Nitrogen transport and transformations in a coastal plain watershed: Influence of geomorphology on flow paths and residence times

Anthony J. Tesoriero,[1] Timothy B. Spruill,[1] H. E. Mew Jr.,[2] Kathleen M. Farrell,[3] and Stephen L. Harden[1]

Received 11 December 2003; revised 20 August 2004; accepted 10 November 2004; published 8 February 2005.

[1] Nitrogen transport and groundwater-surface water interactions were examined in a coastal plain watershed in the southeastern United States. Groundwater age dates, calculated using chlorofluorocarbon and tritium concentrations, along with concentrations of nitrogen species and other redox-active constituents, were used to evaluate the fate and transport of nitrate. Nitrate is stable only in recently recharged (<10 years) water found in the upper few meters of saturated thickness in the upland portion of a surficial aquifer. Groundwater with a residence time between 10 and 30 years typically has low nitrate and elevated excess N_2 concentrations, indications that denitrification has reduced nitrate concentrations. Groundwater older than 30 years also has low nitrate concentrations but contains little or no excess N_2, suggesting that this water did not contain elevated concentrations of nitrate along its flow path. Nitrate transport to streams varies between first- and third-order streams. Hydrologic, lithologic, and chemical data suggest that the surficial aquifer is the dominant source of flow and nitrate to a first-order stream. Iron-reducing conditions occur in groundwater samples from the bed and banks of the first-order stream, suggesting that direct groundwater discharge is denitrified prior to entering the stream. However, nitrogen from the surficial aquifer is transported directly to the stream via a tile drain that bypasses these reduced zones. In the alluvial valley of a third-order stream the erosion of a confining layer creates a much thicker unconfined alluvial aquifer with larger zones of nitrate stability. Age dating and chemical information (SiO_2, Na/K ratios) suggest that water in the alluvial aquifer is derived from short flow paths through the riparian zone and/or from adjacent streams during high-discharge periods.

Citation: Tesoriero, A. J., T. B. Spruill, H. E. Mew Jr., K. M. Farrell, and S. L. Harden (2005), Nitrogen transport and transformations in a coastal plain watershed: Influence of geomorphology on flow paths and residence times, *Water Resour. Res.*, *41*, W02008, doi:10.1029/2003WR002953.

1. Introduction

[2] Nitrate is considered the most ubiquitous contaminant of groundwater in the world [*Spalding and Exner*, 1993] and often poses a serious threat to the quality of public drinking water supplies. Furthermore, according to the United States's Clean Water Action Plan [*U.S. Environmental Protection Agency and U.S. Department of Agriculture*, 1998], overenrichment by nutrients is the largest overall source of impairment of the nation's rivers and streams. In the southeastern United States, streams and receiving waters have been adversely affected by eutrophication [e.g., *Pinckney et al.*, 1997], increased hypoxia [e.g., *Paerl et al.*, 1998], fish kills [*Burkholder et al.*, 1995], and outbreaks of toxic species [*Burkholder and Glasgow*, 1997]. Increased nutrient loading to streams and ultimately to estuaries of the Albemarle and Pamlico Sounds has been implicated in all of these effects.

[3] Within the Neuse River basin (Figure 1), nonpoint source nutrient loads, particularly from confined animal feeding operations (CAFOs), have been identified as a major component of estuarine nutrient loading. The predominant wastewater treatment system used in these CAFOs is lagoons and spray fields; waste is flushed from confined animal housing into large earthen lagoons and then periodically sprayed onto agricultural fields in accordance with state regulations. Nitrogen in the spray volatilizes into the atmosphere, is assimilated by crops, runs off into adjacent streams, and infiltrates into the groundwater system. CAFOs may have a substantial effect on N and P loading to streams in the Neuse River basin based on the amount of waste produced, empirical data showing significant nitrate contamination in receiving waters from CAFOs, and atmospheric contributions from these operations [*Glasgow and Burkholder*, 2000]. While more than 70% of the flow of coastal plain streams in the Albemarle-

[1]U.S. Geological Survey, Raleigh, North Carolina, USA.
[2]North Carolina Department of Environment and Natural Resources, Raleigh, North Carolina, USA.
[3]Coastal Plain Office, North Carolina Geological Survey, Raleigh, North Carolina, USA.

Copyright 2005 by the American Geophysical Union.
0043-1397/05/2003WR002953$09.00

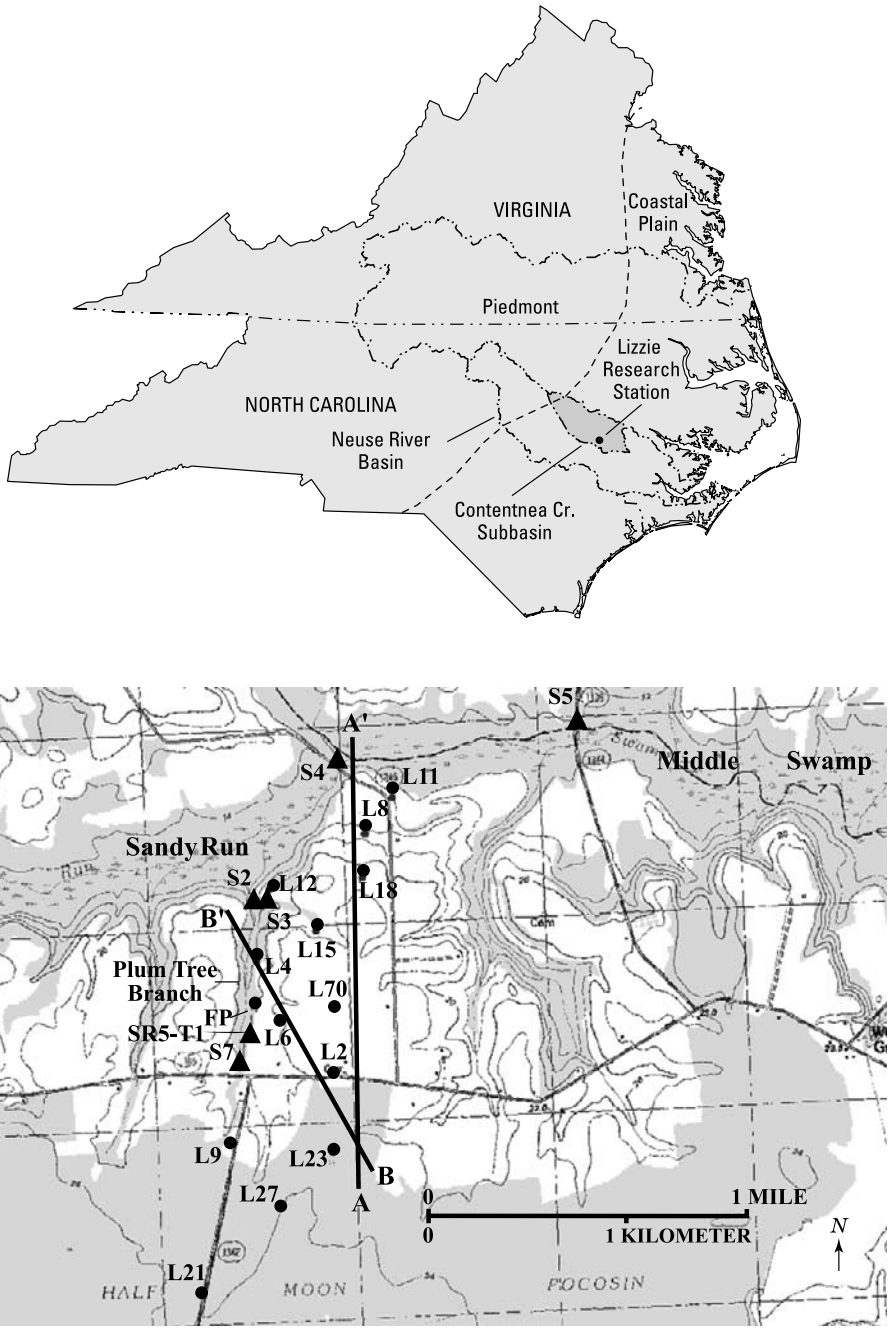

Figure 1. (top) Locations of Neuse River and Contentnea Creek basins and (bottom) sampling sites at the Lizzie Research Station and surrounding area in North Carolina. Triangles and circles indicate surface water and groundwater sampling sites, respectively.

Pamlico drainage is derived from groundwater [*McMahon and Lloyd*, 1995], the fate and transport of nitrate (NO_3^-) from these CAFOs, as it moves from fields to streams through the groundwater system, remain uncertain.

[4] The dominant pathways for nutrient transport from groundwater to streams are a function of hydrology, geology, and nitrate stability in the groundwater system. The presence of confining layers near the surface is thought to have a significant influence on nitrate removal, as these layers may cause more water to be routed through the riparian zone [*Hill*, 1996] where denitrification occurs. Denitrification refers to a microbial respiratory process in which nitrate is used as a terminal electron acceptor and is reduced to N_2 by the following generalized half-reaction:

$$2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O. \quad (1)$$

Most denitrifying bacteria are facultative anaerobes [*Firestone*, 1982] and begin to use nitrate as an electron acceptor when O_2 becomes limited. Anaerobic conditions are commonly found in shallow groundwater in the coastal plain of North Carolina [*Tesoriero et al.*, 2004]. In addition to denitrification, dissimilatory nitrate reduction to ammonium is a potential pathway for nitrate reduction.

[5] While nitrate reduction may occur in all anaerobic parts of the aquifer system, much attention has been given to the influence of riparian zones. As flow paths intersect these zones, N loading to streams from nonpoint sources often is reduced [e.g., *Mengis et al.*, 1999; *Spruill*, 2000; *Maître et al.*, 2003]. Stream riparian zones are defined as areas that have direct interaction between terrestrial and aquatic ecosystems with boundaries of the riparian zone extending outward to the extent of flooding [*Gregory et al.*, 1991]. The interface at the upland edge of the riparian zone often is denoted by steep chemical gradients that occur when aerobic upgradient groundwater enters the typically more reduced riparian zone [e.g., *Tesoriero et al.*, 2001].

[6] It is possible to chronicle the history of nitrate contamination and provide an assessment of groundwater vulnerability by relating water chemistry with sample age and position along a flow path [*Böhlke and Denver*, 1995; *Tesoriero et al.*, 2000, *Böhlke*, 2002]. Specifically, it is possible to deduce whether low nitrate levels are due to denitrification or simply because the water was recharged at a time that predates intensive fertilizer applications [e.g., *Böhlke et al.*, 2002; *Puckett et al.*, 2002]. Linking age-dating information with chemical data also improves assessments of groundwater vulnerability. Groundwater that has a short residence time is derived primarily from young or recently recharged water and is more likely to exhibit major effects of human activities. Residence times are more difficult to measure in surface water because many age-dating techniques (e.g., chlorofluorocarbons) are complicated by interactions with the atmosphere. A study based on long-term tritium data indicated that almost 75% of the annual discharge from the Neuse River had a watershed residence time of less than 1 year [*Michel*, 1992]. Currently, however, there is little information on the residence times of smaller drainages.

