Transport and Fate of Nitrate and Pesticides: Hydrogeology and Riparian Zone Processes

Larry J. Puckett* and W. Brian Hughes

ABSTRACT

There is continuing concern over potential impacts of widespread application of nutrients and pesticides on ground- and surface-water quality. Transport and fate of nitrate and pesticides were investigated in a shallow aquifer and adjacent stream, Cow Castle Creek, in Orangeburg County, South Carolina. Pesticide and pesticide degradate concentrations were detected in ground water with greatest frequency and largest concentrations directly beneath and downgradient from the corn (*Zea mays* L.) field where they were applied. In almost all samples in which they were detected, concentrations of pesticide degradates greatly exceeded those of parent compounds, and were still present in ground waters that were recharged during the previous 18 yr. The absence of both parent and degradate compounds in samples collected from deeper in the aquifer suggests that this persistence is limited or that the ground water had recharged before use of the pesticide. Concentrations of NO_3^- in ground water decreased with increasing depth and age, but denitrification was not a dominant controlling factor. Hydrologic and chemical data indicated that ground water discharges to the creek and chemical exchange takes place within the upper 0.7 m of the streambed. Ground water had its greatest influence on surface-water chemistry during low-flow periods, causing a decrease in concentrations of Cl^-, NO_3^-, pesticides, and pesticide degradates. Conversely, shallow subsurface drainage dominates stream chemistry during high-flow periods, increasing stream concentrations of Cl^-, NO_3^-, pesticides, and pesticide degradates. These results point out the importance of understanding the hydrogeologic setting when investigating transport and fate of contaminants in ground water and surface water.

W IDESPREAD USE of agricultural chemicals, particularly nitrate (NO_3^-) and various organic pesticides, has generated concern over their potential impacts on ground- and surface-water quality (Puckett, 1995; Barbash and Resek, 1996; Mueller and Helsel, 1996; Larson et al., 1997). United States Geological Survey (USGS) data (Barbara Ruddy, USGS, written communication, 2003) indicate that since 1945, the use of nitrogen as commercial fertilizer in the United States has increased more than 20-fold, and information on pesticide use suggests a similar pattern (Barbash and Resek, 1996). Under reducing conditions NO_3^- is converted to N_2 gas by denitrification, a process reviewed in detail by Korom (1992). Denitrification has been shown to occur within aquifers (e.g., Trudell et al., 1986; Postma et al., 1991; Puckett and Cowdery, 2002), and interest has focused

on the ability of riparian buffer zones to remove NO_3^- from ground water through denitrification and plant uptake (e.g., Haycock et al., 1993; Hill, 1996; Puckett et al., 2002).

Hill (1996) reviewed NO_3^- transformation and removal processes in riparian zones and concluded that previous research had failed to adequately consider hydrogeologic controls on biogeochemical processes. He also felt that most studies had been conducted in similar settings, making it difficult to extrapolate findings to other areas. Devito et al. (2000) concluded that "conceptual models that link riparian lithology to ground water NO_3^- dynamics are necessary to improve our ability to predict the effectiveness of riparian zones to remove NO_3^- in a range of landscapes." Puckett (2004) examined results of 13 riparian zone studies from around the United States and concluded that NO_3^- removal effectiveness may be limited by several hydrogeologic factors. These factors include (i) total denitrification in the upgradient aquifer; (ii) long residence times along ground-water flow paths allowing even slow reactions to completely remove NO_3^-; (iii) dilution of NO_3^-–enriched waters with older ground water containing low concentrations of NO_3^-; (iv) bypassing of riparian zones due to extensive use of drains and ditches; and (v) movement of ground water along deep flow paths below shallower, organic-rich reducing zones. In spite of some recent research, there is still inadequate information on hydrogeologic controls on NO_3^- transport through riparian zones in a wide enough range of settings to develop the type of conceptual model envisioned by Devito et al. (2000).

Studies of the transport and fate of pesticides in ground water have shown that biotransformation rates are much faster in the shallow soil zone than in either the deep unsaturated or saturated zones (Wehtje et al., 1983; McMahon et al., 1992; Vinther et al., 2001). Furthermore, a number of studies suggest that biotransformation rates may be limited by the lack of organic carbon and/or microbial populations, which generally have been shown to decrease with depth in aquifers (McMahon et al., 1992; Chapelle, 1993; Loague et al., 1994; Vinther et al., 2001). For at least some pesticides, such as atrazine, abiotic transformations may be more important than microbial processes, particularly under acidic conditions (Armstrong and Chesters, 1968; Accinelli et al., 2001).

Recent surveys of the occurrence and distribution of organic pesticides in ground waters (Kalkhoff et al., 1998; Burkart et al., 1999; Kolpin et al., 2001) and surface waters of the midwestern United States (Kalkhoff et

L.J. Puckett, U.S. Geological Survey, 413 National Center, Reston, VA 20192. W.B. Hughes, U.S. Geological Survey, 3039 Amwiler Road, Norcross, GA 30360. The use of trade names in this paper is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey. Received 28 Mar. 2005. *Corresponding author (lpuckett@usgs.gov).

Abbreviations: CFC, chlorofluorocarbon; DOC, dissolved organic carbon; ESA, ethane-sulfonic acid; MCL, maximum contaminant level; OA, oxanilic acid.

al., 1998, 2003) have revealed that degradates of the most commonly used triazine and chloroacetanilide herbicides often persisted in greater frequency and concentration than the parent compounds. Kolpin et al. (1995) provided direct information on ground-water age and pesticide detection frequency. However, their results were limited to a pre- and post-1953 classification based on tritium concentrations. More recently, Spurlock et al. (2000) showed that selected pesticides had persisted in ground water dated to have recharged from 2 to 33 yr before the time of sample collection. Because they sampled domestic wells with variable-length screened intervals, it is difficult to know exactly when the pesticides reached the wells. Wilson et al. (1983) and McMahon et al. (1992) suggested that slow ground-water flow rates may result in significant degradation of organic contaminants, but there is little information as to how long these compounds may actually persist in the natural environment (Kalkhoff et al., 2003). Consequently, little is known about the long-term transport and fate of many pesticides.

In the study reported here we examined the transport and fate of NO_3^-, and the persistence of selected pesticides and their degradates in a surficial aquifer and hydraulically connected stream. One specific objective was to determine the role of the hydrogeologic setting in the transport and fate of these contaminants. Our hypotheses were that due to long travel times in the ground-water system (i) NO_3^- would be removed because of denitrification in the shallow aquifer and the riparian zone, and (ii) pesticides and selected pesticide degradates would be mineralized to undetectable levels before they reached the adjacent creek.

STUDY AREA

The study area is located in Orangeburg County, South Carolina (Fig. 1), in an area of a series of low relief, eroded escarpments with low-gradient streams and swamps. The surficial water-table aquifer is composed of Pleistocene-age, coastal terrace deposits and Holocene-age floodplain deposits (McCartan et al., 1984) typically up to 12 m thick. The surficial aquifer is separated from the Floridan aquifer and other underlying aquifers by a confining unit, comprising a variety of materials, with estimated hydraulic conductivities ranging from 3×10^{-5} to 2.8×10^{-4} m d^{-1} (Aucott, 1996). The ground-water system is stratified, comprising a series of shallow, intermediate, and regional flow systems (Aucott, 1996); much of the water moves through the shallow flow system and discharges to nearby streams.

The study site is part of a dairy farm, adjacent to Cow Castle Creek (Fig. 1), and consists of wooded areas and several fields. Near-surface geology at the study site is characterized by interbedded sand, clay, and calcareous deposits (Fig. 2). The deepest unit encountered at the site is a thin and discontinuous sandy limestone, described by McCartan et al. (1984). The floodplain is underlain by coarse to very coarse sand interbedded with shell beds and some organic horizons; upland areas are underlain by sand, silty sand, and clayey sand. Soils at the study site were classified by DeFrancesco (1988) as Goldsboro (fine-loamy, siliceous, subactive, thermic Aquic Paleudults), Noboco (fine-loamy, siliceous, subactive, thermic Oxyaquic Paleudults), and Rains (fine-loamy, siliceous, semiactive, thermic Typic Paleaquults). Drain tiles and ditches are used to lower the seasonally high water table in agricultural areas. Pine (*Pinus* spp.) trees are grown in areas with poorly drained soils that are not tiled.

Annual average temperature is 17.5°C, and precipitation is approximately 1200 mm yr^{-1} (Owensby and Ezell, 1992). Soil permeability is relatively high at 7.4 cm h^{-1} (Wolock, 1997), and overland flow has been estimated to account for only 3.4 to 4.3% of total streamflow (Wolock, 2003a, 2003b). Consequently, most water moving to Cow Castle Creek reaches it either as shallow subsurface drainage through tile drains and ditches or as discharging ground water. In the vicinity of the study site, Cow Castle Creek has a 200-m-wide floodplain with a deciduous riparian forest. The creek has been straightened and channelized throughout the study area. The stream channel is about 6 m wide and is incised 2 m below the surrounding floodplain surface.

Within the 62-km² Cow Castle Creek watershed above the USGS streamgaging station, nitrogen and phosphorus inputs as fertilizer, manure, and atmospheric deposition during 1997 totaled 185 Mg N and 36 Mg P (Barbara Ruddy, USGS, written communication, 2003). Fertilizer is applied to the crop areas of the study site in the form of animal manure and commercial chemical fertilizer. Farm records indicate that in 1996, nitrogen was applied as liquid chemical fertilizer to the hay field at a rate of 220 kg ha^{-1}. Manure applied to the corn field in 1996 provided 340 kg ha^{-1} of nitrogen and 310 kg ha^{-1} phosphorus.

Pesticide use in the Cow Castle Creek watershed during 1997 consisted of 600 kg atrazine, 380 kg metolachlor, 230 kg alachlor, 250 kg chlorpyrifos, and 10 kg simazine (Naomi Nakagaki, USGS, written communication, 2003). Pesticides used at the study site in 1996, according to farm records, included the herbicides ametryn, atrazine, metolachlor, and 2,4-D, which were applied to the corn field at rates of 1.3, 0.7, 0.9, and 0.6 kg ha^{-1} of active ingredient, respectively. The herbicide 2,4-D was applied to the hay field at a rate of 0.8 kg ha^{-1} of active ingredient; no insecticides were applied.

METHODS

Water Sample Collection

In the summer of 1996, 15 shallow water-table wells were installed to determine the predominant direction of ground-water flow and seasonal fluctuations in the water table. These wells were constructed with 5-cm-diameter, threaded polyvinyl chloride (PVC) pipe with 1.5-m-long slotted PVC screens. Information collected during well installation and subsequent monitoring of water levels was used to develop a water-table map and plan the installation of the second network of wells.

