Effects of decline on groundwater - OM contact

Channel incision and water table decline at the urban and suburban sites caused a significant reduction in contact between floodplain groundwater and surface O- and A-horizon soils. Though groundwater levels showed no contact with surface soil during baseflow conditions at all 3 sites (Figure 4A), groundwater at the rural site made frequent contact with surface soil during storm events (Figure 4A). Aside from 0.5 hours of contact observed at the suburban site following a storm on 4/5/2008 (Figure 4A), near total loss of contact between groundwater levels and surface soil (Figure 4A) at the incised urban and suburban sites suggests that incision driven water table decline has the potential to shift near-stream groundwater out of contact with surface soil adjacent to incised urban streams.

Despite notable loss of contact between near-stream groundwater and surface soil at the urban and suburban sites, deep and laterally extensive peat at both sites sustained high (2.1 to 14.2 mg/L) median DOC concentrations in shallow wells (Figure 5). Elevated DOC concentrations in samples from wells screened in and near peat have been reported in other studies (Boettger, 2002; Devito et al. 2000; and Hill et al. 2000) and improve conditions for denitrification across floodplain aquifers where buried soil horizons occur. Significant increases in DOC concentrations across the floodplain of the rural site may be sustained by dissolution from buried, decomposing hotspots of organic matter that occurs as groundwater at the rural site enters the floodplain.

Effects of decline on NO_3^-attenuation

Results of this study suggest the NO_3^-attenuation capacity of the floodplain, riparian areas of low-order Coastal Plain streams are substantially influenced by the contact of floodplain groundwater and both surface and buried organic matter. Water table decline may have inhibited NO_3^-attenuation across floodplains of the urban and suburban sites of this study by: 1) shifting groundwater out of contact with the root zones of riparian vegetation, 2) shifting groundwater out of contact with surface soil that typically denitrifies floodplain groundwater, and 3) accelerating N contribution from buried peat to groundwater by exposing peat to more aerobic conditions. The positive correlation of groundwater levels with % difference in NO_3^-N may have also been influenced by high (> 9 mg/L) incoming NO_3^-N likely sustained by septic discharge at the rural site. The effect of elevated incoming NO_3^-N in shallow, up-gradient wells at the rural site would be to allow for greater consumption of NO_3^-N the floodplain, and thus greater % difference in NO_3^-N , but it is worth noting that despite much higher incoming NO_3^-N at the rural site than at the urban and suburban sites, 99% of the incoming NO_3^-N consumed every month that NO_3^-N were measured. Dilution from a cross-lateral or confined groundwater source may also have influenced the observed relationship between water table decline and floodplain NO_3^-attenuation.

Plant uptake via assimilation of NO_3^-N by the roots of riparian vegetation likely did little to remove NO_3^-N $^-$ groundwater at all three sites of 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 the urban and rural sites (Harnsberger, 2009). Sod root systems were based at about 6 cm below the land surface at the developed urban and rural sites and did not occur at the undeveloped suburban site. Evidence for the active root systems of trees and shrubs in cores from the suburban site suggests that active roots did not extend beyond 30 cm depth.

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. The strong spatial patterns of elevated groundwater DOC concentrations and low NO_3^-N DO concentrations in shallow wells in floodplain sediments at the urban and suburban sites of this study are consistent with patterns observed by several similar studies (Spruill, 2004; Hill et al., 2004, 2000). These patterns provide further support for the view that biogeochemical alteration to dissolved chemical constituents in riparian groundwater are primarily influenced by: i) microbial metabolic consumption and ii) supplies of electron donors and acceptors (Hill et al., 2000; Hedin et al. 1998). The occurrence of significantly greater NO_3^-N concentrations along deep flowpaths relative to shallow flowpaths at the urban and suburban sites also reinforces the perspective that NO_3^-N across floodplain, riparian buffer zones via plant-uptake and denitrification may be notably diminished when groundwater travels along deep, unconfined flowpaths before converging and discharging rapidly upward to streams (Bohlke and Denver, 1995). Though doubt remains as to the microbial availability of DOC contributed to groundwater by buried soil horizons, Gurwick et al. (2008b) have suggested that C availability in buried soils is more likely determined by the abundance and quality of organic matter at the time of horizon formation as opposed to horizon depth or age.

