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Hydrology of a first-order riparian zone and stream, mid-Atlantic coastal plain, Maryland

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Abstract

Riparian buffer strips are considered to provide natural remediation for groundwater contaminants, but this function is partly based on a relatively simple model of riparian zone hydrology; specifically, horizontal matrix flow through the shallow subsurface. Deviation from horizontal flow leads to asymmetrical groundwater emergence onto the surface and greater propensity for contaminant delivery to the stream. The study site, at the USDA-Beltsville Agricultural Research Center, is in the mid-Atlantic coastal plain of Maryland. The site contains a small first-order stream that is instrumented with five stations for monitoring stream flow and chemistry, and 170 nested piezometers (mostly in transects) for evaluating groundwater hydrology and geochemistry. Subsurface microstratigraphy and macroporosity are largely responsible for observed spatial and temporal variations in groundwater contributions to the stream. The portion of the stream that shows the highest rate of flow increase per stream length contains discrete zones of enhanced groundwater discharge (upwelling) to the surface, which supply most of the additional stream flow. These upwelling zones display high (positive) vertical hydraulic heads, which relate to the amount of groundwater discharged from those points. One particular area of intense groundwater upwelling supplies approximately 4% of the total stream outflow, yet comprises only 0.006% of the riparian zone. The upwelling zones also supply most of the NO_3^- to the surface. Zones of focused groundwater exfiltration that sustain stream baseflow do not correspond with erosional features, and have a great impact on stream flow characteristics and NO_3^- behavior. Few studies to date have elucidated and quantified contributions from specific surface features (e.g. upwelling zones, discharging macropores). More emphasis and research needs to be directed to the importance of focused groundwater exfiltration points for stream flow generation and NO_3^- transport, with the goal of devising more effective management regulations for preserving and enhancing riparian zone mitigation function.
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1. Introduction

Riparian buffer zones are considered potential lines of defense against contamination of larger surface water bodies by excess agricultural nutrients and other pollutants. First-order streams may include the most

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effective riparian buffers for contaminant mitigation (Brinson, 1988; Peterson et al., 2001). In terms of nutrient flow, phosphorus applied to fields can enter surface waters through storm runoff (Sims, 1993; Sharpley et al., 1998). NO_3^- can be transported to surface waters through groundwater (Crum et al., 1990; Martin et al., 1999; Tesoriero et al., 2000). Evaluating riparian zone contaminant mitigation function thus requires knowledge of the hydrological settings common to these environments. This is especially true for groundwater-borne contaminants (such as NO_3^-), which are typically delivered under baseflow conditions (Cooper, 1990; Pionke et al., 1996). While riparian zones often present conditions (e.g. soils high in organic C, anaerobic conditions near the surface, wide vegetated corridors) that presumably make them suitable for NO_3^- removal (Brinson, 1988; Mitsch and Gosselink, 1993; Emmet et al., 1994; Peterson et al., 2001), significant groundwater NO_3^- may nevertheless enter surface water within the riparian zone (Bohlke and Denver, 1995; Hill et al., 2000; McCarty and Angier, 2001; Angier et al., 2002). The specific circumstances under which riparian zones function at mitigating NO_3^- pollution remain poorly understood. This study examined the hydrological processes that can limit NO_3^- removal (and, more generally, groundwater contaminant remediation) under seemingly favorable conditions. The hydrology of the riparian system for the small first-order watershed in this study changed markedly on both temporal and spatial scales. Detailed understanding of the hydrological setting is therefore required in order to adequately evaluate overall riparian zone function.

Initial conceptual models for riparian zone hydrology often assumed lateral subsurface flow from an agricultural field (upland site), through a riparian buffer strip, to a stream channel (Jordan et al., 1993; Bosch et al., 1994; Crownover et al., 1995). In such settings, the upland area was considered a recharge zone and the stream (and its immediate border) a discharge point. With these models, no substantive consideration was given to the interceding riparian zone regarding the effects of infiltration and exfiltration on groundwater flowpaths and contaminant transport. Some studies, though, have indicated that vertical groundwater recharge (O'Connell, 1998; Sharratt, 2001) or discharge (Devito et al., 2000; Angier et al., 2002) can predominate in riparian environments. Deep aquifers will allow more vertical groundwater movement (Bohlke and Denver, 1995; Devito et al., 2000) and deviation from horizontal flow. Assumption of uniform horizontal groundwater flow without corroborating piezometric data may be inaccurate. Even in the presence of an aquiclude at shallow depth (forcing groundwater to move essentially horizontally through the shallow subsurface), much of the groundwater may travel through, and be delivered to the surface via, preferential subsurface flow pathways. Preferential subsurface flow, particularly macropore flow, can have a substantial impact on the quality (and quantity) of water delivered to the surface, especially for riparian areas (Hill et al., 2000; Angier et al., 2001; McCarty and Angier, 2001). The objectives of this study included elucidating spatial and temporal differences in subsurface hydrology and groundwater flow direction(s), how these differences affected stream flow patterns, and the impact of non-uniform groundwater discharge characteristics on stream NO_3^- loads. In addition, the importance and extent of subsurface preferential (macropore) flow was assessed. First-order and other low-order basins (such as in this study) are expected to be most effective at removing groundwater contaminants (Brinson, 1988; Peterson et al., 2001), so studying these sites should be useful for testing the validity of a 'horizontal flow' riparian hydrologic model.