Seven multiport wells with three to five sampling ports each, comprising 27 sampling ports, were installed in a transect parallel to the predominant direction of ground-water flow (Fig. 1 and 2). These wells were constructed following a procedure outlined by Delin and Landon (1996). Well sites were labeled numerically (1 through 7) beginning in Cow Castle Creek and proceeding in increasing order upgradient. Individual screened intervals were labeled using Roman numerals (I through V) beginning at the shallowest interval and increasing with depth (Fig. 2).

At multiport Well Sites 4 through 7, 5-cm-diameter PVC wells with a 1.5-m-long screen were also installed. Construction of these wells was similar to the water-table wells described above. These wells generally were completed 1 to 3 m below the deepest multiport sampler at depths where it was difficult to install the multiport wells. Two other wells of this type were installed at multiport Well Sites 2 and 3 to serve as water-level reference wells. Water levels in the 5-cm-diameter PVC wells were measured using an electric tape whereas water levels in the multiport wells were measured using a portable manometer (Winter et al., 1988).
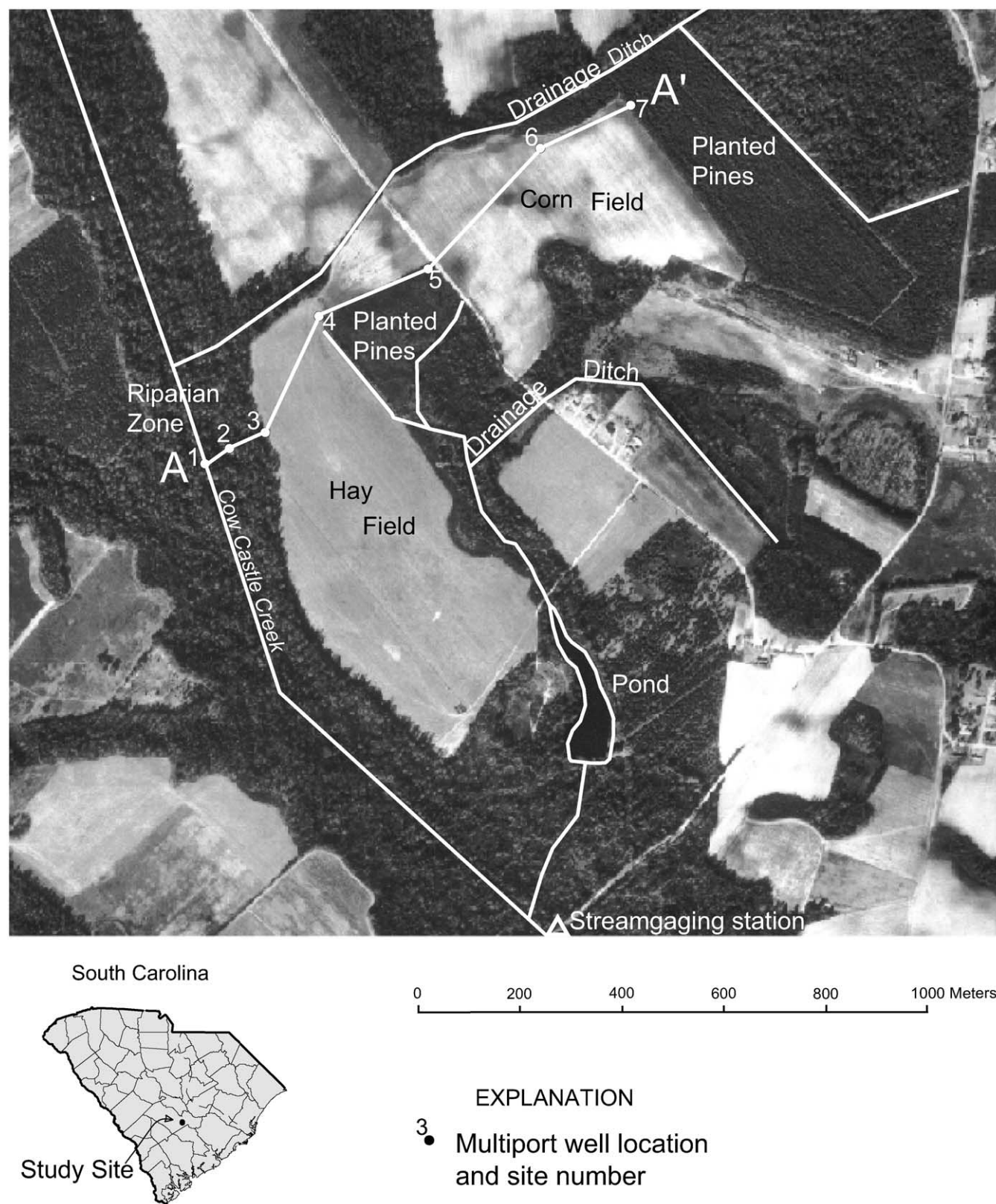
Fig. 1. Location map and aerial photograph (recorded 22 Feb. 1995) of the study site showing locations of important landscape features and the study transect A–A′. The study transect is shown in cross-section view in Fig. 2.
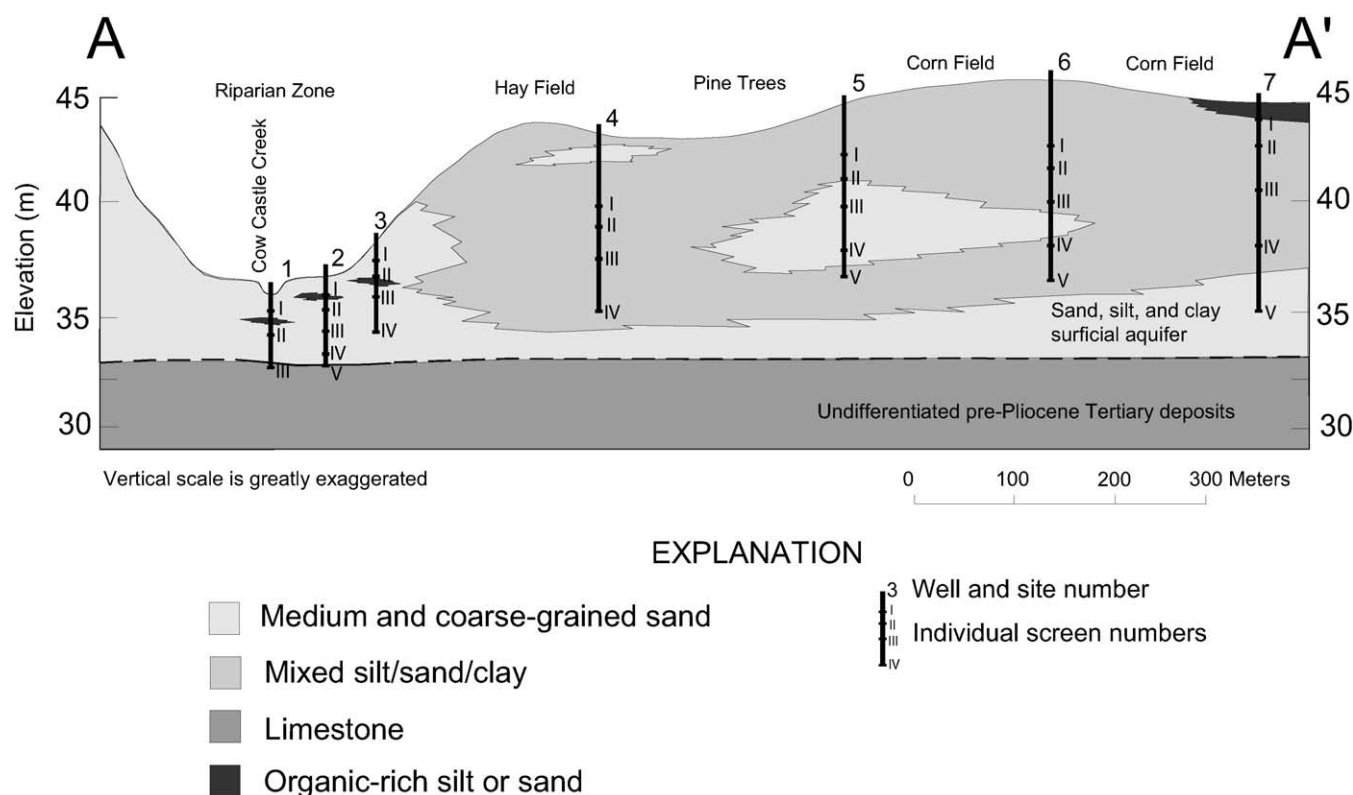
Fig. 2. Hydrogeologic units and sample well locations along the study transect A–A′ in Fig. 1.

Water samples were collected from Cow Castle Creek approximately monthly from October 1995 through September 1998, at a streamgaging station about 1 km downstream from the intersection of the well transect and the creek (Fig. 1); during February 1996 through October 1996, samples were collected weekly. Surface-water samples were collected in multiple vertical sections using a USGS DH-81 depth-integrating sampler with a 7.9-mm Teflon nozzle and a 3-L Teflon bottle. Water levels at the streamgaging station were recorded hourly and converted to discharge based on a calibrated rating curve. On 3 Dec. 1998, flow was measured with a current meter (Buchanan and Somers, 1969) at five sites within a 168-m-long reach bracketing the multiport well transect, to test for changes in discharge that may have occurred as a result of ground-water discharge within the reach.

Ground-water samples were collected from the multiport samplers in November 1997, April 1998, and August 1998. The large-diameter wells were sampled using standard protocols (Koterba et al., 1995). The multiport wells were sampled using a peristaltic pump. Teflon tubing was attached to the stainless steel tubing and a 30.5-cm section of Viton tubing was used in the peristaltic pump head. The Teflon tubing was cleaned according to standard protocols (Koterba et al., 1995) and the Viton tubing was discarded after each multiport was sampled to prevent cross contamination. Before sampling, wells were purged of at least three well volumes with pumping continuing until field parameters, including dissolved O_2, specific conductance, pH, and temperature, stabilized (Koterba et al., 1995).

Sediment Analyses

Sediment samples collected from various distinctive sediment horizons from Sites 2 and 6 (Fig. 2) were sorted into bulk and <1-μm-size fractions and analyzed for mineralogy by X-ray diffraction. Samples for these analyses were selected to provide a description of mineralogy at several points across the thickness of the aquifer at these locations. A separate aliquot of each sample was analyzed for total carbon (C) using a Carlo Erba elemental analyzer (CE Elantach, Lakewood, NJ). A duplicate sample was exposed to hydrochloric acid fumes to remove inorganic C, after which organic C content was measured; inorganic C was calculated as the difference between total and organic C (Hedges and Stern, 1984).

Water Sample Analysis

Water samples were filtered through 0.45-μm nitrocellulose filters (a silver filter was used for dissolved organic carbon [DOC] samples). Temperature, pH, conductance, and alkalinity were measured in the field. Samples were analyzed by the USGS National Water Quality Laboratory (NWQL) in Denver, CO, for cations, anions, nutrients, pesticides, and organic carbon; samples collected for cation analyses were preserved with nitric acid. Cations and silica were analyzed by inductively coupled plasma spectroscopy, anions by ion chromatography, nutrients by colorimetric methods, and DOC by persulfate oxidation and infrared spectrometry (Fishman and Friedman, 1989; Fishman, 1993; Wershaw et al., 1987).