Repeated drying and rewetting of organic matter typically accelerates organic matter decomposition (Sorensen, 1974). Significantly greater NH_4^+N concentrations in shallow wells of the urban site relative to NH_4^+N concentrations in deep wells at the site ($p < 0.01$; Table 3) were likely motivated by excess contribution of NH_4^+N from peat soil pore water during groundwater recharge across the urban floodplain. Declining water tables at the urban site have exposed once saturated peat to aerobic conditions that accelerate floodplain N production. In a study of 13 riparian zones across a European climatic gradient, Hefting et al. (2004) found that in riparian zone settings where average groundwater levels were deeper than 30 cm, such as those determined for all 3 sites of this study, soil pore water NO_3^-N concentrations typically increase as a result of high net nitrification in unsaturated soils. Thus, elevated NO_3^-N in near-stream groundwater discharging from the floodplain to incised, low-order streams observed in this study and in similar studies (Angier and McCarthy, 2008; and Schilling et al., 2006) likely begins as excess NH_4^+N in soil pore water that is nitrified prior to transfer across the floodplain water table (Groffman et al., 2002) and accumulates in groundwater in advance of being discharged to incised streams. The occurrence of significantly greater groundwater DO concentrations at the urban site relative to the suburban and rural sites may also have been promoted by exposure of floodplain sediments to aerobic conditions by substantial decline of the near-stream water table at the urban site.

Dilution of NO_3^-N along lateral groundwater flowpaths by cross-lateral groundwater flow or upwelling from the confined aquifer may also affect the decline-removal capacity relationship. Chloride concentration change of 13.4% from wells at the urban site (Table 4) suggest that NO_3^-N concentrations may be diluted by groundwater upwelling from the clay confining unit. Evidence for this perspective is reinforced by the median ($N = 12$), upward vertical hydraulic head gradient

(-0.01 m/m) measured between shallow and deep near-stream wells of the urban site. Chloride concentrations at the suburban site were 32.9% higher at the near-stream wells than at the up-gradient wells (Table 4). It is unclear if dilution by upwelling groundwater occurs at this site. The notable decrease in median Cl^-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 up to 19.7% (Table 4). In general, monthly % differences in Cl^-concentrations were <1/3 of % differences in NO_3^-N suggesting that the observed NO_3^- values for each site were not primarily controlled by dilution.

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) groundwaterNO_3^-N concentrations measured in agricultural settings of the central and eastern US (Table 6). Floodplain groundwater $_3^-$N data of this study is compared to data measured in agricultural settings because very little work has been conducted investigating N-dynamics in groundwater discharging to incised streams of urban watersheds. Comparison of near-stream groundwater nitrate concentrations at sites listed in Table 6 to floodplain NO_3^-N attenuation at each respective site suggests that near-stream groundwater NO_3^- concentrations > 0.5 mg/L may be indicative of impaired floodplain $_3^-$N

Table 6. Median NO_3^--N concentrations and floodplain NO_3^- attenuation reported by studies assessing the effectiveness of riparian buffers in agricultural catchments of the central and eastern United States.

				[NO_3^--N] (mg/L)			
Study Location	**Land use context**	**Site label**	**Flowpath Length (m)**	**Up-gradient**	**Near-stream**	**% NO_3^-N Attenuated**	**Reference**
Eastern North Carolina	agriculture	Site 5A[a]	65	6.4	< 0.05	> 99	Harden & Spruill, 2008
		Site 5B	380	41.3	0.1	> 99	
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	
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
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%	

[a]NO_3^- conc. values are mean ± standard error

[b]NO_3^- conc. values are reported in-text by the referred author(s).

attenuation (concentration declines of < 85% across the floodplain). In all cases where near-stream groundwater $_{3}^{-}$N concentrations were < 0.5 mg/L, floodplain NO_3^--attenuation was > 95%. The general pattern of nearly complete (> 95 %) floodplain $_{3}^{-}$N attenuation at sites with "up-gradient" NO_3^--N concentrations > 8.0 mg/L at each site (e.g. sites 5B, 1, A-A' (ENC), B-B' (ENC) and A-A' Transect; Table 6) suggests that elevated incoming NO_3^- concentrations may improve floodplain $_{3}^{-}$N attenuation. Impaired floodplain NO_3^- attenuation observed at the incised urban and suburban sites of this study may be at least partially due to the lack of a substantial NO_3^--N source.

Finally, despite the positive correlation between near-stream groundwater levels and floodplain NO_3^-N , NO_3^-N did not vary in coordination with near-stream groundwater levels. The product of monthly near-stream NO_3^-N concentrations and monthly floodplain groundwater discharge, the latter being partially controlled by the hydraulic properties of floodplain sediments, caused NO_3^-N to be greatest at the suburban site (Table 5). NO_3^-N estimates presented in Table 5 may overestimate the mass (g/mo) of NO_3^-N enters each stream channel since streambed hyporheic processes often act to remove NO_3^-N groundwater (Harden and Spruill, 2008; Gu et al. 2007; Spruill, 2004; and Storey, 2004) when hyporheic sediments have sufficient organic matter to sustain denitrification.

Improved NO_3^-attenuation in floodplain aquifers could be achieved by reconstructing and stabilizing stream channels to elevate in-stream water levels and adjacent groundwater levels and improve contact between groundwater and organic-rich soil. Geomorphic restoration whereby streams are reconnected with riparian, floodplain areas should be considered for reaches where reconnection will not flood residential property. This type of restorative effort could improve surface water quality for incised urban streams and decrease nitrogen loading to downstream water bodies (Kaushal et al., 2008).

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