[7] The specific objectives of this paper are to (1) link chemical, hydrologic, and geologic data to obtain a mechanistic understanding of the fate and transport of nitrate in groundwater in a coastal plain environment; (2) combine age-dating and chemical analyses of groundwater to estimate historical groundwater nitrate levels and fate; and (3) define the dominant pathways of nutrients moving from groundwater to surface water by using chemical tracers and by tracking chemical changes along flow paths.

2. Site Description and Geomorphic Setting

[8] The study area is located in the Contentnea Creek subbasin of the Neuse River (Figure 1). The 180 ha Lizzie Research Station study site lies south of the confluence of the Sandy Run and Middle Swamp headwater streams in the 110 km^2 Middle Swamp watershed. The site encompasses a first-order drainage, known locally as Plum Tree Branch, that drains to Sandy Run, a third-order stream (Figure 1). Land use in the area is primarily agricultural, with row crops composed typically of corn and soybeans.

[9] In 1993, the North Carolina Department of Environment and Natural Resources (Division of Water Quality, Groundwater Section) established the Lizzie Research Station to investigate groundwater recharge and pollutant pathways in a typical coastal plain landscape. Independently, a local farmer purchased a portion of the study site in 1994, constructed a CAFO facility with lagoon and spray field waste treatment, and began operating in early 1995.

[10] Geologically, the Lizzie site lies in the Coastal Plain physiographic province, a landscape characterized by a series of progressively younger paleoshorelines and intervening terraces that step down in elevation and age toward the coast and into drainages. Landforms characterizing the Plum Tree Branch catchment include the poorly drained, upland wet flat headwaters, known locally as Half Moon Pocosin, and the generally well-drained to moderately well-drained upland dry flats and valley side slopes composing the Plum Tree Branch upland valley (Figure 2). Plum Tree Branch drains into Sandy Run, an alluvial paleovalley with riverine landforms along the valley bottoms [*Mew et al.*, 2003].

[11] A generalized hydrogeologic framework for the Lizzie site indicates that a late Cretaceous marine shelf deposit resembling the Peedee Formation functions as the basement of the shallow groundwater system of near-surface aquifers and confining units (Figure 2). Overlying the Cretaceous section is the Yorktown Formation of Pliocene age and several poorly exposed Pliocene to Pleistocene units that are difficult to age date and correlate because of widespread carbonate dissolution.

[12] Lithologically, the Yorktown aquifer is composed of gravelly sands and a phosphatic gravelly, shelly sand (Ty-2 and Ty-3 (Figure 2a)) overlain by a sandy, clayey silt with beds of *Mulinia congesta* that function as the 1- to 7-m-thick Yorktown confining unit (Ty-4). The tidally bedded surficial deposits of the Wicomico Plain (W unit (Figure 2)) form the upland surficial or terrace aquifer at the Lizzie site. These deposits of medium- to fine-grained flaser-bedded sand and silt initially settled into low-lying depressions in the relic landscape (W-1 unit), infilling paleovalleys and other channel-like features that cut into the Yorktown. Overlying these sands is a sheet-shaped, heterogeneous, extensively bioturbated, 1- to 3-m-thick, surficial layer (W-2 unit) that formed as a tidal flat or bay-like deposits that evolved upward into salt marsh deposits.

[13] Within the Sandy Run paleovalley, earlier erosion truncated the surficial and Yorktown Formations, with the Yorktown confining unit completely eroded below the 16 m scarp. Subsequent Middle Pleistocene fluvial to estuarine deposition, associated with later sea level rises, overlaid fine to coarse sands within the valley (PL and N units (Figure 2)) that compose the alluvial aquifer. Modern (Holocene) floodplain deposits that are several meters thick and rich in detrital plant debris form a riparian zone along Sandy Run and lower parts of Plum Tree Branch.

3. Methods

[14] Wells sampled in this study were installed by the North Carolina Department of Environment and Natural Resources (Table 1). Surface water sampling sites include a tile drain (SR5-T1 (Figure 1)), drainage ditch (S3), Plum Tree Branch (S2), Sandy Run (S4), and Middle Swamp (S5). Water quality sampling was performed according to the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) protocols [*Koterba et al.*, 1995]. Vertical coordinate information is referenced to the North American Vertical Datum of 1929.

[15] Dissolved oxygen and pH were measured with electrodes placed in a flow cell chamber to minimize atmospheric

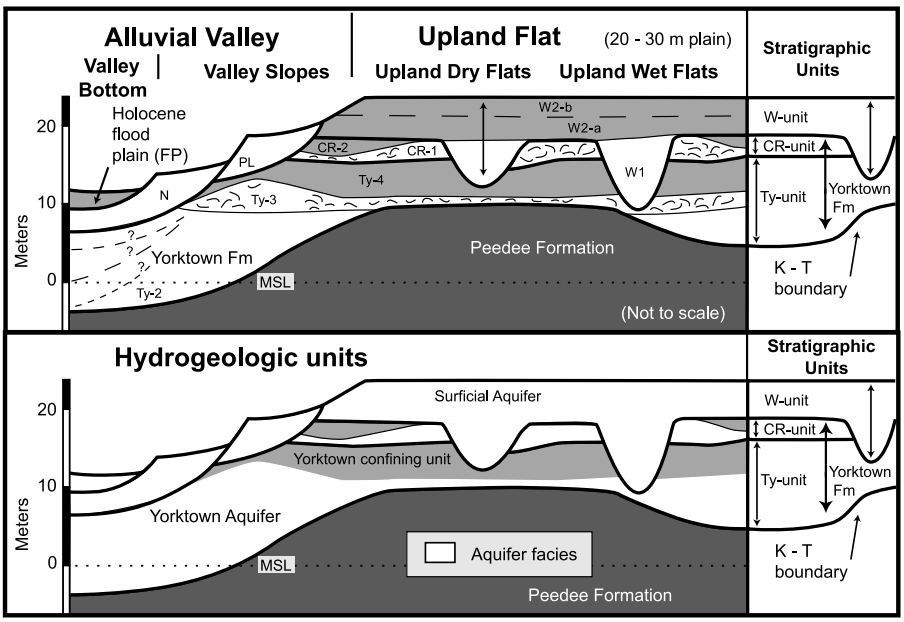

Figure 2. Conceptual model of the (top) stratigraphy and (bottom) hydrogeologic units at the Lizzie Research Station study site. Stratigraphic units are as follows: FP, quartz sand, upward fining to mud and detrital plant debris; N, PL, quartz sand fining upward to muddy sand and mud; W2, mud, sandy mud, and sand; W-1, flaser to wavy bedded quartz sand; CR-2, sandy mud; CR-1, muddy phosphatic shelly sand and gravel; Ty-4, sandy mud with thin shell beds; Ty-3, phosphatic gravelly shelly sand; Ty-2, gravelly sand with detrital wood; Peedee Formation, very fine to fine muddy sand. K-T boundary refers to the Cretaceous-Tertiary boundary.

interactions. Alkalinity was determined in the field by titration. Water samples for major ions and nutrients were filtered with a 0.45 μm capsule filter. Sulfate (SO_4^{2-}) was analyzed by ion chromatography. Magnesium, silica (SiO_2), iron, and manganese were analyzed by inductively coupled plasma and mass spectrometry. Nitrate, nitrite, ammonium, and bromide were analyzed using colorimetric methods. Detailed descriptions of the analytical methods for major ions and nutrients are provided by *Fishman* [1993]. Dissolved organic carbon was analyzed by ultraviolet promoted persulfate oxidation and infrared spectrometry [*Brenton and Arnett*, 1993]. All of the analyses were conducted at the USGS laboratories in Denver, Colorado and Ocala, Florida. Samples were collected and analyzed for chlorofluorocarbons (CFCs: trichlorofluoromethane, CFC-11; dichlorodifluoromethane, CFC-12; trichlorotrifluoroethane, CFC-113) as described by *Busenberg and Plummer* [1992]. Chlorofluorocarbon concentrations coupled with the relations between atmospheric chlorofluorcarbon concentrations and time were used to provide estimates of groundwater ages. Tritium analyses were performed using electrolytic enrichment and liquid scintillation. Tritium concentrations in the atmosphere are derived from atmospheric testing of nuclear weapons and are particularly helpful markers of whether recharge occurred before or after the onset of atmospheric testing (approximately 1953).

[16] Selected samples were collected and analyzed for N_2 and Ar gas to estimate the amount of nitrogen derived from denitrification [*Busenberg et al.*, 1993]. N_2 and Ar are incorporated in groundwater during recharge by air-water equilibration processes and excess air [*Heaton and Vogel*, 1981]. First, aerobic samples were used to determine the relation between N_2 and Ar and to ultimately determine the recharge temperature, because N_2 from denitrification is not expected in aerobic samples [*Dunkle et al.*, 1993]. Denitrification estimates were then calculated by subtracting the estimate of atmospheric nitrogen (both water-air equilibration and excess air) from the total amount of nitrogen gas measured in the sample.

[17] Dominant terminal electron-accepting processes (TEAPs) were determined by using the classification system of *Chapelle et al.* [1995]. Oxygen-reducing conditions were considered dominant when concentrations of dissolved oxygen exceeded 0.5 mg/L. Nitrate-reducing conditions were considered dominant when dissolved oxygen levels were less than 0.5 mg/L and nitrate concentrations exceeded 0.5 mg/L. Iron-reducing conditions were considered dominant when both dissolved oxygen and nitrate levels were less than 0.5 mg/L and dissolved iron concentrations exceeded 0.5 mg/L. In most instances, determinations of more reduced environments were not made, so when iron-reducing conditions are indicated, conditions may indeed be more reducing (e.g., sulfate reducing).

[18] A multiple comparison test using the Tukey method was performed on the ranks of SiO_2 concentration data in aquifers and streams to test the null hypothesis that groups were not significantly different based on an overall significance level of 0.05 [*Helsel and Hirsch*, 1992].