Samples for analyses of pesticides were filtered through 0.7-μm baked-glass fiber filters into two amber, baked-glass bottles. One bottle was shipped to the NWQL and the other to the USGS Organic Research Laboratory (ORL) in Lawrence, KS (Table 1). The NWQL sample was analyzed for 88 organic compounds (Reuber, 2001) including acetochlor, alachlor, metolachlor, atrazine, deethylatrazine, simazine, prometon, tebuthiuron, cyanazine, and chlorpyrifos by gas chromatography–mass spectrometry (GC–MS) with selected ion monitoring after extraction on C-18 solid-phase cartridges; reporting limits for these compounds ranged from 0.001 to 0.018 μg L^{-1}. The ORL sample was analyzed for 23 compounds

Table 1. Herbicides and herbicide degradation products analyzed by the Organic Research Laboratory for this study.

Common name	Chemical name	Use or origin	Method†
Acetochlor	2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide	herbicide	GC–MS
Acetochlor ethane-sulfonic acid (ESA)	2-[(2-ethyl-6-methylphenyl)(ethoxymethyl)amino]-2-oxoethane sulfonic acid	herbicide degradate (acetochlor)	HPLC
Acetochlor oxanilic acid (OA)	2-[(2-ethyl-6-methylphenyl)(ethoxymethyl)amino]-2-oxoacetic acid	herbicide degradate (acetochlor)	HPLC
Alachlor	2-chloro-2′-6′-diethyl-*N*-(methoxymethyl)-acetanilide	herbicide	GC–MS
Alachlor ESA	2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoethane sulfonic acid	herbicide degradate (alachlor)	HPLC
Alachlor OA	2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoacetic acid	herbicide degradate (alachlor)	HPLC
Ametryn	2-(ethylamino)-4-isopropylamino-6-methyl-thio-*s*-triazine	herbicide	GC–MS
Atrazine	2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine	herbicide	GC–MS
Deethylatrazine (DEA)	2-amino-4-chloro-6-(isopropylamino)-*s*-triazine	herbicide degradate (atrazine, propazine)	GC–MS
Deisopropylatrazine (DIA)	2-amino-4-chloro-6-(ethylamino)-*s*-triazine	herbicide degradate (atrazine, cyanazine, simazine)	GC–MS
Hydroxyatrazine (HA)	2-hydroxy-4-(ethylamino)-6-(isopropylamino)-*s*-triazine	herbicide degradate (atrazine)	HPLC
Cyanazine	2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methyl propionitrile	herbicide	GC–MS
Cyanazine amide	2-chloro-4-(1-carbamoyl-1-methyl-ethylamino)-6-ethylamino-*s*-triazine	herbicide degradate (cyanazine)	GC–MS
Metolachlor	2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methyl ethyl) acetamide	herbicide	GC–MS
Metolachlor ESA	2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoethanesulfonic acid	herbicide degradate (metolachlor)	HPLC
Metolachlor OA	2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoacetic acid	herbicide degradate (metolachlor)	HPLC
Metribuzin	4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one	herbicide	GC–MS
Prometon	2,4-bis(isopropylamino)-6-methyoxy-*s*-triazine	herbicide	GC–MS
Prometryn	2,4-bis(isopropylamino)-6-(methylthio)-*s*-triazine	herbicide	GC–MS
Propachlor	2-chloro-*N*-isopropylacetanilide	herbicide	GC–MS
Propazine	2-chloro-4,6-bis(isopropylamino)-*s*-triazine	herbicide	GC–MS
Simazine	2-chloro-4,6-bis(ethylamino)-*s*-triazine	herbicide	GC–MS
Terbutryn	2-tert-butylamino-4-ethylamino-6-methylthio-*s*-triazine	herbicide	GC–MS

† GC–MS, gas chromatography–mass spectrometry; HPLC, high-performance liquid chromotography.

(Kolpin et al., 1998) including acetochlor, alachlor, meto-lachlor, and their oxanilic acid (OA) and ethane-sulfonic acid (ESA) degradates, as well as atrazine and simazine. Reporting limits for compounds analyzed by the ORL were about an order-of-magnitude greater than those at the NWQL, and ranged from 0.05 μg L^{-1} for parent compounds to 0.2 μg L^{-1} for degradates. Because of differences in the reporting limits, results are reported separately. The latter analytes were ana-lyzed by high-performance liquid chromatography (HPLC) with diode-array detection and quantitation after extraction on C-18 solid-phase cartridges (Thurman et al., 1990; Meyer et al., 1993). Analyte groups measured in ground- and surface-water samples collected during various time periods of the study are presented in Table 2.

Dissolved Gases

Dissolved N_2 and Ar in ground-water samples collected in November 1997 were analyzed by gas chromatography after extraction in headspaces of glass samplers (Busenberg et al., 1998). Results were corrected for solubility in sample water

at laboratory temperatures and have an error of ± 2 to 4%. Under most conditions, the N_2 gas produced by denitrification will remain in solution until the ground water discharges to a surface-water body and equilibrates with the atmosphere (Heaton and Vogel, 1981; Blicher-Mathiesen et al., 1998). Therefore, concentrations of N_2 and Ar gases dissolved in water were used to estimate the amount of nitrogen resulting from denitrification (Heaton and Vogel, 1981; Vogel et al., 1981; Puckett et al., 2002).

Chlorofluorocarbon Age Dating

Samples for analyses of the chlorofluorocarbons $CFCl_3$ (CFC-11), CF_2Cl_2 (CFC-12), and $C_2F_3Cl_3$ (CFC-113) were col-lected in November 1997 using a stainless steel sampling appa-ratus under an ultra-pure nitrogen atmosphere and were flame sealed in 62-cc borosilicate glass ampoules (Busenberg and Plummer, 1992). Samples were analyzed by electron-capture gas chromatography with a detection limit of 0.3 pg kg^{-1} for CFC-11 and CFC-12, and 1.0 pg kg^{-1} for CFC-113 (Busenberg and Plummer, 1992). Sample ages were assigned on the basis

Table 2. Analytes determined in ground- and surface-water samples collected at various time periods during the study.

Sample type	Time period	Cations	Anions	Nutrients	Organic carbon	Pesticides† NWQL	Pesticides† ORL
Surface water	October 1995–September 1998, monthly	X	X	X	X	NA‡	NA
	February–October 1996, weekly	X	X	X	X	X	NA
	April 1997–March 1998, monthly	X	X	X	X	NA	X
Ground water	November 1997	X	X	X	X	X	X
	April 1998	X	X	X	X	X	NA
	August 1998	X	X	X	X	NA	NA

† Pesticide samples labeled NWQL were analyzed at the USGS National Water Quality Laboratory in Denver, CO, and those labeled ORL were analyzed at the USGS Organic Research Laboratory in Lawrence, KS.
‡ Not analyzed for the respective analytes.

of a comparison of CFC equilibrium partial pressures, corrected for recharge temperature, with a chronology of atmospheric partial pressures (Busenberg and Plummer, 1992).

RESULTS

Surface Water Hydrology

The median discharge of Cow Castle Creek during the October 1995 through September 1998 sampling period was 0.21 m^3 s^{-1}, and ranged from 0.003 to 10.7 m^3 s^{-1} (Table 3). Comparisons of discharge at five points on the creek during December 1998 indicated that discharge increased by as much as 22% through the 85-m-long section of the reach upstream from the transect site and increased by 13.4% overall. Although discharge decreased somewhat through the 68-m-long section downstream from the well transect site, these changes were within measurement error. This increase in flow during the low-flow period with no tile drain discharges would be expected for a stream that receives ground-water discharge. Therefore, overall ground-water discharge within the 168-m-long reach was about 2 $\times$ 10^{-6} m^3 s^{-1} m^{-1}.

Surface Water Chemistry

The analytes having the largest concentrations in stream water (Table 3) were Ca^{2+} and HCO_3^-. Concentrations of these two analytes, along with pH, were at a maximum during the period of lowest stream flow, reflecting the carbonate content of the deeper sediments underlying the riparian zone and the increased importance of ground-water discharge as a major component of stream baseflow at that time. Conversely, Ca^{2+}, HCO_3^-, and SiO_2 were at their lowest concentrations during periods of high flow, due to dilution of the discharging ground water by shallow subsurface drainage from tile drain discharges. Concentrations of DOC, Cl^-, and O_2, which were lower in ground-water samples at depth beneath the stream than in samples from the stream, were at a minimum during the period of lowest

stream flow, again due to the dominant influence of ground-water discharge. Concentrations of Cl^-, NO_3^-, and O_2 in stream water were greatest during periods of high flow, due to shallow subsurface drainage from agricultural fields. Given the widespread agricultural land use in the watershed, the range in NO_3^- concentration (33.6–279 μmol L^{-1}) seemed relatively small values and were only about one-third the maximum contaminant level (MCL) set by the USEPA (2005). However, concentrations were still as great as 6.5 times the 42.8 μmol L^{-1} considered background (Mueller and Helsel, 1996). Concentrations of most other inorganic analytes either varied less than about 10% from the 3-yr median or were negligible.

Among the 88 pesticides analyzed in the 39 surface-water samples collected during February through October 1996, 23 were detected above the reporting limit, but only 7 of the compounds were present in more than 25% of samples (Table 4). Metolachlor was present in all 39 samples at concentrations ranging from just above the reporting limit to 1.1 μg L^{-1}. The results for simazine and tebuthiuron are interesting given their low agricultural use (10 kg and 0 kg, respectively, in 1997) within the watershed. These results probably indicate nonagricultural sources because simazine also is used in aquatic weed control and on turfgrass, and tebuthiuron is used on roadways and rights of way (Hoffman et al., 2000).

The median concentrations of chlorpyrifos, alachlor, and deethylatrazine were near their respective reporting limits, and the maximum concentrations were only about an order-of-magnitude greater than their medians. The median concentration of deethylatrazine was only slightly greater than its reporting limit, and its maximum was only about 3% of the maximum atrazine concentration, reflecting insufficient residence time in the soil for the biologically mediated degradation process responsible for creating deethylatrazine (McMahon et al., 1992; Bayless, 2001; Kalkhoff et al., 2003). Furthermore, maximum concentrations of both atrazine and deethylatrazine occurred during periods of high flow in

Table 3. Stream discharge and concentrations of selected constituents in 78 samples collected from Cow Castle Creek, October 1995 through September 1998.†

Constituent	Median value for the period					
	January–March	April–June	July–September	October–December	Three years	Three-year range
pH	6.5	6.6	7.0	6.6	6.7	5.4–7.4
O_2	303.1	256.3	237.5	260.9	259.4	190.6–381.3
HCO_3^-	262.2	368.8	671.9	516.3	467.1	65.6–950.6
Ca^{2+}	194.6	247.0	374.3	336.8	274.5	69.9–449.1
Mg^{2+}	82.3	82.3	74.0	84.3	80.2	41.1–127.5
Na^+	165.3	156.6	156.6	158.8	160.9	73.9–213.2
K^+	33.2	46.0	53.7	58.8	46.0	2.55–104.8
SiO_2	108.2	133.9	136.4	143.1	131.5	56.6–158.1
Fe^{2+}	3.04	2.42	1.65	1.60	2.06	0.555–7.16
Mn^{2+}	0.36	0.31	0.22	0.22	0.30	0.10–0.87
Cl^-	253.9	244.0	208.8	231.3	234.4	98.7–338.5
SO_4^{2-}	39.6	43.8	41.7	50.0	43.2	23.9–104.2
PO_4^{3-}	0.32	0.65	0.97	0.61	0.65	0.32–1.81
Total P	0.97	1.21	1.29	1.03	1.13	0.32–7.55
NO_3^-	128.6	128.6	85.7	121.4	121.4	33.6–278.6
NH_4^+	1.43	3.43	2.14	1.43	2.14	1.07–6.43
DOC	341.7	341.7	233.3	345.8	304.2	166.7–916.7
Discharge	0.59	0.21	0.03	0.19	0.21	0.003–10.7

† All concentrations are μmol L^{-1} with the exception of pH, which is in standard units; dissolved organic carbon (DOC) is reported as μmol L^{-1} C; discharge units are m^3 s^{-1} as measured at the time of sample collection.

Table 4. Concentrations of selected pesticides detected in at least 25% of 39 surface-water samples collected from Cow Castle Creek during February 1996 through October 1996, and on 4 Feb. 1998.

Pesticide	Detection frequency ($n = 39$)	Concentration		
		Minimum	Median	Maximum
		— μg L^{-1} —		
Metolachlor	39	0.004	0.028	1.1
Atrazine	37	<0.001†	0.010	1.1
Simazine	35	<0.005	0.075	1.6
Alachlor	29	<0.002	0.010	0.045
Deethylatrazine	26	<0.002	0.003	0.033
Chlorpyrifos	25	<0.004	0.006	0.057
Tebuthiuron	24	<0.01	0.012	0.03

† Values reported as "<" were less than the reporting limit.

the spring following pesticide applications. Similar patterns were observed for alachlor, chlorpyrifos, metolachlor, simazine, and tebuthiuron, suggesting rapid losses following spring applications.

Among the 12 monthly water samples collected from April 1997 through March 1998 and analyzed for 23 pesticides including atrazine and its degradates, and acetanilide parent and degradate compounds, only five compounds were detected at concentrations above the reporting limit (Table 5). It is important to remember that the reporting limits based on the HPLC method used for these samples was about an order-of-magnitude greater than for the samples analyzed by GC–MS during 1996, resulting in a lower frequency of detection. Again metolachlor was the most frequently detected pesticide, occurring in eight samples, followed by metolachlor ESA in five samples; metolachlor OA was detected in only one sample. The ratio of metolachlor ESA to metolachlor was 0.25 in May 1997 after application, increasing to 5.4 in July, 5.3 in October, 7.5 in November, and 6.3 in December, due to degradation of the parent compound in the months following application; this pattern also was reported by Phillips et al. (1999). Alachlor ESA was detected in three samples, but at a maximum concentration only slightly greater than its reporting limit. Atrazine was detected twice, in April and May 1997, but no atrazine degradates were detected. At no time during the study were any pesticides detected above the USEPA (2005) established MCLs, although atrazine and simazine concentrations in surface water were the largest detected during the study at about one-third their MCLs.

Ground Water Hydrology

The water-table elevation and piezometric heads generally were at their maximum during the winter and spring, 1997–1998, and then decreased to their lowest levels during the late summer and fall, 1998. The depth to water below land surface was greatest at the upgradient end of the flow system in the corn field and was at or above land surface at the downgradient end of the flow system in the riparian forest. Overbank flow from Cow Castle Creek during December 1997 contributed to the water level rising above land surface in the riparian zone. Piezometric heads in the streambed were consistently greater relative to surface-water stage. In addition, there was a pattern of increasing heads with depth below the streambed, a condition commonly associated with ground-water discharge zones (Winter, 1976). Water-table elevations and ground-water flowlines shown in Fig. 3 provide a representation of the flow system along Section A–A′ at the study site in November 1997. At the time, there was a ground-water mound near Site 6, which resulted in potential movement of ground water from Site 6 toward Site 7. This ground-water mound and flow potential persisted through the April 1998 sampling, but by August 1998 the mound had dissipated and ground-water flow was all toward Cow Castle Creek. These patterns in the water table and heads are consistent with the stratified flow systems common to the study area, as described by Aucott (1996), where water enters at topographic highs and along flow paths and travels through the shallow flow system, discharging to nearby streams.

Sediment Chemistry

The bulk fraction of the shallow sediment in the riparian zone (Site 2 in Fig. 2) was predominantly quartz sand with a <1-μm clay fraction comprising kaolinite, chlorite, smectite, and illite. At 0.97% organic carbon, this sample contained the greatest organic carbon fraction among the samples analyzed; organic carbon con-

Table 5. Concentrations of selected pesticides and degradates detected in 12 monthly surface-water samples collected from Cow Castle Creek during April 1997 through March 1998.

Pesticide†	Detection frequency ($n = 12$)	Concentration		
		Minimum	Median	Maximum
		— μg L^{-1} —		
Metolachlor	8	<0.05‡	0.05	0.93
Metolachlor ESA	5	<0.2	<0.2	0.4
Metolachlor OA	1	<0.2	<0.2	0.3
Atrazine	2	<0.05	<0.05	0.14
Alachlor ESA	3	<0.2	<0.2	0.3

† OA = oxanilic acid degradate; ESA = ethane-sulfonic acid degradate.
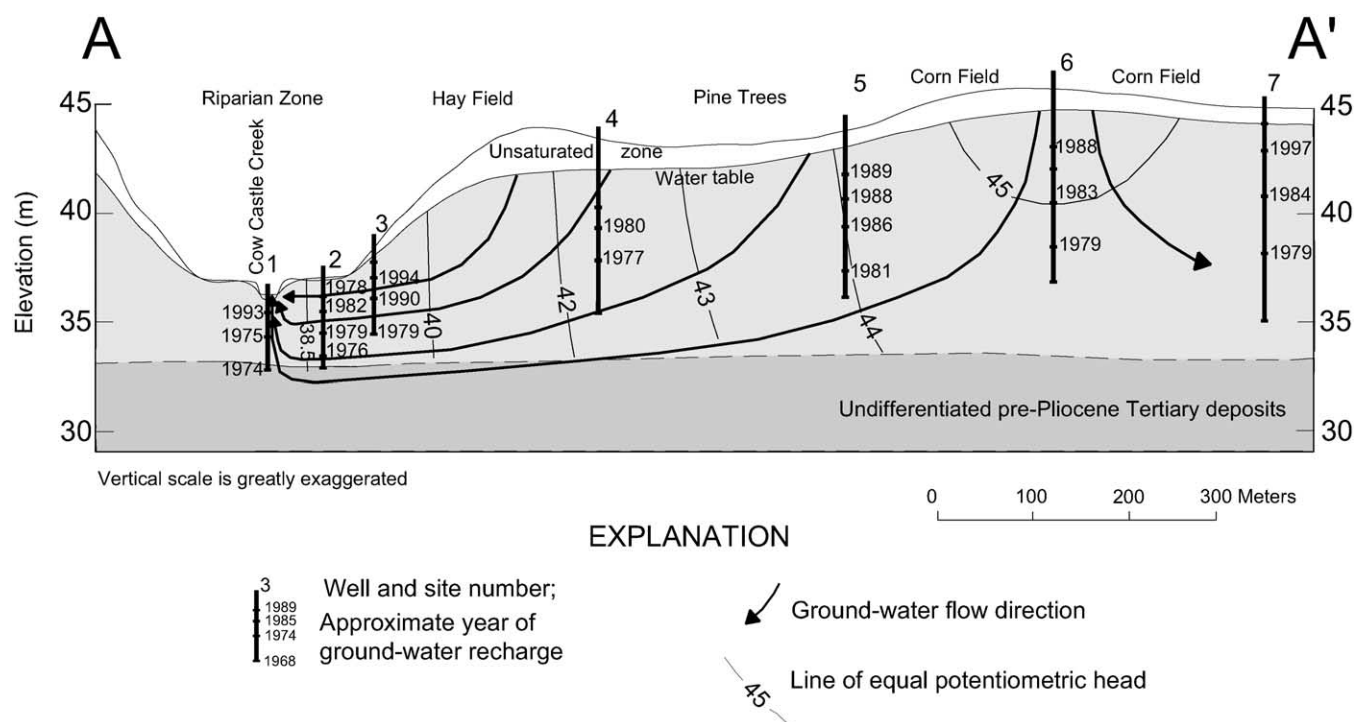‡ Values reported as "<" were less than the reporting limit.

Fig. 3. Water-table elevations, ground-water flow directions, and approximate year of ground-water recharge in the surficial aquifer, November 1997.

tent declined with depth to 0.39 to 0.29%. Deeper in the sediment at Site 2, the bulk fraction contained plagioclase in addition to the quartz sand, and in the deepest sample, calcite, dolomite, and potassium feldspar were detected along with the quartz and plagioclase. The <1-μm clay fraction in these two deeper samples was virtually the same as that in the shallow sample.

In the corn field (Site 6 in Fig. 2), the bulk fraction near the surface was fine to medium quartz sand with calcite and dolomite. Calcite and dolomite were not present at the two greater depths, suggesting they may have been of agricultural origins. However, chlorite was present. The <1-μm clay fractions at all three depths at Site 6 were similar, comprising a mixture of kaolinite, smectite, illite, and chlorite. Organic carbon content at Site 6 was greatest near the surface with a concentration of 0.21%, and then decreased to 0.02 to 0.04% with depth.

Dissolved Gases

Concentrations of Ar ranged from 13.1 to 17.2 μmol L^{-1} with a median of 15.5 μmol L^{-1} (Table 6). The N$_2$ concentrations ranged from 464.5 to 992.1 μmol L^{-1} with a median of 637.2 μmol L^{-1} (Table 6). Excess N$_2$, calculated as the difference between the measured N$_2$ and the air–water equilibrium plus the contribution from excess air, ranged from 0 to 355.3 μmol L^{-1} with a median of 46.4 μmol L^{-1} (Table 6). The distribution of excess N$_2$ was variable but the largest concentrations were found in samples from beneath the riparian zone. A linear regression fit through the N$_2$ and Ar data indicated a recharge temperature of 17.3°C; near the 17.5°C average annual temperature.