4. Results and Discussion

4.1. Groundwater Flow and Residence Times

[19] Head values for 13 December 2000 are shown for the surficial and Yorktown aquifers (Figure 3). Flow directions in the surficial aquifer indicate that much of the groundwa-

Table 1. Screened Intervals and Median Constituent Concentrations Dissolved in Groundwater Samples Collected From Aquifers and Riparian Zones at the Lizzie Research Station, North Carolina[a]

Well Name	Well Location in Figure 1	Screened Interval (m above msl)[b]		DO	pH	Ca	Mg	K	Na	HCO_3^-	Cl	SiO_2	SO_4^{2-}	NH_4^+ (as N)	NO_3^- (as N)	Fe
		Bottom	Top													
Surficial Aquifer																
L2	L2	18.6	21.6	3.4	4.6	3.5	3.6	0.7	2.4	1.2	9.1	5.6	9.3	<0.04	4.1	0.21
L2S	L2	22.1	23.0	4.2	5.1	2.2	2.5	0.7	5.3		10	6.7	3.4	0.12	2.6	0.17
L2D	L2	17.5	18.1	0.6	5.2	6.0	1.1	3.9	14	10	23	9.9	10	<0.04	0.89	0.63
L3	L2	11.9	16.5	0.4	5.1	2.4	0.4	2.0	4.3	3.1	11	17	8.5	<0.04	<0.05	5.06
L4	L4	16.6	18.1	5.5	5.3	27	4.6	5.2	3.9	10	20	4.9	14	<0.04	15	<0.003
L4S	L4	17.2	18.1	4.2	4.2	28	7.1	9.1	6.5	1.0	33	5.4	16	<0.04	19	0.02
L4D	L4	16.0	16.6	3.1	5.0	35	5.4	7.0	7.1	7.5	37	5.6	36	<0.04	19	0.17
L5	L6	13.5	16.5	0.1	4.4	3.5	0.6	1.5	4.8		9.8	16	14	<0.04	0.14	0.79
L6	L6	20.2	21.2	2.8	4.3	41	15	9.2	39	1.2	95	7.9	17	<0.04	41	0.07
L6S	L6	21.5	22.1	1.0	4.7	41	14	13	30	7.0	76	9.6	18	0.10	35	0.02
L6D	L6	16.9	17.5	0.3	4.5	1.9	0.7	1.9	7.4	2.2	10	13	17	<0.04	0.12	0.70
L9	L9	16.1	19.1	0.2	6.0	38	2.5	1.7	5.2	38	26	13	60	0.03	<0.05	2.48
L15	L15	16.1	19.2	1.7	4.1	15	7.6	2.4	3.7		25	6.7	16	<0.04	12	0.02
L15D	L15	15.4	16.0	1.1	5.9	25	3.7	1.5	4.6	19	20	9.8	41	<0.04	1.4	0.06
L18D	L18	14.2	14.8	1.9	5.3	13	0.9	1.4	7.8	5.0	11	8.4	26	<0.04	0.46	0.03
L20	L21	18.1	21.1	0.1	4.9	3.3	0.3	0.5	3.4	8.0	7.1	15	0.9	0.03	<0.05	0.66
L23	L23	21.0	22.5	2.1	5.3	3.6	0.1	0.2	17	9.0	22	12	12	0.07	0.07	0.31
L24	L23	16.4	17.9	0.5	7	88	1.8	0.9	17	293	20	37	5.1	<0.04	<0.05	1.49
L27	L27	18.2	21.2	4.5	5.0	0.8	0.2	0.1	2.1	3.0	3.4	4.7	1.3	<0.04	<0.05	0.11
L70S	L70	21.8	23.0	6.9	4.3	90	23	20	47		122	7.2	61	<0.04	85	0.04
L70D	L70	19.7	20.9	0.8	4.6	28	6.9	2.8	17		53	15	10	<0.04	20	0.11
Alluvial Aquifer																
L7	L8	6.3	12.4	7.8	4.7	13	7.4	4.5	2.4	2.0	18	6.2	3.9	<0.04	12	<0.01
L8S	L8	12.4	14.0	6.7	4.3	12	6.2	4.4	2.1	1.0	17	6.5	6.3	<0.04	12	0.01
L8D	L8	7.9	8.5	1.8	4.7	15	6.6	4.3	2.7	2.0	15	6.4	34	<0.04	6.5	0.05
L11S	L11	12.2	13.7	3.4	5.1	9.1	2.2	5.0	2.3	4.0	9.2	2.8	8.6	<0.04	5.2	<0.01
L11D	L11	7.5	8.1	4.3	4.5	16	5.7	7.1	2.1	1.0	24	3.4	16	<0.04	7.7	0.01
L11	L11	9.7	12.7	3.2	5.0	7.9	2.3	4.6	2.2	4.0	8.3	2.4	9.0	<0.04	3.9	
Yorktown Aquifer																
L10	L11	0.7	5.2	0.2	6.2	32	1.4	1.6	4.7	49	13	11	39	<0.04	0.05	1.15
L12	L12	2.6	8.7	0.1	7.5	59.0	2.2	2.0	8.5	200	5.5	35	5.2	0.07	<0.05	0.27
L14	L15	5.5	8.6	0.1	7.45	51.9	2.0	1.1	4.1	151	7.5	16	16	<0.04	<0.05	0.86
L16	L4	4.3	8.9	0.4	7.4	60.5	1.7	2.2	7.1	210	3.1	40	1.7	0.06	<0.05	0.29
L17	L18	3.5	9.6	0.1	7.4	55.0	1.8	1.7	6.4	184	3.4	29	3.2	<0.04	<0.05	0.93
L19	L21	3.7	11.4	0.1	7.5	61.1	1.4	1.4	4.9	198	4.1	25	1.1	<0.04	<0.05	1.19
L22	L23	5.4	11.5	0.1	7.3	66	1.4	1.1	7.2	226	5.1	33	0.8	0.03	<0.05	2.45
L26	L27	2.4	8.5	0.6	7.5	52.5	1.2	1.3	17	193	4.2	25	6.2	<0.04	<0.05	0.83
Peedee Formation																
L25	L23	−10.2	−7.9	0.1	7.3	61.2	2.4	2.2	8.6	218	4.4	27.0	0.4	0.06	<0.05	1.2
L55	L2	2.2	8.4	0.1	7.2	35.1	1.3	1.9	4.1	116	7.0	23.0	5.0	0.02	<0.05	2.3
Streambed and Riparian Zone																
Streambed-Center	Drainage Ditch @ S3	0.6	0.5	0.1	5.2	8.2	2.3	2.9	7.1	23	27	16	3.1	0.09	0.63	8.0
Riparian/Upland Boundary	FP	1.6	1.5	0.3	4.5	7.2	5.5	4.0	9.0		29	6.6	11	<0.04	6.4	0.09
Streambed-Center	Plum Tree nr FP	0.6	0.5	0.3	5.5	15	2.7	4.0	6.9	54	41	8.2	4.3	1.1	<0.05	14
Streambank-Right	Plum Tree nr FP	0.8	0.7	0.2	5.3	9.8	3.1	7.9	10	32	44	10	10	0.63	<0.05	9.6
Streambed-Center	Plum Tree @ S2	0.6	0.5	0.3	5.0	5.4	1.1	1.7	8.2	7.5	25	12	10	0.29	<0.05	8.2
Streambed-Center	Plum Tree @ S2	1.3	1.2	1.1	5.1	6.0	1.1	1.2	7.8	15	23	12	9.0	0.22	<0.05	10
Streambed-Center	Sandy Run @ S4	0.8	0.7	0.3	6.0	28	1.8	2.3	7.4	81	12	18	1.3	0.84	<0.05	0.04
Streambed-Right	Sandy Run @ S4	0.8	0.7	0.3	6.0	20	1.2	1.9	8.1	59	13	11	28	0.60	<0.05	0.08
Streambed-Right	Sandy Run @ S4	0.6	0.5	0.3	5.7	17	1.5	3.4	6.6	66	13	16	2.0	4.3	<0.05	4.1
Streambank-Right	Sandy Run @ S4	0.4	0.3	0.2	5.7	11	1.5	1.8	5.3	49	14	9.8	0.7	1.6	<0.05	6.2

[a]Units are milligrams per liter unless otherwise noted. Most samples were collected from March 1999 to June 2002.
[b]Abbreviation msl, mean sea level; for streambed and riparian wells, the screened interval is given as depth below land surface, in meters.

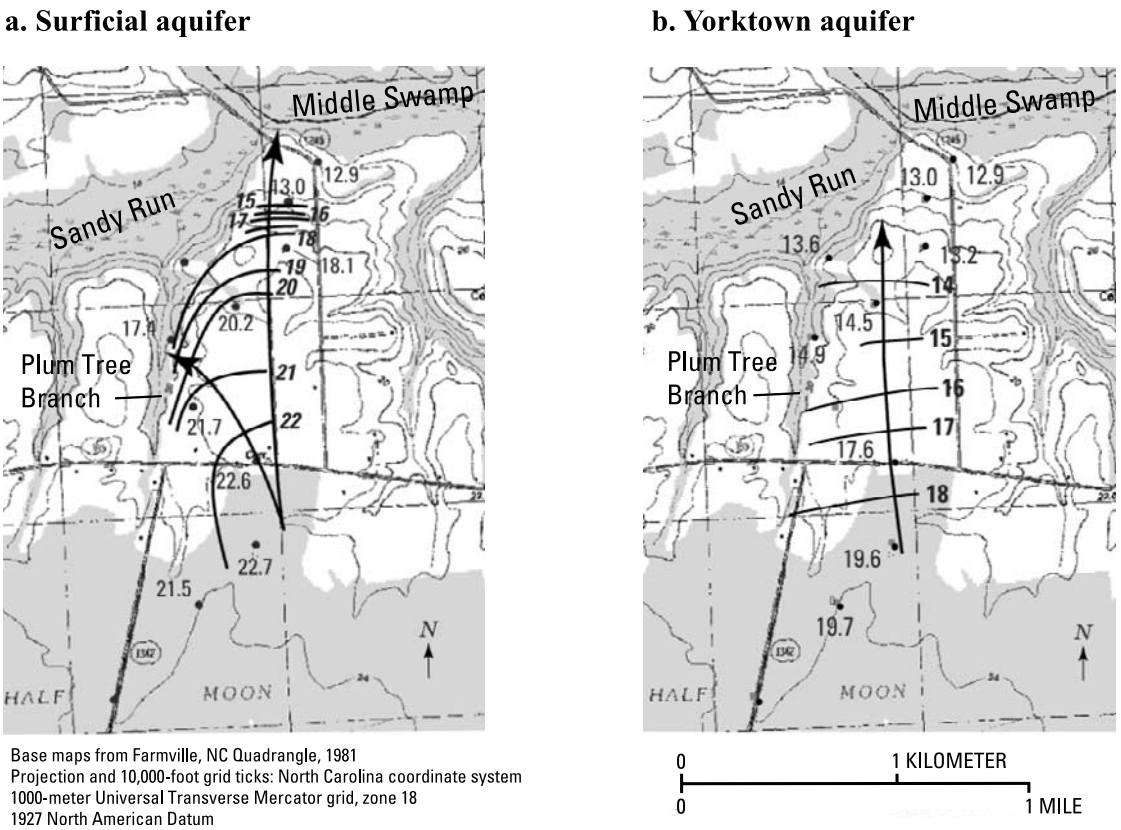

Figure 3. Piezometric head values and contours (in meters above mean sea level) and flow directions for the (a) surficial and (b) Yorktown aquifers. Measurements were taken on 13 December 2000.

ter underlying the western part of the study site flows toward Plum Tree Branch and may be a significant source of stream flow. Interactions between the Yorktown aquifer and Plum Tree Branch are limited because Plum Tree Branch does not breach the Yorktown confining unit (section B-B′ (Figure 4)) but flows above it. Not surprisingly, groundwater from the Yorktown aquifer does not discharge to Plum Tree Branch, as large downward gradients occur between the surficial and Yorktown aquifers as the stream is approached (Figure 4).