Dissolved oxygen concentrations ranged from 3.1 to 297 μmol L^{-1} with a median of 168 μmol L^{-1}. Given the calculated equilibrium value of 297 μmol L^{-1} at 17.5°C, most samples, although oxic, showed signs of some oxygen depletion, as a result of oxidation of or-

Table 6. Concentrations Ar, N$_2$, NO$_3^-$, excess N$_2$, reconstructed NO$_3^-$ (ΣNO$_3^-$), and chlorofluorocarbon (CFC)-assigned recharge year of ground-water samples collected in November 1997.†

Site	Ar	N$_2$	Excess N$_2$	NO$_3^-$	ΣNO$_3^-$	Assigned CFC year
			μmol L^{-1}			
1-I	15.8	602.4	2.5	321.4	326.4	1993
1-II	16.1	670.0	59.7	200.0	319.4	1975
1-III	15.7	667.2	68.3	200.0	336.6	1974
2-I	16.1	701.8	90.5	28.6	209.6	1978
2-II	15.5	654.3	64.4	171.4	300.2	1982
2-III	15.9	747.8	145.0	228.6	518.6	1979
2-IV	15.9	653.7	47.9	178.6	274.4	1976
3-II	15.1	591.8	15.9	885.7	917.5	1994
3-III	15.6	628.1	33.3	1014	1081	1990
3-IV	16.0	645.3	38.2	242.9	319.3	1979
4-II	15.6	658.6	65.7	171.4	302.8	1980
4-III	15.8	690.5	89.2	<3.6	178.4	1977
5-I	13.1	464.5	0	1157	1157	1989
5-II	15.5	635.3	44.9	1407	1496	1988
5-III	15.5	639.1	50.2	1100	1200	1986
5-IV	14.9	611.6	40.3	700.0	780.6	1981
6-I	15.2	608.6	26.9	1264	1318	1988
6-III	NA	NA	NA	1257	1257	1983
6-IV	14.6	583.0	24.4	364.3	413.1	1979
7-I	13.6	513.3	0	371.4	371.4	NA
7-II	13.7	525.9	0	1521	1521	1997
7-III	NA	NA	NA	335.7	335.7	1984
7-IV	14.3	617.6	67.9	50.0	185.8	1979
7-V	15.5	622.0	33.0	135.7	201.7	NA

† Values reported as "<" were less than the reporting limit; values of excess N$_2$ reported as "0" were calculated to have no excess N$_2$; "NA" were not sampled.

ganic carbon. All of the shallow samples from the riparian zone, as well as all of the samples at Site 4, were suboxic or near suboxic (<64 μmol L^{-1}).

Chlorofluorocarbon Age Dates

Chlorofluorocarbon-based ages of ground water ranged from near modern in the shallow piezometer at Site 1 to 23 yr in the deepest sampling port at Site 1 (Table 6). As might be expected, ground-water ages increased with depth and distance along the flow system (Fig. 3), and there was a strong correlation between age and depth ($r = 0.92$) for the samples in the recharge zone. Several age dates were older than expected based on their depth and position in the flow system. Specifically, the shallowest sample from Site 2 was 4 yr older than the one immediately below it. Here, ground water must pass through the chemically reducing, organic-carbon-rich sediments of the riparian zone, resulting in sorption and/or biodegradation of CFCs, and consequently older apparent age dates. Samples from Site 4 appear to have been similarly affected due to organic horizons in that area as well. The nine age dates for the samples from Site 1-I in the streambed (0.7 m) ranged from 1990 to 1997, with a median of 1993, due to varying degrees of exchange and mixing with the overlying surface water.

We used the exponential age gradient equation presented by Vogel (1967) to estimate recharge rate:

$$A = \left(Z\frac{n}{r}\right)\ln\left(\frac{Z}{Z-z}\right) \qquad [1]$$

where A is age in yr, Z is aquifer thickness (m), z is depth below the water table (m), n is effective porosity, and r is average long-term recharge rate (m yr^{-1}). By substituting various values for initial literature values of porosity and recharge rate for each sample port, we arrived at an effective porosity of 0.4 and an average long-term recharge rate of 0.143 m yr^{-1} in the recharge zone.

Ground Water Chemistry

There were distinct differences in the chemistry of ground water along the study transect, with the riparian zone samples being dominated by Ca^{2+}, HCO_3^-, and in some cases NO_3^-, whereas the upland samples were dominated by Na^+, Cl^-, and NO_3^-. Sodium and Cl^- concentrations were greatest under and immediately downgradient of the fertilized areas. Both Na^+ and Cl^- commonly occur as a contaminant in fertilizer as NaCl and as KCl, and both are a common contaminant associated with agricultural areas (Anderson, 1993; Puckett et al., 1999). Dissolved organic carbon concentrations were highly variable, probably reflecting mineralization of organic C in the sediments, which itself was highly variable due to the depositional history of the sediments.

Probably the greatest differences were in pH, which ranged from 3.8 to 5.4 with a median of 4.4 in the upland samples, and 5.0 to 8.0 with a median of 6.6 in the riparian zone samples. These patterns in pH can be easily attributed to the nitrification of NH_4^+ in fertilizer with the subsequent production of H^+ in the cultivated upland. Because of this nitrification, there was almost

total loss of HCO_3^- to neutralize the resulting H^+. In addition, NH_4^+ concentrations were negligible, with a median of 1.4 μmol L^{-1} in the riparian zone and 2.5 μmol L^{-1} in the upland areas receiving fertilizer. On the other hand, NO_3^- concentrations generally were greatest in the shallow upland samples where fertilizer was applied and in a number of samples exceeded the USEPA (2005) established MCL by as much as 2.5 times.

The initial or reconstructed concentrations of NO_3^- (ΣNO_3^-), before denitrification, calculated as (Table 6, Fig. 4):

$$\Sigma NO_3^- = [NO_3^-] + 2[\text{excess } N_2] \qquad [2]$$

are similar to the results for measured NO_3^-, with concentrations decreasing with depth below the fertilized areas and in the riparian zone. In a few cases the reconstructed concentrations indicate that NO_3^- concentrations in the past were somewhat greater than might have initially been assumed on the basis of measured NO_3^- alone, particularly at Site 2-III. Given the calculated recharge rate of 0.143 m yr^{-1}, and the available N-application rate information for the corn field of 340 kg N ha^{-1} in 1996, we estimate that only about 10% of the N applied would be required to reach the water table to account for the maximum ground-water NO_3^- concentration of 2021 μmol L^{-1}. Smaller reconstructed ground-water NO_3^- concentrations may be attributed to larger recharge rates, smaller N-application rates, or a combination of the two. It is particularly noteworthy that the large decreases in NO_3^- in the shallow samples between Sites 3 and 2 were only partly accounted for in the excess N_2 data and therefore the reconstructed NO_3^- concentrations. This discrepancy arises because the decreases in NO_3^- concentrations were due to denitrification, plant uptake, and mixing with low NO_3^- waters that recharged in the riparian zone.

Concentrations of NO_3^- in ground water at 0.7 m beneath Cow Castle Creek (Table 7) at the time of sampling in November 1997 were similar to that measured in surface water, as were concentrations of Cl^-; O_2 concentrations were also near those of surface water and Fe^{2+} concentrations were negligible. At the time of the April 1998 sampling, NO_3^- in ground water and surface water had declined to about one-third of the November values, and the O_2 concentration of the shallow ground water had declined by about 90% relative to both its November value and the April surface water value. Concentrations of Fe^{2+} increased markedly in the shallow ground water sample as well while Cl^- concentrations remained comparable in all the April samples. By the time of the August 1998 sample collection, NO_3^- and O_2 concentrations in shallow ground water had declined even further, Fe^{2+} was elevated relative to the November samples, and Cl^- concentrations were essentially identical in both shallow ground water and surface water. These results indicate that during the April and August time periods, conditions at 0.7 m beneath the streambed were sufficiently reducing for Fe^{2+} to remain in solution and for denitrification to occur, therefore accounting for the small NO_3^- concentrations. While there may be sufficient organic C buried in stream sedi-
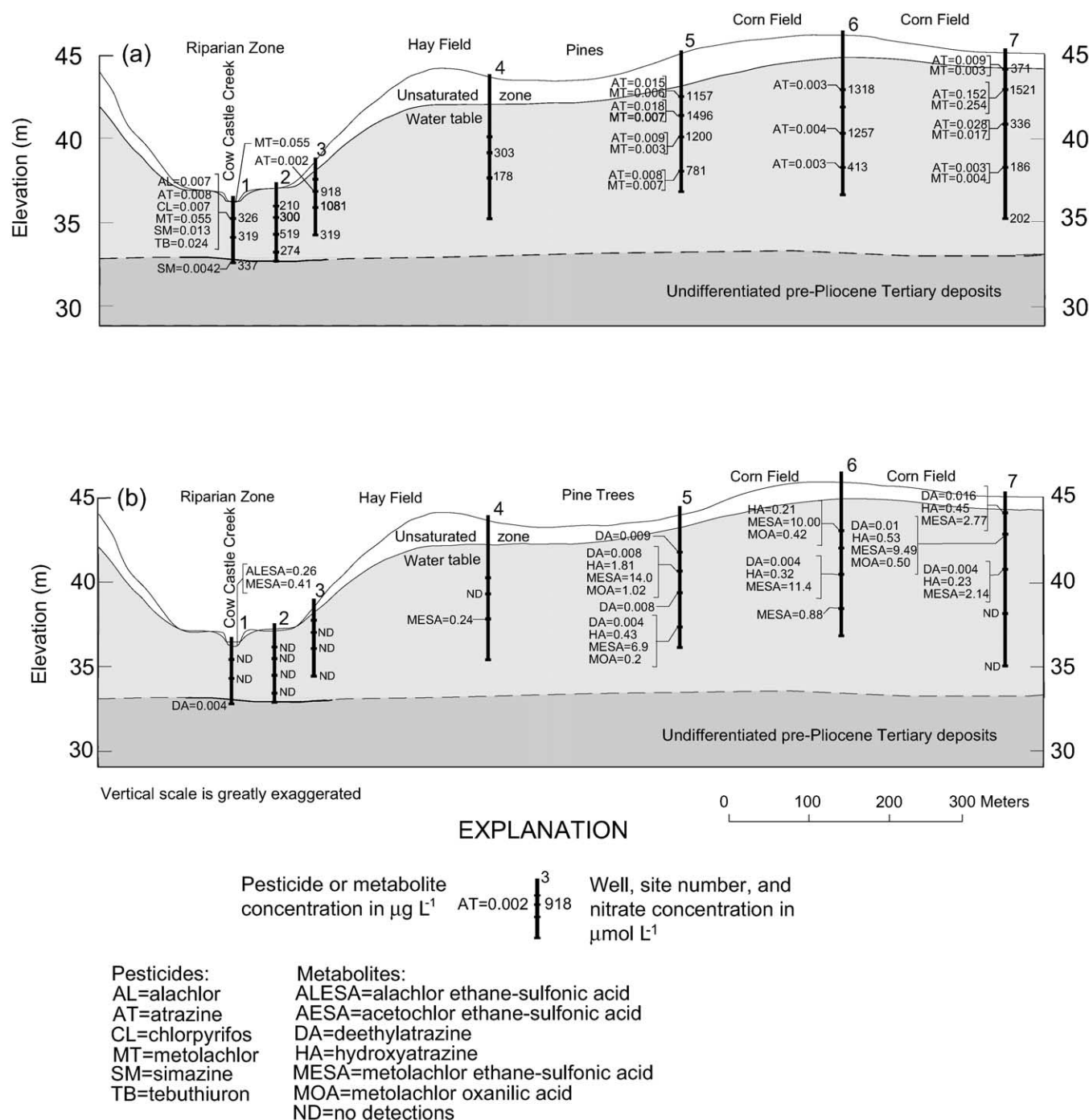
Fig. 4. Concentrations of selected (a) pesticides and reconstructed nitrate and (b) pesticide degradates in ground water sampled during November 1997.

ments to support denitrifying and iron-reducing bacteria, it is also likely that the dissolved organic C in stream water was mixing with shallow ground water; this possibility is supported by the similarity between Cl⁻ concentrations in shallow ground water and surface water.