[20] Direct discharge to streams also occurs along the northern part of the site, with flow to both Sandy Run and Middle Swamp (Figure 3). Head differences between the surficial and Yorktown aquifers along the south-north cross section A-A′ are several meters in the upland areas but decrease to less than 0.1 m along the paleovalley slope terrace (Figure 4). Beneath this paleovalley stream terrace the confining unit has been eroded, and the Yorktown aquifer sediments have been overlain by fluvial to estuarine deposits, creating a 10-m-thick unconfined alluvial aquifer (Section A-A′ (Figure 4)).

[21] Age dating of groundwater provides another line of evidence regarding the prevailing flux through the groundwater flow system and the fate of contaminants. Three distinct flow regimes are present at the site and can be characterized by the overlying landscape settings: poorly drained upland wet flats, moderate- to well-drained upland valleys (dry flats), and broad riverine alluvial valleys (Figures 2 and 4). These landscape features typically are found in the middle coastal plain environment and have been mapped across the entire North Carolina Coastal Plain [*Haven*, 2003]. The south-north transect A-A′ (Figure 5; Table 2) illustrates the three flow regimes. The poorly drained upland wet flats to the south appear to have a recharge age profile indicative of slow percolation rates. While data are limited in this portion of the aquifer, recharge age contours based on chlorofluorocarbon data are closely spaced, with old water (1955 or earlier) found at the base of the surficial aquifer (Figure 5). In contrast, along the upland dry flats, moderately well-drained soils are present; faster recharge is indicated by the spreading of the recharge age contours. Groundwater at the base of the upland surficial aquifer in this part of the flow system is 20-30 years old. Along the alluvial valley slopes, recent recharge date contours occur at greater depths than in upland areas, suggesting that the alluvial aquifer is a recharge area that does not receive appreciable flow from deeper portions of the groundwater system. Along the B-B′ transect (Figure 5), the surficial aquifer thins as Plum Tree Brach is approached, with groundwater near the stream having a recharge date (i.e., 1983) that is consistent with being derived from a mixture of upgradient water from the surficial aquifer (Figure 5).

4.2. Chemical Indicators of Groundwater–Surface Water Interactions

[22] Chemical indicators were used to examine the interactions between the surficial, Yorktown, and alluvial aquifers and adjacent streams. By comparing the major ion chemistry of the aquifers and streams, it is often possible to discern the origin of ground and surface waters. Groundwater from the Yorktown aquifer is dominated by Ca^{2+}-

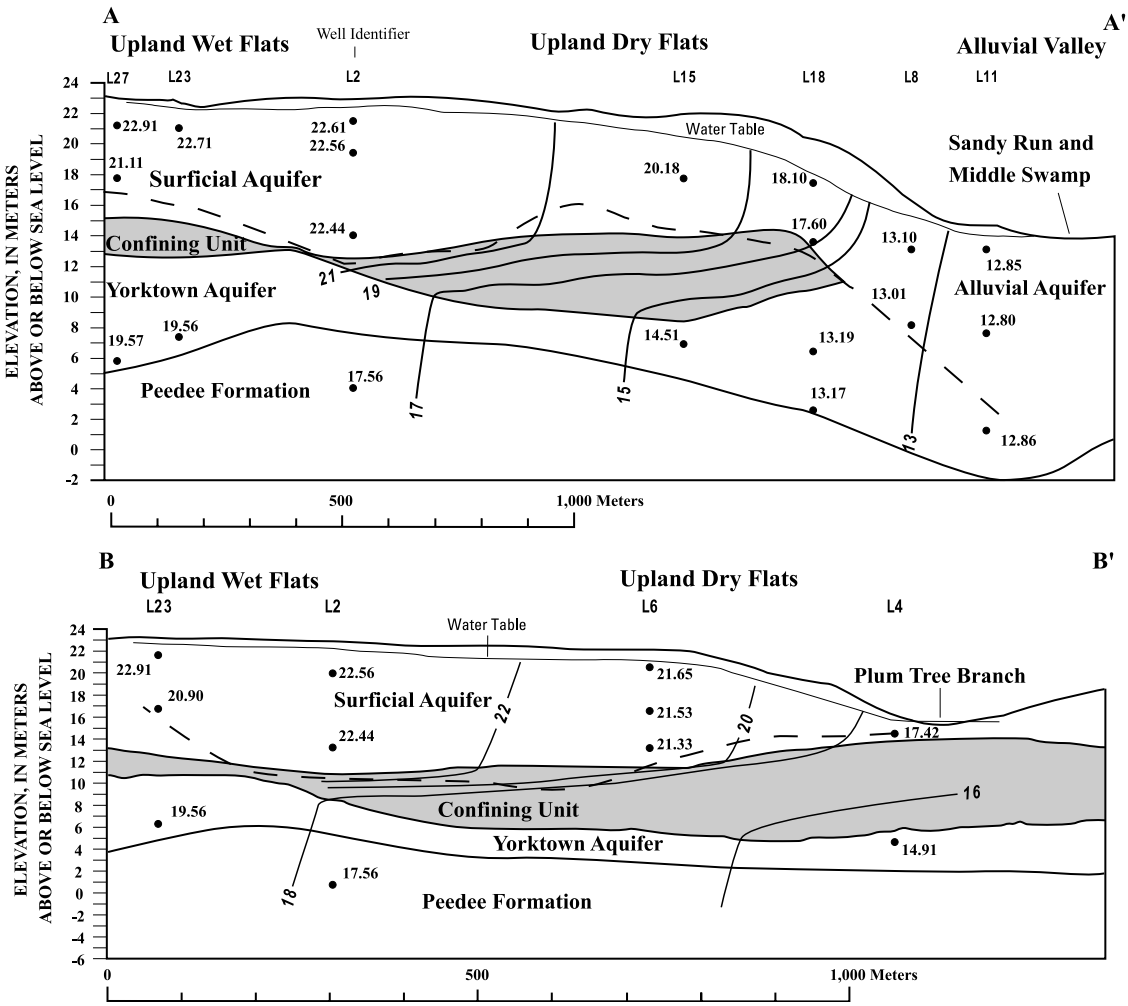

Figure 4. Piezometer head values (in meters above mean sea level) and contours along cross sections (top) A-A′ and (bottom) B-B′. The area above the dashed line indicates where calcareous sediments have been dissolved.

HCO_3^- (Figure 6). In contrast, water from the surficial aquifer has a more varied mix of cations, with anion chemistry dominated by Cl^- and NO_3^-. The alluvial aquifer has similar anion chemistry as the surficial aquifer; however, the cation chemistries of these two aquifers are different, with the alluvial aquifer having a smaller contribution from Na. One sample from the Yorktown (L10) differs from the rest of the samples from this aquifer (Table 1; Figure 6). This sample is at the interface of the alluvial, surficial, and Yorktown aquifers (Figure 5) and may be a mixture of these waters. This finding is supported by the recharge date of this sample (1974 (Figure 5)), which is intermediate between the younger water in the surficial and alluvial aquifers (1990s) and the older water in the Yorktown aquifer (1950s).

[23] The cation chemistry of Plum Tree Branch, Sandy Run, and Middle Swamp is bounded by the range in cation chemistry found in the surficial and alluvial aquifers. In contrast, the anion chemistry of all three streams, but particularly Sandy Run and Middle Swamp, trends from Cl-NO_3^--dominated water similar to the surficial aquifer to HCO_3^--dominated water similar to that of the Yorktown aquifer (Figure 6). HCO_3^-, however, is not conservative and may be generated by biologically mediated reactions occurring in the stream. It is hypothesized that the primary sources of groundwater discharge to these streams are from the surficial and alluvial aquifers, not the Yorktown aquifer.

[24] Interactions between ground and surface water can be complex, and the influence of riparian zone recharge can complicate flow path delineation in this zone [*Cey et al.*, 1999]. The water source and areal extent of the alluvial aquifer can be estimated by examining the chemistry of groundwater in this environment relative to other waters. Na/K, SiO_2 and chlorofluorocarbons are useful indicators of water sources in this study area. Na/K ratios are highest in the surficial and Yorktown aquifers with values commonly greater than 3 (Figure 7). In contrast, the alluvial aquifer is dominated by K, with Na/K ratios less than 0.7. Reduced Na/K ratios may be associated with increased soil leaching of K during high-discharge periods [e.g., *Cresser and Edwards*, 1988] and/or direct recharge through organic-rich soils [*Hem*, 1985]. Both mechanisms are plausible in this system. K concentrations increase during high-discharge periods in Middle Swamp and Sandy Run, with Na/K ratios typically less than 0.7. Direct discharge through the organic-rich riparian zone (Table 1) above the alluvial aquifer may also lead to K dominance.

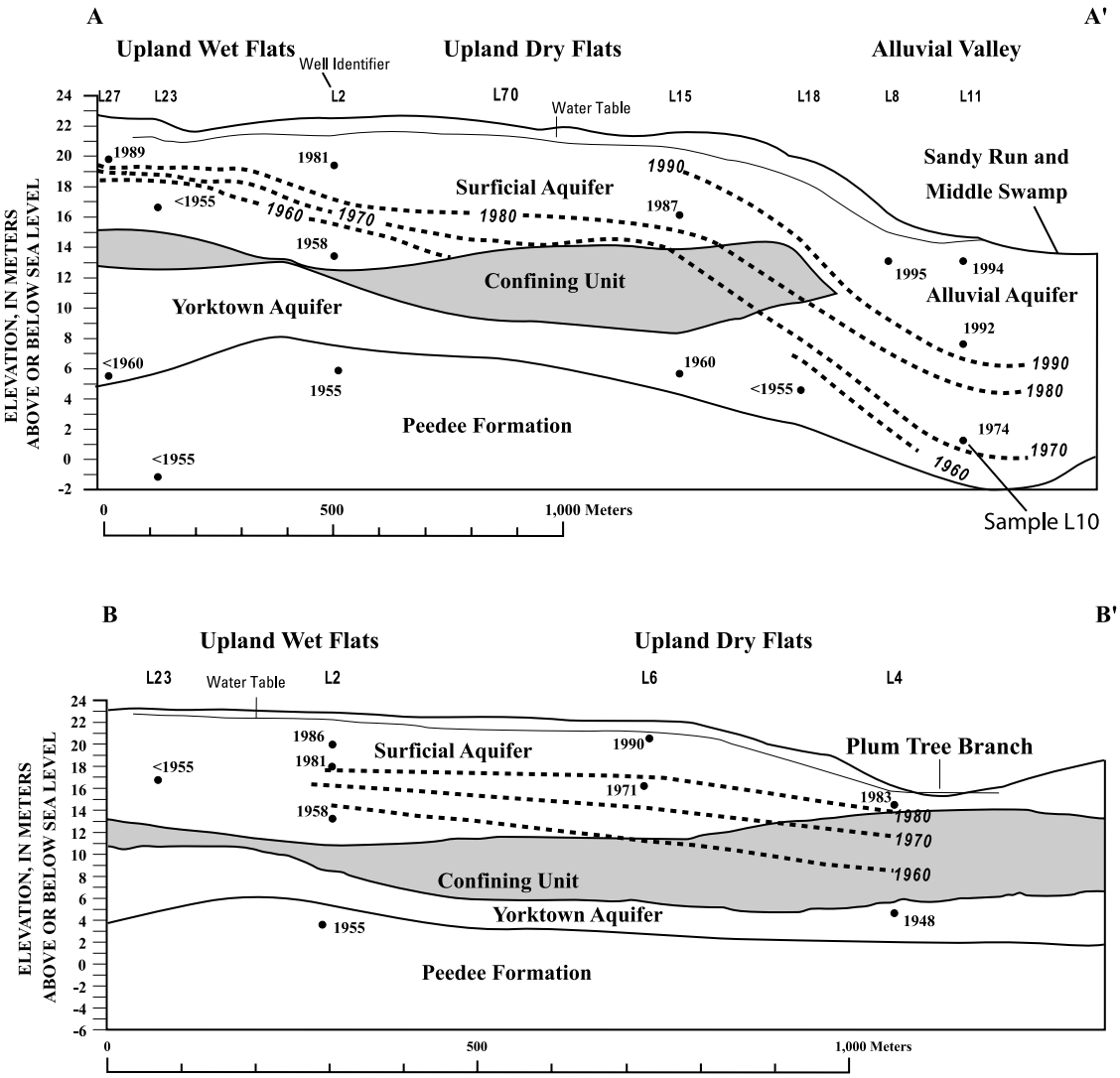

Figure 5. Recharge dates and contours using chlorofluorocarbon and tritium concentrations along sections (top) A-A′ and (bottom) B-B′.