Atrazine and metolachlor were the most frequently detected parent compounds in ground water during November 1997 (Fig. 4) and April 1998 (Table 8). At both sampling times, their concentrations were barely above the reporting limit in most samples, although there were notable exceptions such as at Sites 7-II and 7-III. Most detections were in the sample ports located under or immediately downgradient from the corn field, where these pesticides were applied. Atrazine and metolachlor were detected in the shallowest sample port at Site 1-I, in the middle of the creek. Alachlor, carbofuran, chlorpyrifos, simazine, and tebuthiuron also were detected on one occasion in the sample port at Site 1-I. None of the concentrations of any of the compounds detected in ground water during the study exceeded the maximum contaminant level (MCL) set by the USEPA (2005).

Among the pesticide degradates, only those derived from atrazine and metolachlor were detected in ground water. Both deethylatrazine and hydroxyatrazine were

Table 7. Concentrations of selected constituents in ground- and surface-water samples collected during November 1997, April 1998, and August 1998.

Site	Depth	NO_3^-	O_2	DOC†	Cl^-	Fe^{2+}
	m	— μmol L^{-1} —		μmol L^{-1} C	— μmol L^{-1} —	
				November 1997		
1-I	0.7	318.6	246.9	258.3	338.5	0.38
1-II	1.9	202.1	143.8	25.1	152.3	0.06
1-III	3.1	202.1	131.3	8.3	163.6	0.06
Creek	–	278.6	300.1	333.3	338.5	1.2
				April 1998		
1-I	0.7	105.7	21.9	191.7	189.0	13.8
1-II	1.9	285.7	178.1	75.0	169.3	0.18
1-III	3.1	323.6	200.0	33.3	186.2	0.18
Creek	–	102.9	228.1	633.3	208.8	5.7
				August 1998		
1-I	0.7	27.9	15.6	233.3	211.6	19.7
1-II	1.9	320.0	200.0	25.0	172.1	0.18
1-III	3.1	336.4	218.8	16.7	172.1	0.18
Creek	–	140.0	231.3	241.7	208.8	1.58

† Dissolved organic carbon.

detected at concentrations ranging from just above the reporting limit to a maximum of 1.8 μg L^{-1} in the case of hydroxyatrazine (Table 8). Hydroxyatrazine concentrations generally were greatest in samples from the second sampling port below the water table then decreased with depth (Fig. 4). Deethylatrazine concentrations generally were greatest in samples from the shallowest sample ports and decreased with depth.

Metolachlor ESA was the most frequently detected metolachlor degradate with nine detections above the reporting limit, whereas metolachlor OA was detected at less than half that frequency. In addition, concentrations of metolachlor ESA were the largest of any detected, reaching a maximum of 14.1 μg L^{-1}, which is about one order-of-magnitude greater than that for metolachlor OA and two orders greater than for the parent metolachlor. On a molar basis the sums of atrazine and metolachlor and their degradates only accounted for about 0.002 and 0.007%, respectively, of the parent compounds applied on the field in 1996.

DISCUSSION

Nitrate Transport and Fate

We hypothesized that long travel times in the ground-water system would allow denitrification to completely remove NO_3^- in the shallow aquifer and the riparian zone. Because most of the surficial aquifer is oxic, the potential for widespread denitrification is limited and NO_3^- was not completely removed, leading to rejection of the hypothesis. However, the observed changes in NO_3^- concentrations along the flow path and in the excess N_2 measurements indicate that some denitrification has taken place. One reason for this variability in denitrification is the heterogeneous nature of the Pleistocene-age coastal terrace deposits, Holocene-age floodplain deposits, and the scattered recent wetland deposits that make up the surficial aquifer. This heterogeneity results in pockets of high organic matter content, creating scattered local conditions capable of supporting some limited denitrification. In addition, because buried organic C commonly is refractory, and may limit microbial processes, its reactivity controls the temporal and spatial extent of denitrification (Chapelle, 1993; Appelo and Postma, 1996).

Although limited in the upland areas, denitrification plays a role as a sink for NO_3^- in the shallow portions of the riparian zone where organic C is in greater abundance. As shown in Fig. 4 and Table 6, large NO_3^- concentrations, originating as fertilizer applied to the hay field, decreased by approximately an order-of-magnitude by the time they had traversed about halfway through the riparian zone. As reflected in the net increase in excess N_2 gas, however, denitrification can account for only about 7 to 28% of the net decrease in NO_3^- concentrations. Therefore, the remaining decreases in NO_3^- concentrations are attributed either to plant uptake or to mixing of low-NO_3^- waters that recently recharged in the riparian zone with the shallow ground water. More importantly, NO_3^- remained in ground water below the riparian zone and in ground water beneath the creek, meaning that the chemically reducing conditions present in shallow portions of the riparian zone were being bypassed. Furthermore, excess N_2 gas accounts for only about 37 to 41% of the reconstructed NO_3^- concentrations in the 23-yr-old ground water in the discharge zone. Even if the larger NO_3^- concentrations in ground water that recharged since the mid-1980s are decreased by these same percentages, we can expect that at some time in the coming decade, as this ground water reaches the end of

Table 8. Concentrations of pesticides and degradates detected in 24 ground-water samples collected during November 1997, and pesticides in 29 ground-water samples collected during April 1998. Only 22 of the 24 samples collected during November 1997 were analyzed by the Organic Research Laboratory for the triazine and acetanilide degradates.

Pesticide†	Detection frequency		Concentration		
	November 1997	April 1998	Minimum	Median	Maximum
			— μg L^{-1} —		
Atrazine	13	10	<0.001‡	<0.001	0.15
Deethylatrazine	9	9	<0.002	<0.002	0.021
Hydroxyatrazine	7	NA	<0.2	<0.2	1.8
Metolachlor	9	6	<0.002	<0.002	0.25
Metolachlor ESA	9	NA	<0.2	<0.2	14.1
Metolachlor OA	4	NA	<0.2	<0.2	1.0
Alachlor	1	0	<0.002	<0.002	0.007
Carbofuran	0	1	<0.003	<0.003	0.007
Chlorpyrifos	1	0	<0.004	<0.004	0.004
Simazine	1	0	<0.005	<0.005	0.013
Tebuthiuron	1	0	<0.01	<0.01	0.02

† OA = oxanilic acid degradate; ESA = ethane-sulfonic acid degradate.
‡ Values reported as "<" were less than the reporting limit; "NA" were not sampled.

its flow path, we will see NO_3^- concentrations of about 430 to 700 μmol L^{-1} beneath Cow Castle Creek. It is also possible, however, that the NO_3^- decreases will be only on the order of the 120 to 140 μmol L^{-1} that we observed, and NO_3^- concentrations of about 1000 to 1600 μmol L^{-1} may occur in ground water beneath the creek.

It is important to note that at least during April and August some NO_3^- was removed from shallow ground water as the result of denitrification in the upper 0.7 m of the streambed. The fact that the greatest decrease in NO_3^- occurred during the August low-flow period helps to explain why even though ground water had its greatest influence on surface-water chemistry at that time, surface-water NO_3^- concentrations were at their smallest and were only about one-quarter of what might be expected given NO_3^- concentrations in deeper ground water beneath the stream. A more intensive study of hyporheic zone processes would be required at the study site to determine the degree to which the potential increases in ground-water NO_3^- concentrations will affect in-stream NO_3^- concentrations.

Pesticides and Pesticide Degradates

We also hypothesized that long travel times in the ground-water system would allow pesticides and their degradates to be mineralized to undetectable levels before they reached the adjacent creek, and with minor exceptions this appears to be true. Our results indicate that some of these compounds (atrazine, deethylatrazine, hydroxyatrazine, metolachlor, metolachlor ESA, and metolachlor OA) may persist in ground water for periods up to 18 yr. In the case of the degradates, it might be argued that their presence in ground water is the result of continued degradation of the parent compound, or it may be due to their assumed slower degradation rates than the parent compounds. Where detected in this study, the concentrations of parent compound often were just above the reporting limit whereas the degradate concentrations were commonly one or more orders-of-magnitude greater than those of the parent compounds. Therefore, continued transformation of the parents is not likely to have accounted for the persistence of the degradates.

In spite of this persistence, there is little evidence that the parent compounds or their degradates have migrated very far downgradient from the corn field where they originated. At this location the configuration of the ground-water flow system results in moderately long residence times ($>$20 yr), giving degradation processes sufficient time to reduce pesticide concentrations to relatively small values. The absence of virtually all pesticides in samples from the riparian zone, and especially beneath the stream at depths greater than 0.7 m, indicates that, at least at this location, ground water is not a direct source of pesticides or their degradates to Cow Castle Creek.

The pesticide and pesticide degradate results agree with a number of recent studies that have reported the presence of numerous pesticides and their degradates in ground water and surface water in the midwestern United States (e.g., Kolpin et al., 2000; Kalkhoff et al.,

2003). The relatively large surface-water concentrations of pesticides we observed in the spring are indicative of runoff following applications (Phillips et al., 1999; Kalkhoff et al., 2003). Most of the relevant degradation processes are biologically mediated and occur in the shallow soil zone (Phillips et al., 1999; Kalkhoff et al., 2003). Therefore, the absence of, or relatively small concentrations of pesticide degradates in the same surface-water samples, indicates that they had not been in the shallow soil zone long enough after application for biodegradation to occur to a measurable extent. The increases in the ratio of pesticide degradates, such as metolachlor ESA, to the parent compound during the growing season (from 0.25 in May to 7.5 in November) reflect the production of the degradates because of transformation processes in the shallow soil zone (Phillips et al., 1999).