[25] Concentrations of SiO_2 in Sandy Run, Middle Swamp, Plum Tree Branch, and the major aquifers in the study area were compared to examine possible sources of ground and surface water. SiO_2 is an excellent indicator of groundwater residence time (Figure 8) and groundwater source (Figure 9) in this system. Inferences about the watershed residence times of surface water also can be made by comparing SiO_2 concentrations in surface water to the relation between SiO_2 and groundwater residence time [e.g., *Burns et al.*, 2003]. The usefulness of SiO_2 concentrations as indicators of both the source and residence times of stream flow is limited by the effect that biological activity has on SiO_2 concentrations in streams. A bloom dominated by diatoms is indicated by a decrease in SiO_2 concentrations in Middle Swamp, Sandy Run, and Plum Tree Branch during late winter or early spring followed by a return to normal levels. This pattern has been observed in streams elsewhere and been attributed to a spring diatom bloom followed by summer blooms with a mixed phytoplankton population [e.g., *Garnier et al.*, 1995]. As a result, some of the lowest SiO_2 concentrations (e.g., bottom quartile) observed in Middle Swamp, Sandy Run, and Plum Tree Branch may not be reliable indicators of watershed residence time. Removing these low values does not alter the statistical groupings shown in Figure 9.

[26] SiO_2 concentrations are highest in the Yorktown aquifer, somewhat lower in the surficial aquifer, and lowest in the alluvial aquifer (Figures 7 and 9). The low SiO_2 concentrations in the alluvial aquifer are further evidence that water in this aquifer is not derived from a simple mixture of the Yorktown and surficial aquifers. Rather, a source with low SiO_2 concentrations, such as Middle Swamp and Sandy Run or perhaps direct discharge through overlying sediments, is indicated. Recharge in the riparian zone has been shown to cause water from a surficial aquifer to migrate deeper into the groundwater system and subsequently flow along an alluvial valley [*Cey et al.*, 1999]. The deeper migration of young water (containing low SiO_2 and high nitrate) in the alluvial aquifer and the mixed water chemistry just below the alluvial aquifer (i.e., sample L10) suggest that this process may also be occurring in this watershed.

Table 2. Recharge Dates and Concentrations of Dissolved Gases and Tritium for Selected Groundwater Samples at the Lizzie Research Station, North Carolina[a]

Well Name	Well Location in Figure 1	CH_4	N_2	Ar	Excess N_2	Tritium (pCi/L)	CFC-12 (pg/kg)	Recharge Date	Age-Dating Method
				Surficial Aquifer					
L2D	L2	0.001	22.4	0.689	2.1	33	171	1981	CFC-12
L3	L2	0.001	22.6	0.695	1.8	29	14	1958	CFC-12
L4	L4	<0.001	18.9	0.558				1983	CFC-113
L6D	L6	<0.001	22.8	0.668	3.6	48	75	1971	CFC-12
L6S	L6	0.002	18.8	0.646	1	26	259	1990	CFC-12
L15D	L15	0.005	24.3	0.635	7	30	236	1987	CFC-12
L18D	L18					31		>1953	Tritium
L20	L21	0.014	21.3	0.681	1.3	36	12	1957	CFC-12
L23	L23					29		>1953	Tritium
L24	L23					<1		<1955	Tritium
L27	L27	<0.001	17.3	0.650	<1	18	256	1989	CFC-12
				Alluvial Aquifer					
L7	L8	<0.001	17.7	0.630	<1	23	284	1994	CFC-12
L8S	L8	<0.001	16.0	0.595	<1	19	288	1995	CFC-12
L8D	L8	<0.001	19.3	0.638	1.9	22			
L11S	L11	0.005	18.0	0.641	0.4	19	281	1994	CFC-12
L11D	L11	<0.001	19.1	0.685	<1	19		1992	SF_6
				Yorktown Aquifer					
L10	L11	0.155	27.3	0.667	8.2	28	108	1974	CFC-12
L14	L15	0.002	22.3	0.704	1.1	10	19	1960	CFC-12
L16	L4	0.011	22.1	0.743	<1	<1	2	1948	CFC-12
L17	L18	0.004	21.7	0.732	<1	<1		<1955	Tritium
L19	L21	0.003	22.4	0.743	<1	<1	5	1952	CFC-12
L26	L27	<0.001	21.7	0.722	<1	2.6	32	<1960	Tritium
				Peedee Formation					
L25	L23	0.003	23.0	0.752	<1	<1		<1955	Tritium
L55	L2	0.006	23.0	0.742	<1	11	9	1955	CFC-12
				Streambed and Riparian Zone					
Streambed-Center (GR089)	Drainage Ditch @ S3	0.001[b]	17.2[b]	0.531[b]					
Streambed-Center (GR149)	Plum Tree @ S2	0.090[b]	16.3[b]	0.542[b]			51.8	1968	CFC-12
Streambed-Center (GR148)	Plum Tree @ S2	0.002	18.8	0.612	2.1		68.5	1970	CFC-12
Streambed-Center (GR155)	Plum Tree nr FP	7.2[b]	11.5[b]	0.364[b]					
Streambank-Right (GR156)	Plum Tree nr FP	0.430	20.1	0.638	2.8				
Riparian/Upland Boundary (GR157)	FP	<0.001	20.1	0.632	3.1				
Streambed-Center (GR152)	Sandy Run @ S4	14.9[b]	1.4[b]	0.045[b]					
Streambed-Right (GR151)	Sandy Run @ S4	6.63[b]	3.8[b]	0.150[b]					
Streambed-Right (GR150)	Sandy Run @ S4	14.7[b]	2.2[b]	0.105[b]					

[a]Units are milligrams per liter unless otherwise noted. Most samples were collected from March 1999 to June 2002.
[b]Samples have outgassed. Values shown underestimate actual concentrations.

[27] SiO_2 concentrations in the surficial aquifer are not significantly ($p < 0.05$) different from those found in Plum Tree Branch (Figure 9), which is consistent with this aquifer being a significant source of stream flow during base flow conditions. The first-order Plum Tree Branch is narrowly cut into the surficial aquifer and appears to have a similar chemical composition during base flow conditions. However, it should be noted that during high-flow conditions Plum Tree Branch likely has a different chemical signature than the surficial aquifer, but this water is quickly transported to Sandy Run. In contrast, Middle Swamp and Sandy Run flow along a paleovalley where the Yorktown confining unit has been eroded, allowing significant groundwater-surface water interactions. SiO_2 concentrations in Middle Swamp and Sandy Run are not significantly different from those found in the alluvial aquifer (Figure 9), further evidence of a strong link between these systems. Low SiO_2 concentrations in these streams also suggest that stream flow is largely derived from sources having short watershed residence times (e.g., <3 years). It is hypothesized that the broad alluvial valleys of these larger streams allow greater storage of recently recharged water, and this water becomes a significant portion of stream base flow. The short resi-

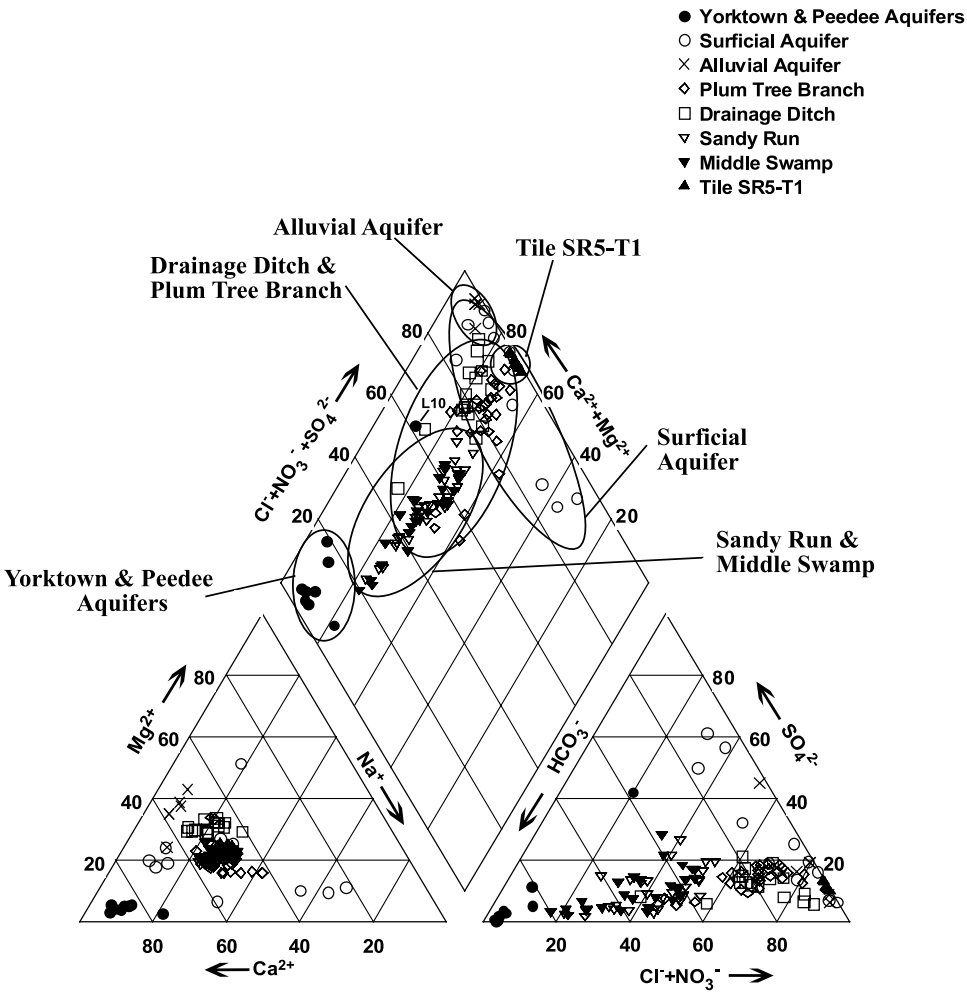

Figure 6. Trilinear diagrams of water chemistry in groundwater, streams, and artificial drainages.

dence times and low Na/K ratios in the alluvial aquifer also are evidence of the significant interaction that this aquifer has with adjacent streams.

4.3. Nitrogen Transformations and Transport

[28] Denitrification can be an important process affecting the fate and transport of nitrate in groundwater systems [*Korom*, 1992]. To evaluate this process, selected groundwater samples were analyzed for dissolved nitrogen and argon gas to estimate the amount of nitrogen derived from denitrification (Table 2). Aerobic samples have N_2/Ar ratios that plot on or near the lines for air-saturated water plus excess air (ASWEA) for recharge temperatures varying from 12 to 16°C (Figure 10). Therefore, a recharge temperature of 14° ± 2°C was used in the calculations of excess N_2. The uncertainty in the recharge temperature (±2°C) translates to approximately ±1 mg/L excess N_2. Most post-1953 (defined by detectable levels of tritium) anaerobic samples from the surficial aquifer and alluvial aquifer plot to the right of the ASWEA line for 14°C, indicating that varying amounts of denitrification have occurred in these areas (Figure 10). This suggests that these water samples contained elevated nitrate levels prior to entering an anaerobic part of the aquifer where nitrate was subsequently denitrified. In contrast, pre-1953 samples, while anaerobic, plotted on or near the 12°C ASWEA line, indicating that these samples have little or no excess N_2. Fertilizer use increased markedly after 1950, so it is likely that nitrogen applications to the land surface were much lower when these samples recharged the aquifer than they have been recently.

[29] A delineation of the dominant TEAPs along transects A-A′ and B-B′ indicates that nitrate is expected to be stable only in the uppermost part of the surficial aquifer (e.g., <3 m below the water table (Figure 11)). Nitrate concentrations decrease quickly with depth in the upland, with levels below 1 mg/L less than 3 m below the water table (Figure 11). Flow is generally horizontal in the surficial aquifer, limiting the transport of dissolved oxygen into deeper areas of the aquifer. As a result, the consumption of oxygen by aerobic respiration quickly exceeds the supply, with groundwater becoming anaerobic at relatively shallow depths. In deeper parts of the surficial aquifer and in most of the Yorktown aquifer, iron-reducing conditions are present; nitrate is not stable in this environment. Only in the alluvial aquifer at the northern terminus of the A-A′ transect are oxygen-reducing conditions found at significant depth. The absence of the Yorktown confining unit in this area allows for the forma-

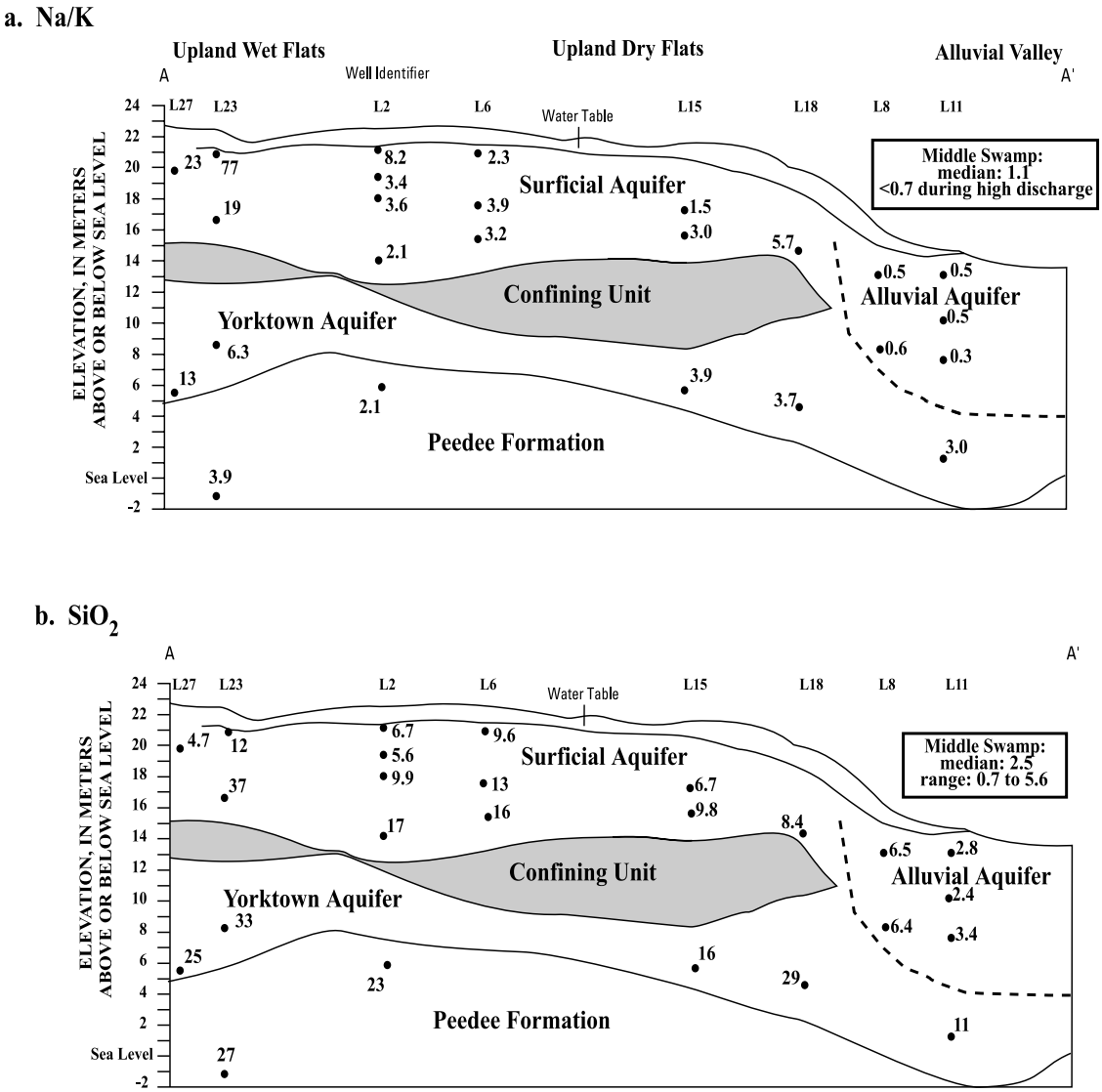

Figure 7. Cross section along transect A-A′ showing (a) Na/K mass ratios and (b) SiO_2 concentrations in mg/L.

tion of a large alluvial aquifer that contains recently recharged water, either from adjacent streams and/or direct recharge through the riparian zone (Figure 5). While oxygen-reducing conditions are observed at significant depth in the alluvial aquifer, it is important to note that bank and bed wells adjacent to Middle Swamp and Sandy Run are strongly reducing (methanogenic and iron-reducing conditions (Tables 1 and 2; Figure 11)). As a result, nitrate in water that moves from streams into the alluvial aquifer during high-flow periods may be denitrified prior to discharging back to streams when flows recede.

[30] Along the B-B′ transect, TEAP delineation is similar to the A-A′ transect in the upland areas but differs at the groundwater-surface water interface (Figure 11). Oxygen-reducing conditions pinch out as Plum Tree Branch is approached rather than widen as observed adjacent to Middle Swamp and Sandy Run. Reducing conditions adjacent to the stream coupled with older groundwater age suggests that this narrowly cut channel allows for little bank storage.

[31] The combined use of age dating, nitrate, excess N_2 and other redox-active constituent concentrations provides insight into the fate and history of nitrate contamination in the surficial, alluvial, and Yorktown aquifers (Figure 12). Specifically, these data can help discern if the sharp decrease in nitrate with depth occurs because nitrate-contaminated water from agricultural activity may not have reached this point in the flow system (i.e., the age of deep, low-nitrate groundwater predates intensive fertilizer and hog waste spray applications), and/or nitrate is denitrified as it moves deeper in the aquifer system. Three regimes regarding the history of nitrate contamination are apparent. First, groundwater that is younger than 10 years tends to be oxic and have elevated nitrate concentrations, reflecting both the oxic conditions in the upper part of the surficial aquifer and a recharge time period of high-nitrogen applications. Second, groundwater that is older than 10 years but younger than 30 years has low nitrate and dissolved oxygen concentrations, and increased excess N_2 values. These conditions indicate that these waters once contained elevated

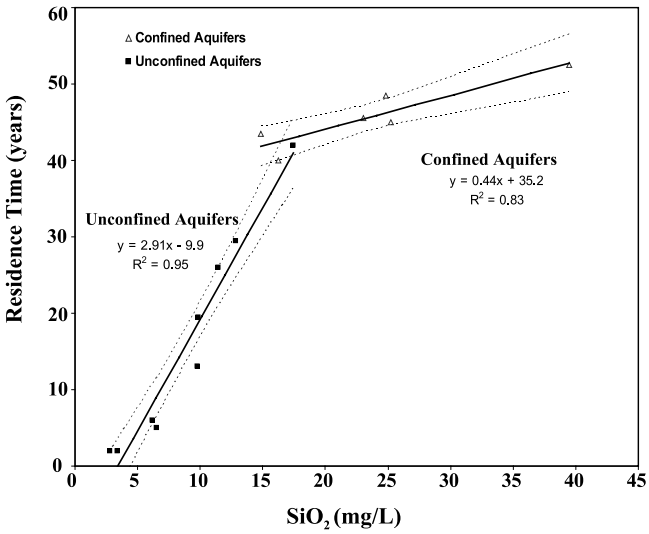

Figure 8. Groundwater residence times interpreted from chlorofluorocarbon concentrations plotted against SiO_2 concentrations. Unconfined aquifer data include the surficial and alluvial aquifers. Confined aquifer data include the Yorktown aquifer and the Peedee Formation. Dashed lines show 95% confidence levels.

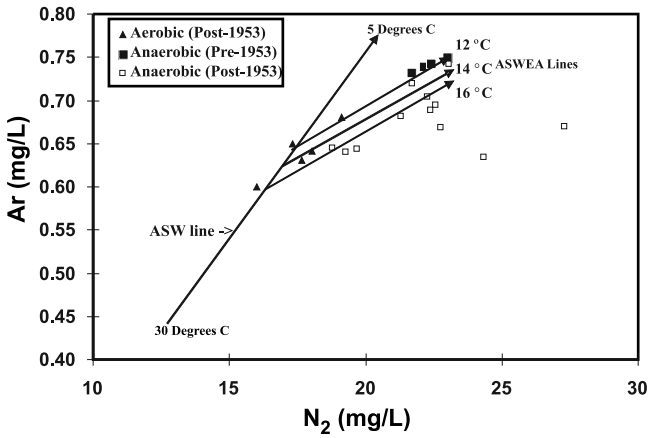

Figure 10. Dissolved Ar and N_2 concentrations in groundwater. ASW line depicts range of values expected for air-water equilibrium at varying temperatures. ASWEA lines depict range of values for one recharge temperature but with varying amounts of excess air. Values to the right of the ASWEA line representing the recharge temperature for the sample indicate excess N_2 from denitrification.

nitrate concentrations that have since been reduced by denitrification. Third, groundwater that is older than 30 years also has low nitrate and dissolved oxygen concentrations and high levels of iron but little or no excess N_2, suggesting that this water never contained elevated nitrate concentrations along its flow path.