Hydrogeologic Controls

Several hydrogeologic factors combine in the study area to influence the transport and fate of NO_3^- and pesticides from the cultivated fields to Cow Castle Creek. First, this is a low-gradient hydrologic setting with a seasonally high water table, requiring tile drains and ditches to remove excess water. The net result of this practice is to route shallow subsurface drainage directly from the cultivated fields to Cow Castle Creek, bypassing biogeochemical processes in the riparian zone. Another effect of artificial drainage is a decrease in the effective recharge rate, resulting in an increase in ground-water residence times within the flow system. This increased residence time allows more time for slow processes such as pesticide degradation, and in part, accounts for why the pesticides have not migrated far from the corn field where they were applied. Finally, the depositional history of the sediments that make up the surficial aquifer plays a very important role as well. These sediments are a mixture of finer-grained sands, silts, and clays in the uplands, coarser-grained sands at depth near the creek, and a thin ($<$1 m thick) chemically reducing surficial layer in the riparian zone, most of which contain small amounts of organic C. The small amounts of organic C are inadequate to support widespread denitrification. The coarser-grained sediments provide a preferential flow path that allows NO_3^- in ground water to pass beneath the shallow reducing layer in the riparian zone and discharge directly into the streambed.

Several lines of evidence indicate that Cow Castle Creek receives ground water from the adjacent aquifer and that there is active exchange of water within the streambed. Head measurements made at various depths under the streambed were consistently positive throughout the year, indicating a strong discharge potential. Measurements of flow at various points in a 168-m-long stream reach during a relatively stable period of discharge in winter confirmed a net increase in discharge of 13.4%, indicating that ground water was contributing to stream flow. Furthermore, (i) the relatively modern age date for samples from the shallow (0.7 m) sampling port under the streambed, (ii) the fact that the dissolved N_2 concentration measured there was virtually the same
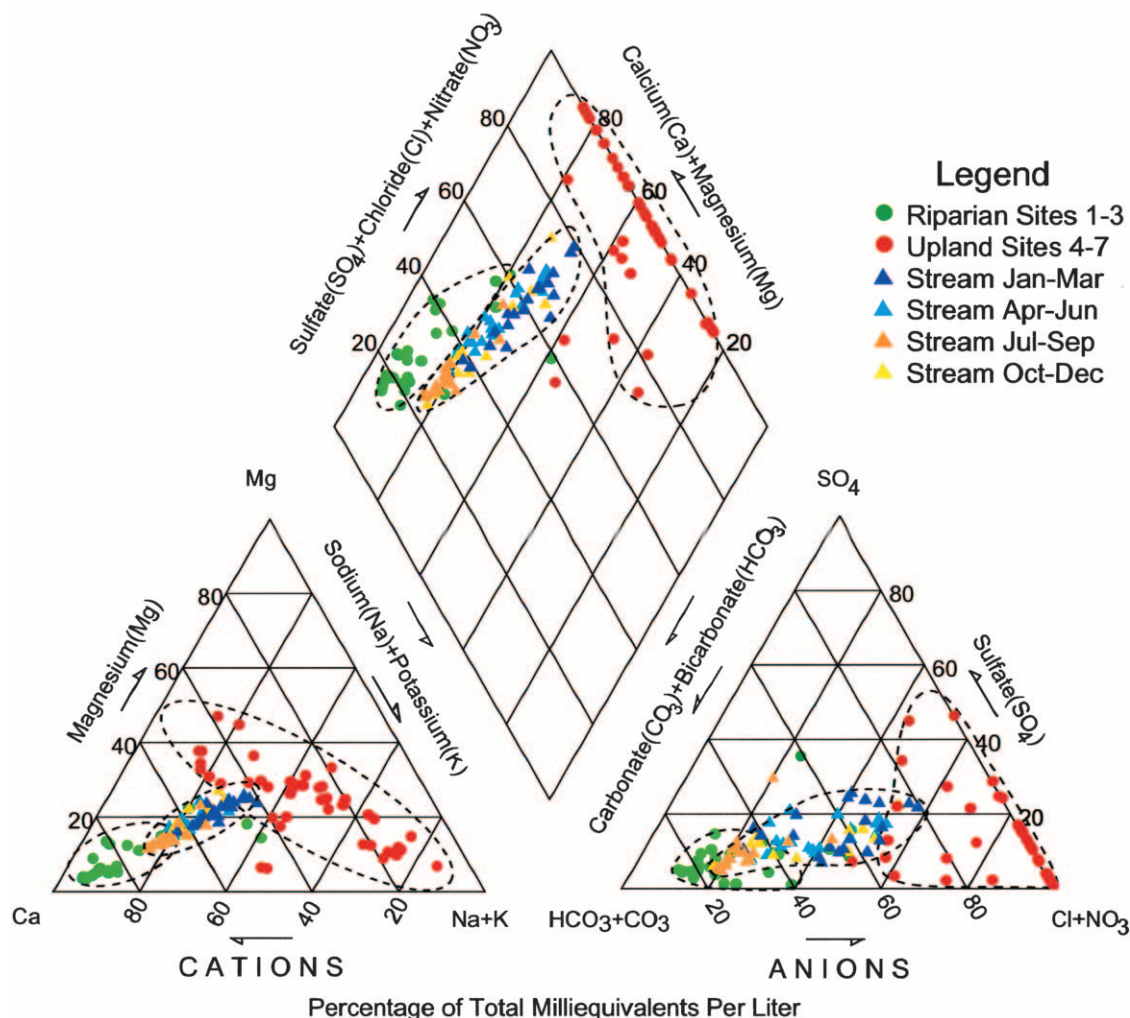
Fig. 5. Piper diagram of ground- and surface-water chemistry, October 1995 through September 1998.

as the air-water equilibrium value, and (iii) the presence of numerous pesticides found in the stream but not in deeper ground water at Site 1, confirm that exchange is occurring in the upper 0.7 m of the streambed.

The water-chemistry data for the creek and ground-water samples shown in the Piper diagram in Fig. 5 illustrate the relative importance of different ground-water sources to the stream. As shown in the "CAT-IONS" panel in Fig. 5, ground water in the riparian zone is dominated by Ca^{2+}, whereas in the cultivated upland area the water chemistry is much more variable and trends toward Na^+, K^+, and Mg^{2+}. This pattern is also discernible in the "ANIONS" panel, although not as pronounced because the Cl^- and NO_3^- applied in fertilizer in the upland area are, for the most part, transported conservatively downgradient into the riparian zone. In the combined chemistry panel, the three groupings of water chemistry are still evident, with the stream samples again falling between the two distinct groupings of ground-water samples. In all three panels, Cow Castle Creek samples fall on a line or in a cluster between the two ground water groupings, with stream samples collected during the low-flow months (July–September) plotting closer to the riparian zone samples and those

collected during the high-flow months (January–March) plotting closer to the upland samples. Our interpretation of these data is that during the low-flow period, stream chemistry is strongly influenced by discharging ground water that has most recently passed beneath the riparian zone and, thus, has a similar chemical signature. On the other hand, during periods of higher stream flow, when ditches and tile drains are actively shunting shallow sub-surface drainage water directly from the cultivated areas to the stream, the chemical signature of surface water reflects the upland ground-water chemistry to a greater degree.

CONCLUSIONS

Denitrification was not a strong controlling factor in the transport and fate of NO_3^- at this study site due to the absence of sufficient organic C or other reduced species required to support this process. Even in the riparian zone sediments, other processes accounted for more NO_3^- loss than did denitrification, and NO_3^- in ground water was transported to Cow Castle Creek where it mixed with surface water in the streambed. During the low-flow period, some NO_3^- was lost in the streambed,

limiting the impact of ground water on surface-water NO_3^- concentrations. However, the largest concentrations of NO_3^- measured in surface water were only about half the MCL; maximum NO_3^- concentrations in ground water were up to about 2.5 times the MCL. Since the surficial aquifer is only rarely used for drinking water, these large concentrations do not represent a major health issue. Because this high NO_3^- ground water should reach the stream over the next decade, there is the potential for surface-water NO_3^- concentrations to increase and contribute to eutrophication. It is still uncertain how effective the riparian and hyporheic zones will be in reducing these large NO_3^- concentrations.

Atrazine and simazine concentrations in surface water were the largest detected during the study but were only about one-third their MCLs. In spite of their persistence in ground water, all the pesticides detected were well below the MCLs. However, it is important to note that there are no MCLs for the various degradates studied. The absence of these compounds in samples collected from deeper positions in the aquifer suggests that (i) this persistence is limited; (ii) they were not transported that deep; or (iii) this deeper, older ground water recharged before their use. Furthermore, the fact that these pesticides and pesticide degradates have not migrated very far downgradient from the point of application points out the potentially important role that buffer zones may have in limiting their transport in ground water to streams. By establishing sufficiently wide buffer zones to guarantee adequate residence times, natural processes may eliminate these compounds before they reach surface waters.

Hydrogeologic factors at the site exert strong influences on the transport and fate of NO_3^- and pesticides. Tile drains and ditches route contaminants directly to the steam, bypassing the riparian zone. Long groundwater residence times allow sufficient time for most pesticides and their degradates to be reduced to negligible concentrations. Coarse sediments below the riparian zone provide preferential flowpaths for NO_3^- in ground water to pass beneath the chemically reducing layer there and reach the stream. Ground water has its greatest influence on surface-water chemistry during the low-flow periods of the year, whereas shallow subsurface drainage dominates stream chemistry during high-flow periods. These dynamics of the hydrogeologic setting result in larger concentrations of NO_3^- and pesticides and their degradates during periods of high stream flow, and lower concentrations during periods of low stream flow.

ACKNOWLEDGMENTS

REFERENCES

Accinelli, C., G. Dinelli, A. Vicari, and P. Catizone. 2001. Atrazine and metolachlor degradation in subsoils. Biol. Fertil. Soils 33:495–500.

Anderson, H.W. 1993. Effects of agricultural and residential land use on ground-water quality, Anoka Sand Plain Aquifer, east-central Minnesota. Water-Resour. Investigations Rep. 93-407. USGS, Mounds View, MN.

Appelo, C.A.J., and D. Postma. 1996. Geochemistry, groundwater and pollution. A.A. Balkema, Rotterdam, the Netherlands.

Armstrong, D.E., and G. Chesters. 1968. Adsorption catalyzed chemical hydrolysis of atrazine. Environ. Sci. Technol. 2:683–689.

Aucott, W.R. 1996. Hydrology of the Southeastern Coastal Plain aquifer system in South Carolina and parts of Georgia and North Carolina. USGS Professional Paper 1410-E. U.S. Gov. Print. Office, Washington, DC.

Barbash, J.E., and E.A. Resek. 1996. Pesticides in ground water: Distribution, trends, and governing factors. Ann Arbor Press, Chelsea, MI.