[32] High nitrate concentrations in the upper part of the surficial aquifer are the likely source of nitrate in Plum Tree Branch (median nitrate concentration as N = 3.6 mg/L). Two mechanisms were considered for the transport of nitrate from groundwater to Plum Tree Branch: direct discharge of nitrate in groundwater to surface water and tile drainage.

[33] Groundwater migrates from uplands receiving hog spray through the riparian zone prior to discharging to Plum Tree Branch. Dissolved oxygen analyses indicate that aerobic conditions occur upgradient of the riparian zone with high concentrations of nitrate beneath the spray field (Figure 13). As groundwater enters the riparian zone,

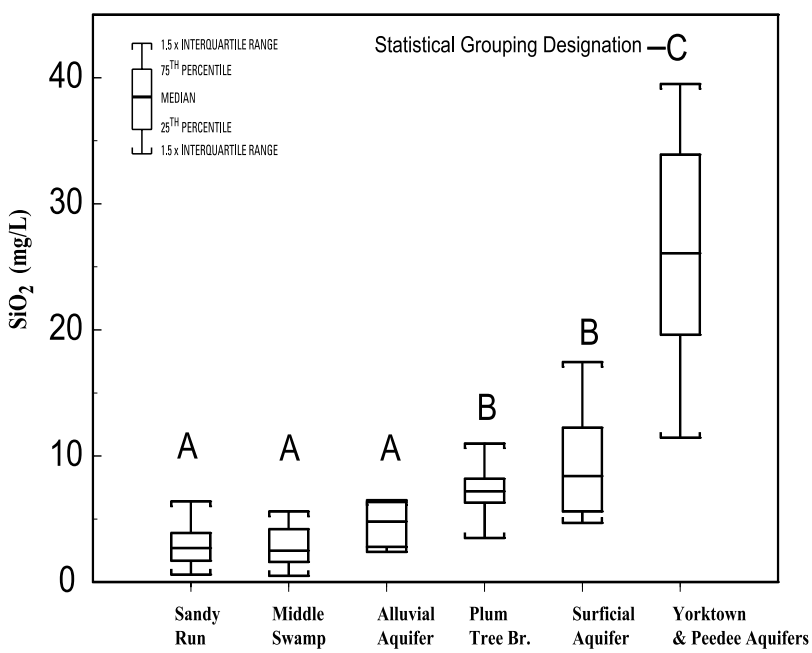

Figure 9. SiO_2 concentrations (in mg/L) for aquifers and streams at the Lizzie Research Station in North Carolina. Groups with different letter designations are statistically ($p < 0.05$) different from each other.

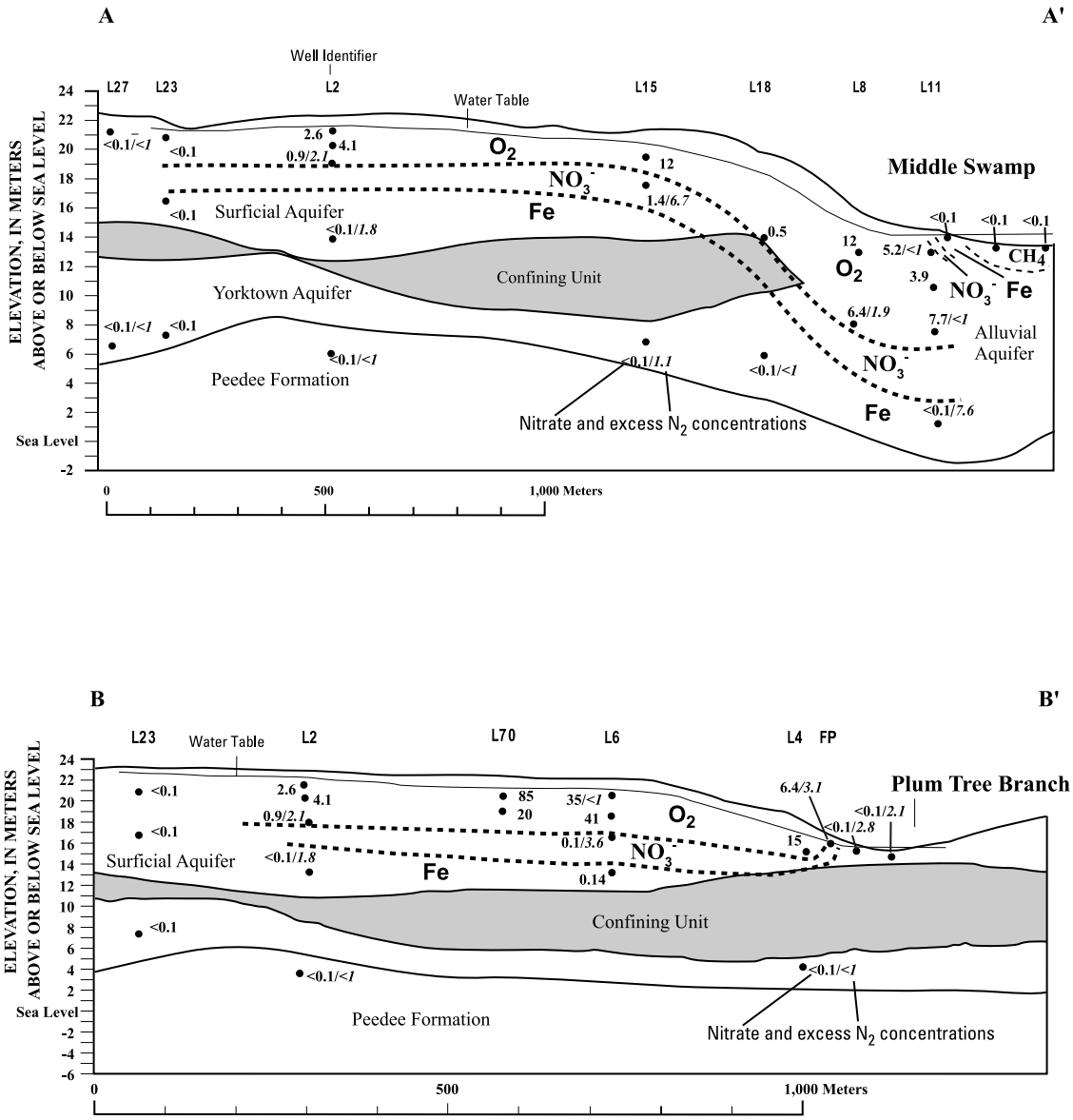

Figure 11. Delineation of terminal electron-accepting processes along transect (top) A-A′ and (bottom) B-B′. O_2, NO_3^-, Fe, and CH_4 denote zones of oxygen reduction, nitrate reduction, iron reduction, and methanogenesis, respectively. Nitrate (roman font) and excess N_2 (italics) concentrations in milligrams per liter also are shown.

dissolved oxygen and nitrate decrease and iron and methane increase, indicating that nitrate passing through this zone will likely be reduced prior to discharging to Plum Tree Branch (Figure 13). While this conclusion is supported by additional samples collected from the bed of Plum Tree Branch (Tables 1 and 2), additional transects would help extrapolate these findings to the entire basin. Excess N_2 determinations were not made in many bed and bank samples from Plum Tree Branch, Middle Swamp, and Sandy Run due to significant outgassing (Table 2). Mineralization of organic matter is a possible source of increases in ammonium levels that occur in the riparian zone.

[34] Groundwater that is intercepted by a tile drain at this site is routed directly to Plum Tree Branch (SR5-T1 (Figure 2)); as a result, riparian zone processes that lower nitrate fluxes are bypassed. Samples were collected from this tile nine times from October 2000 to September 2001 and analyzed for nitrate. Nitrate concentrations (as N) were consistently high, ranging from 30 to 46 mg/L. While a rigorous mass balance of the various nitrate sources is needed to provide a quantitative assessment, these high concentrations suggest that tile drainage has the potential to be a significant component of the nutrient flux in Plum Tree Branch.

[35] Dissolved inorganic nitrogen (DIN) concentrations are much lower in both Sandy Run (avg. DIN = 0.3 mg/L as N) and Middle Swamp (0.3 mg/L as N) than in Plum Tree Branch (5.4 mg/L). This may reflect more efficient nitrogen processing in the riparian zone and/or less intense agricultural land use in these larger basins. Methanogenic conditions are present in the streambed of Sandy Run (Table 2), indicating that direct discharge of nitrate to surface water during base flow conditions is not likely in this drainage.

5. Summary

[36] Chemical, hydrologic, and lithologic data have been used to examine the transport of nutrients in groundwater and their pathways to surface water in a coastal plain setting in the southeastern United States. In the uplands, groundwater in the surficial aquifer drains to a first-order stream. This stream receives little or no influence from deeper aquifers due to the presence of a confining unit at shallow depth. This confining unit is incised along drainages of third-order streams, thus connecting the surficial aquifer to the underlying aquifers, forming a large alluvial aquifer. Age-dating, lithologic, chemical, and piezometric data all suggest that water in the alluvial aquifer is composed of recently recharged water that is derived from direct discharge through the riparian zone and/or from adjacent streams during high-discharge periods.

[37] In the surficial aquifer, the upper few meters of saturated thickness is the only region where nitrate is stable. A deeper zone of nitrate stability occurs in the alluvial aquifer where younger and more oxic water is found at greater depths. Denitrification in deeper parts of the surficial aquifer and in the riparian zones is indicated by redox conditions in the aquifer and by the presence of excess levels of N_2. While conditions in the confined aquifer are favorable for denitrification, groundwater in this aquifer contains little or no excess N_2, suggesting that this groundwater never contained elevated nitrate concentrations along its flow path.

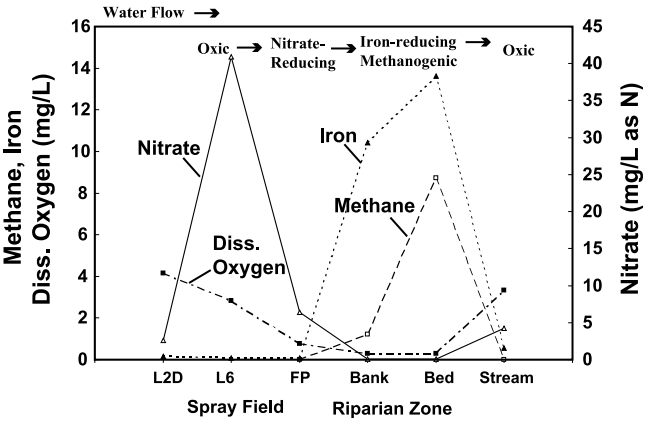

Figure 13. Selected redox-active constituents and terminal electron-accepting zones along the transect from well L2 to Plum Tree Branch near site FP (see Figure 1). Not to scale.