Bayless, E.R. 2001. Atrazine retention and degradation in the vadose zone at a till plain site in central Indiana. Ground Water 39:169–180.

Blicher-Mathiesen, G., G.W. McCarty, and L.P. Nielsen. 1998. Denitrification and degassing in groundwater estimated from dinitrogen and argon. J. Hydrol. (Amsterdam) 208:16–24.

Buchanan, T.J., and W.P. Somers. 1969. Discharge measurements at gaging stations. Techniques of Water-Resour. Investigations, Book 3, Chapter A8. USGS, Denver.

Burkart, M.R., D.W. Kolpin, R.J. Jaquis, and K.J. Cole. 1999. Agrichemicals in ground water of the midwestern USA: Relations to soil characteristics. J. Environ. Qual. 28:1908–1915.

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., L.N. Plummer, R.C. Bartholomay, and J.E. Wayland. 1998. Chlorofluorocarbons, sulfur hexafluoride, and dissolved permanent gases in ground water from selected sites in and near the Idaho National Engineering and Environmental Laboratory, Idaho, 1994–97. Open-File Rep. 98-274. USGS, Idaho Falls, ID.

Chapelle, F.H. 1993. Ground-water microbiology and geochemistry. John Wiley & Sons, New York.

DeFrancesco, D.J. 1988. Soil survey of Orangeburg County, South Carolina. USDA-SCS, Washington, DC.

Delin, G.N., and M.K. Landon. 1996. Multiport well design for sampling of ground water at closely spaced vertical intervals. Ground Water 34:1098–1104.

Devito, K.J., D. Fitzgerald, A.R. Hill, and R. Aravena. 2000. Nitrate dynamics in relation to lithology and hydrologic flow path in a river riparian zone. J. Environ. Qual. 29:1075–1084.

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. Open-File Rep. 93-125. USGS, Denver.

Fishman, M.J., and L.C. Friedman (ed.) 1989. Methods for determination of inorganic substances in water and fluvial sediments. USGS Techniques of Water-Resour. Investigations. Book 5, Chapter A1. U.S. Gov. Print. Office, Washington, DC.

Haycock, N.E., G. Pinay, and C. Walker. 1993. Nitrogen retention in river corridors: European perspectives. Ambio 22:340–346.

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

Hedges, J.L., and J.H. Stern. 1984. Carbon and nitrogen determinations of carbonate-containing solids. Limnol. Oceanogr. 29:657–663.

Hill, A.R. 1996. Nitrate removal in stream riparian zones. J. Environ. Qual. 22:743–755.

Hoffman, R.S., P.D. Capel, and S.J. Larson. 2000. Comparison of pesticides in eight U.S. urban streams. Environ. Toxicol. Chem. 19:2249–2258.

Kalkhoff, S.J., D.W. Kolpin, E.M. Thurman, I. Ferrer, and D. Barcelo. 1998. Degradation of chloroacetanilide herbicides: The prevalence of sulfonic and oxinilic acid metabolites in Iowa groundwaters and surface waters. Environ. Sci. Technol. 32:1738–1740.

Kalkhoff, S.J., K.E. Lee, S.D. Porter, P.J. Terio, and E.M. Thurman. 2003. Herbicides and herbicide degradation products in Upper Midwest agricultural streams during August base-flow conditions. J. Environ. Qual. 32:1025–1035.

Kolpin, D.W., D.A. Goolsby, and E.M. Thurman. 1995. Pesticides in

near-surface aquifers: An assessment using highly sensitive analytical methods and tritium. J. Environ. Qual. 24:1125–1132.

Kolpin, D.W., E.M. Thurman, and S.M. Linhart. 1998. The environmental occurrence of herbicides: The importance of degradates in ground water. Arch. Environ. Contam. Toxicol. 35:385–390.

Kolpin, D.W., E.M. Thurman, and S.M. Linhart. 2000. Finding minimal herbicide concentrations in ground water? Try looking for their degradates. Sci. Total Environ. 248:115–122.

Kolpin, D.W., E.M. Thurman, and S.M. Linhart. 2001. Occurrence of cyanazine compounds in groundwater: Degradates more prevalent then the parent compound. Environ. Sci. Technol. 35:1217–1222.

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. Open-File Rep. 95-399. USGS, Reston, VA.

Larson, S.J., R.D. Capel, and M.S. Majewski. 1997. Pesticides in surface water: Distribution, trends, and governing factors. Ann Arbor Press, Chelsea, MI.

Loague, K., R.N. Miyahira, D.S. Oki, R.E. Green, R.C. Schneider, and T.W. Giambelluca. 1994. Chemical leaching near the Waiawa shaft, Oahu, Hawaii: 1. Field experiments and laboratory analysis. Ground Water 32:986–996.

McCartan, L., E.M. Lemon, and R.E. Weems. 1984. Geologic map of the area between Charleston and Orangeburg, South Carolina. Miscellaneous Investigations Ser. I-1472, 1:250,000, 1 sheet. USGS, Reston, VA.

McMahon, P.B., F.H. Chapelle, and M.L. Jagucki. 1992. Atrazine mineralization potential of alluvial-aquifer sediments under aerobic conditions. Environ. Sci. Technol. 26:1556–1559.

Meyer, M.T., M.S. Milles, and E.M. Thurman. 1993. Automated solid-phase extraction of herbicides from water for gas chromatographic-mass spectrometric analysis. J. Chromatogr. 629:555–559.

Mueller, D.K., and D.R. Helsel. 1996. Nutrients in the nation's waters—Too much of a good thing? USGS Circ. 1136. U.S. Gov. Print. Office, Washington, DC.

Owensby, J.R., and D.S. Ezell. 1992. Climatography of the United States no. 81—Monthly station normals of temperature, precipitation, and heating and cooling degree days, 1961–90. Natl. Climatic Data Center, Ashville, NC.

Phillips, P.J., G.R. Wall, E.M. Thurman, D.A. Eckhardt, and J. Vanhoesen. 1999. Metolachlor and its metabolites in tile drain and stream runoff in the Canojoharie Creek watershed. Environ. Sci. Technol. 33:3531–3537.

Postma, D., C. Boesen, H. Kristiansen, and F. Larsen. 1991. Nitrate reduction in an unconfined aquifer: Water chemistry, reduction processes, and geochemical modeling. Water Resour. Res. 27:2027–2045.

Puckett, L.J. 1995. Identifying the major sources of nutrient water pollution. Environ. Sci. Technol. 29:408A–414A.

Puckett, L.J. 2004. Hydrogeologic controls on the transport and fate of nitrate in ground water beneath riparian buffer zones: Results from thirteen studies across the United States. Water Sci. Technol. 49:47–53.

Puckett, L.J., and T.K. Cowdery. 2002. Transport and fate of nitrogen in a glacial outwash aquifer in relation to ground-water age, land use practices, and redox processes. J. Environ. Qual. 31:782–796.

Puckett, L.J., T.K. Cowdery, D.L. Lorenz, and J.D. Stoner. 1999. Estimation of nitrate contamination of an agro-ecosystem aquifer using a nitrogen mass-balance budget. J. Environ. Qual. 28:2015–2025.

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, doi: 10.1029/2001WR000396.

Reuber, E.J. 2001. Shallow ground-water quality in an agricultural area of the Lower Coastal Plain of South Carolina, 1997. Open-File Rep. 01-377. USGS, Columbia, SC.

Spurlock, F., K. Burow, and N. Dubrovsky. 2000. Chlorofluorocarbon dating of herbicide-containing wells in Fresno and Tulare Counties, California. J. Environ. Qual. 29:474–483.

Thurman, E.M., M.T. Meyer, M.L. Pomes, C.A. Perry, and A.P. Schwab. 1990. Enzyme-linked immunosorbent assay compared with gas chromatography/mass spectrometry for the determination of triazine herbicides in water. Anal. Chem. 62:2043–2048.

Trudell, M.R., R.W. Gillham, and J.A. Cherry. 1986. An in-situ study of the occurrence and rate of denitrification in a shallow unconfined sand aquifer. J. Hydrol. (Amsterdam) 83:251–268.

USEPA. 2005. List of drinking water contaminants & MCLs. Available at http://www.epa.gov/safewater/mcl.html#mcls (verified 20 July 2005). USEPA, Washington, DC.

Vinther, F.P., L. Elsgaard, and O.S. Jacobson. 2001. Heterogeneity of bacterial populations and pesticide degradation potentials in the unsaturated zone of loamy and sandy soils. Biol. Fertil. Soils 33:514–520.

Vogel, J.C. 1967. Investigation of groundwater flow with radiocarbon. p. 355–368. In Isotopes in hydrology. Int. Atomic Energy Agency, Vienna.

Vogel, J.C., A.S. Talma, and T.H.E. Heaton. 1981. Gaseous nitrogen as evidence for denitrification in ground water. J. Hydrol. (Amsterdam) 50:191–200.

Wehtje, G.R., R.F. Spalding, O.C. Lowry, S.R. Burnside, and J.R.C. Leavitt. 1983. Biological significance and fate of atrazine under aquifer conditions. Weed Sci. 31:610–618.

Wershaw, R.L., M.J. Fishman, R.R. Grabbe, and L.E. Lowe. 1987. Methods for the determination of organic substances in water and fluvial sediments. USGS Techniques of Water-Resour. Investigations, Book 5. U.S. Gov. Print. Office, Washington, DC.

Wilson, J.T., J.F. McNabb, D.L. Balkwill, and W.C. Ghiorse. 1983. Enumeration and characterization of bacteria indigenous to a shallow water-table aquifer. Ground Water 21:134–142.

Winter, T.C. 1976. Numerical simulation analysis of the interaction of lakes and ground water. U.S. Geol. Survey Professional Paper 1001. U.S. Gov. Print. Office, Washington, DC.

Winter, T.C., J.W. LaBaugh, and D.O. Rosenberry. 1988. The design and use of a hydraulic potentiomanometer for direct measurement of differences in hydraulic head between groundwater and surface water. Limnol. Oceanogr. 33:1209–1214.

Wolock, D.M. 1997. STATSGO soil characteristics for the conterminous United States. Open-File Rep. 97-656. Available at http://water.usgs.gov/GIS/metadata/usgswrd/XML/muid.xml (verified 20 July 2005). USGS, Reston, VA.

Wolock, D.M. 2003a. Infiltration-excess overland flow estimated from TOPMODEL for the conterminous United States. Open-File Rep. 03-310. Available at http://water.usgs.gov/GIS/metadata/usgswrd/XML/ieof48.xml (verified 20 July 2005). USGS, Reston, VA.

Wolock, D.M. 2003b. Saturation overland flow estimated by TOPMODEL for the conterminous United States. Open-File Rep. 03-264. Available at http://water.usgs.gov/GIS/metadata/usgswrd/XML/satof48.xml (verified 20 July 2005). USGS, Reston, VA.