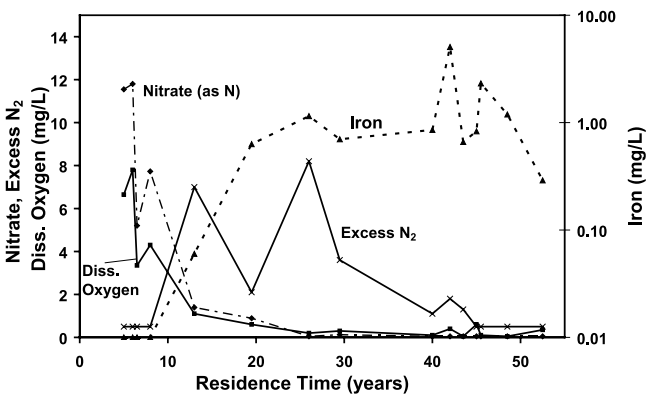

Figure 12. Redox-active species as a function of groundwater residence time. Nondetectable concentrations are plotted at half of the detection limit.

[38] **Acknowledgments.** Funding for this research was provided by the U.S. Environmental Protection Agency and by the U.S. Geological Survey's National Water-Quality Assessment Program. Suggestions made by Steve Kraemer, John Duff, Jeff Barbaro, J. K. Böhlke, two anonymous reviewers, and the Associate Editor that handled this manuscript are greatly appreciated. Eric Sadorf, Terry Middleton, Scott Caldwell, Cassandra Pfeifler, and Gloria Ferrell are gratefully acknowledged for their contributions to various aspects of this project. Although the research described in this article has been funded in part by the U.S. Environmental Protection Agency through assistance agreement number DW14938792-01 to the U.S. Geological Survey, it has not been subjected to agency review and therefore does not necessarily reflect the views of the agency, and no official endorsement should be inferred.

References

Böhlke, J. K. (2002), Groundwater recharge and agricultural contamination, *Hydrogeol. J.*, *10*, 153–179.

Böhlke, J. K., and J. M. Denver (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, *Water Resour. Res.*, *31*, 2319–2339.

Böhlke, J. K., R. Wanty, M. Tuttle, G. Delin, and M. Landon (2002), Denitrification in the recharge area and discharge area of a transient agricultural nitrate plume in a glacial outwash sand aquifer, Minnesota, *Water Resour. Res.*, *38*(7), 1105, doi:10.1029/2001WR000663.

Brenton, R. W., and T. L. Arnett (1993), Methods of analysis by the U.S. Geological Survey National Water-Quality Laboratory—Determination of dissolved organic carbon by UV-promoted persulfate oxidation and infrared spectrometry, *U.S. Geol. Surv. Open File. Rep., 92–480*.

Burkholder, J. M., and H. B. Glasgow Jr. (1997), Pfiesteria piscicida and other Pfiesteria-like dinoflagellates: Behavior, impacts and environmental controls, *Limnol. Oceanogr.*, *42*, 1052–1075.

Burkholder, J. M., H. B. Glasgow Jr., and C. W. Hobbs (1995), Distribution and environmental conditions for fish kills linked to a toxic ambush predator dinoflegellate, *Mar. Ecol. Prog. Ser.*, *124*, 43–61.

Burns, D. A., et al. (2003), The geochemical evolution of riparian ground water in a forested piedmont catchment, *Ground Water*, *41*, 913–925.

Busenberg, E., and L. N. Plummer (1992), Use of chlorofluorocarbons (CCl_3F and CCl_2F_2) as hydrologic tracers and age-dating tools: The alluvium and terrace system of central Oklahoma, *Water Resour. Res.*, *28*, 2257–2283.

Busenberg, E., E. P. Weeks, L. N. Plummer, and R. C. Bartholomay (1993), Age dating groundwater by use of chlorofluorocarbons (CCl_3F and CCl_2F_2), and distribution of chlorofluorocarbons in the saturated zone, Snake River Plain aquifer, Idaho National Engineering Laboratory, Idaho, *U.S. Geol. Surv. Water Resour. Invest. Rep., 93-4054*.

Cey, E. E., D. L. Rudolph, R. Aravena, and G. Parkin (1999), Role of the riparian zone in controlling the distribution and fate of agricultural nitrogen near a small stream in southern Ontario, *J. Contam. Hydrol.*, *37*, 45–67.

Chapelle, F. H., P. B. McMahon, N. M. Dubrovsky, R. F. Fujii, E. T. Oaksford, and D. A. Vroblesky (1995), Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems, *Water Resour. Res.*, *31*, 359–371.

Cresser, M., and A. Edwards (1988), Identification of changes in hydrological pathways during storms by analysis of leachate from intact soil-core lysimeters, *Scot. Geogr. Mag.*, *104*, 84–90.

Dunkle, S. A., L. N. Plummer, E. Busenberg, P. J. Phillips, J. M. Denver, P. A. Hamilton, R. L. Michel, and T. B. Coplen (1993), Chlorofluorocarbons (CCl_3F and CCl_2F_2) as dating tools and hydrologic tracers in shallow groundwater of the Delmarva peninsula, Atlantic coastal plain, United States, *Water Resour. Res.*, *29*, 3837–3860.

Firestone, M. K. (1982), Biological denitrification, in *Nitrogen in Agricultural Soils*, edited by F. J. Stevenson, pp. 289–326, Am. Soc. of Agron., Madison, Wis.

Fishman, M. J. (1993), Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments, *U.S. Geol. Surv. Open File Rep., 930-125*, 217 pp.

Garnier, J., G. Billen, and M. Coste (1995), Seasonal succession of diatoms and Chlorophyceae in the drainage network of the Seine River: Observations and modeling, *Limnol. Oceanogr.*, *40*, 750–765.

Glasgow, H. B., and J. M. Burkholder (2000), Water quality trends and management implications from a five-year study of a eutrophic estuary, *Ecol. Appl.*, *10*, 1024–1046.

Gregory, S. V., F. J. Swanson, W. A. McKee, and K. W. Cummins (1991), An ecosystem perspective of riparian zones, *Bioscience*, *41*, 540–551.

Haven, W. T. (2003), Introduction to the North Carolina Ground Water Recharge Map, *Ground Water Circ. 19*, N.C. Dep. of Environ. and Nat. Resour. Div. of Water Qual., Raleigh.

Heaton, T. H. E., and J. C. Vogel (1981), "Excess air" in groundwater, *J. Hydrol.*, *50*, 201–216.

Helsel, D. R., and R. M. Hirsch (1992), *Statistical Methods in Water Resources*, Elsevier, New York.

Hem, J. D. (1985), Study and interpretation of the chemical constituents of natural water, *U.S. Geol. Surv. Water Supply Pap.*, *2254*.

Hill, A. R. (1996), Nitrate removal in stream riparian zones, *J. Environ. Qual.*, *25*, 743–755.

Korom, S. F. (1992), Natural denitrification in the saturated zone: A review, *Water Resour. Res.*, *28*, 1657–1668.

Koterba, M. T., F. D. Wilde, and W. W. Lapham (1995), Ground-water data-collection protocols and procedures for the National Water Quality Assessment program: Collection and documentation of water-quality samples and related data, *U.S. Geol. Surv. Open File Rep., 95-399*.

Maître, V., A. Cosandey, E. Desagher, and A. Parriaux (2003), Effectiveness of groundwater nitrate removal in a river riparian area: The importance of hydrogeological conditions, *J. Hydrol.*, *278*, 76–93.

McMahon, G., and O. B. Lloyd (1995), Water quality assessment of the Albemarle-Pamlico drainage basin, North Carolina and Virginia, *U.S. Geol. Surv. Open File Rep., 95-136*.

Mengis, M., S. L. Schiff, M. Harris, M. C. English, R. Aravena, R. J. Elgood, and A. MacLean (1999), Multiple geochemical and isotopic approaches for assessing ground water NO_3^- elimination in a riparian zone, *Ground Water*, *37*, 448–457.

Mew, H. E., Jr., D. K. Hirth, D. V. Lewis, R. B. Daniels, and A. J. Keyworth (2003), Methodology for compiling ground water recharge maps in the Piedmont and Coastal Plain provinces of North Carolina, *Ground Water Bull. 25*, N.C. Dep. of Environ. and Nat. Resour. Div. of Water Qual., Raleigh.

Michel, R. L. (1992), Residence times in river basins as determined by analysis of long-term tritium records, *J. Hydrol.*, *130*, 367–378.

Paerl, H. W., J. L. Pinckney, J. M. Fear, and B. L. Peierls (1998), Ecosystem responses to internal and watershed organic matter loading: Consequences for hypoxia in the eutrophying Neuse River estuary, North Carolina, USA, *Mar. Ecol. Prog. Ser.*, *166*, 17–25.

Pinckney, J. L., D. F. Millie, B. T. Vinyard, and H. W. Paerl (1997), Environmental controls on phytoplankton bloom dynamics in the Neuse River estuary, USA, *Can. J. Fish. Aquat. Sci.*, *54*, 2491–2501.

Puckett, L. J., T. K. Cowdery, P. B. McMahon, L. H. Tornes, and J. D. Stoner (2002), Using chemical, hydrologic, and age dating analysis to delineate redox processes and flow paths in the riparian zone of a glacial outwash aquifer-stream system, *Water Resour. Res.*, *38*(8), 1134, doi:10.1029/2001WR000396.

Spalding, R. F., and M. E. Exner (1993), Occurrence of nitrate in groundwater—A review, *J. Environ. Qual.*, *22*, 392–402.

Spruill, T. B. (2000), Statistical evaluation of effects of riparian buffers on nitrate and ground water quality, *J. Environ. Qual.*, *29*, 1523–1538.

Tesoriero, A. J., H. Liebscher, and S. E. Cox (2000), Mechanism and rate of denitrification in an agricultural watershed: Electron and mass balance along groundwater flow paths, *Water Resour. Res.*, *36*, 1545–1559.

Tesoriero, A. J., F. E. Löffler, and H. Liebscher (2001), The fate and origin of 1,2-dichloropropane in an unconfined shallow aquifer, *Environ. Sci. Technol.*, *35*, 455–461.

Tesoriero, A. J., T. B. Spruill, and J. L. Eimers (2004), Geochemistry of shallow ground water in coastal plain environments in the southeastern United States: Implications for aquifer susceptibility, *Appl. Geochem.*, *19*, 1471–1482.

U.S. Environmental Protection Agency and U.S. Dept. of Agriculture (1998), Clean water action plan: Restoring and protecting America's waters, report, 89 pp., Washington, D. C.

K. M. Farrell, Coastal Plain Office, North Carolina Geological Survey, 1620 Mailservice Center, Raleigh, NC 27699, USA. (kathleen.farrell@ncmail.net)

S. L. Harden, T. B. Spruill, and A. J. Tesoriero, U.S. Geological Survey, 3916 Sunset Ridge Road, Raleigh, NC 27607, USA. (slharden@usgs.gov; tspruill@usgs.gov; tesorier@usgs.gov)

H. E. Mew Jr., North Carolina Department of Environment and Natural Resources, 1636 Mailservice Center, Raleigh, NC 27699, USA. (ted.mew@ncmail.net)