2. Site description

The study site is contained within a first-order agricultural watershed in the Maryland inner coastal plain. The entire watershed area is approximately 70 ha. At least 75% of the total land area is in agricultural production; about 65% corn and 10% rotating clover and corn. The riparian corridor runs alongside the entire length of the stream ($\sim$1100 m), and varies in width from about 65 m at its narrowest point, to more than 250 m. The riparian corridor comprises about 10% of the total land area in this watershed. The remainder consists of forested upland and uncropped meadow.

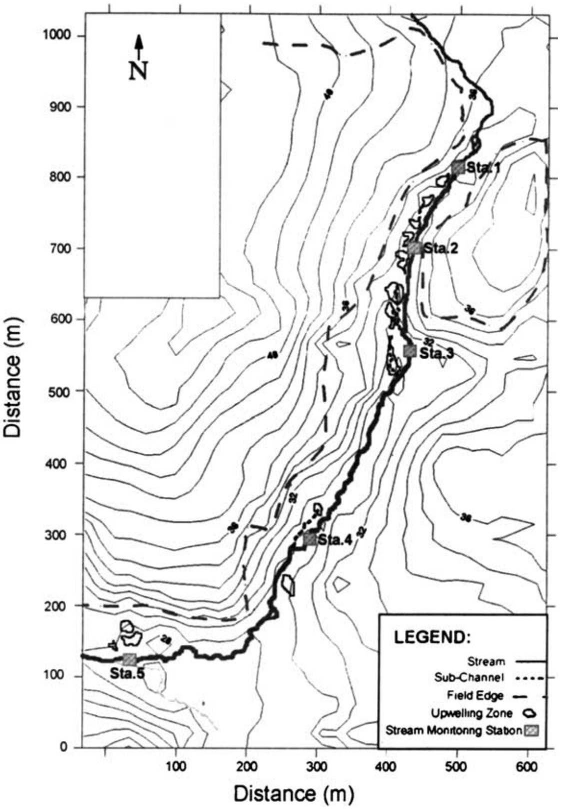

Fig. 1. Plan-view topographic map of study site. Shows locations of key features and instrumentation discussed in text. Riparian zone is forested area between western and eastern field edges (dashed lines on map). Stream station 1 is approximate stream head, station 5 is outflow point of stream (where it joins a higher-order stream, shown in bottom left of map). Note the preponderance of upwelling zones (outlined areas) and sub-channels (dotted lines) in upper part of floodplain (between stations 1–3).

Fig. 1 is a plan-view topographic map of the study watershed. The sub-watershed includes a 20 ha agricultural field that drains into a riparian zone and a small north-to-south flowing first-order stream. To the east of the riparian corridor lies a 8 ha upland field and a low-lying wetland area. The first-order stream flows into a larger stream, marking the termination of the study area. Based on USGS regional 7.5×7.5 min Maps, the geomorphological characteristics and orientation in the landscape of this site are comparable to other first-order streams in this part of the mid-Atlantic coastal plain.

3. Methods

3.1. Surveying and georectification

The riparian zone and adjacent fields were extensively mapped using a land survey system (Topcon Total Station, Tripod Data Systems, Corvallis, OR, USA). Survey data were adjusted to UTM coordinates for georectification. Elevation was corrected for meters above sea level by surveying from a nearby USGS elevation marker to a common point in the field site. GPS (Global Positioning System) was used to orient the survey data, allowing the survey data to be integrated into a larger area of the landscape.

3.2. Surface water measurements

Five channel devices were constructed to rate and monitor the stream, and installed at intervals along the stream channel (see Fig. 1). V-notch weirs were attached to the channel structures. This configuration allowed separate stream lengths to be monitored individually, and compared. Station 1 represented the non-agriculturally-impacted (forested) portion of the system; flow in this station only occurred during winter and wet periods. Station 2 was approximately 100 m downstream from station 1. This part of the channel functioned essentially as the stream head during dry periods; water flowed continuously here, even in drought conditions. Station 3 was about 150 m below station 2 and drained the part of the riparian zone that constituted a perpetual wetland (based on hydrological characteristics and vegetation). Station 4 was approximately 350 m downstream of station 3. Station 5, about 450 m below station 4, marked where the first-order stream drained into a higher-order stream channel. This station was sometimes flooded under wet conditions, but was often dry in summer.

A water level/stream discharge relationship (rating curve) was determined for each station. Manual discharge (Q) measurements were taken for the full range of weir notch heights at each station. A power function equation for the rating curve was established. The coefficients for this equation were estimated by non-linear regression and used to program a water level logger/autosampler (Sigma 900max Portable Sampler, American Sigma Inc., Medina, NY, USA) at each station, so stream discharge was calculated automatically with each level measurement. Water level in the channel was measured with an automatic stream level logger (Sigma 950/960 Ultrasonic Flow Meter), and recorded at 10 min intervals. Stream water samples were collected by hand about once a week, and in response to major precipitation events. At the same time, the level in the stream was measured directly to ensure that the datalogged levels were consistent with real, measured levels.

There are several small sub-channels that feed into the main stream channel within the upstream part of the wetland, shown in Fig. 2. Two of these were particularly important to total stream discharge, and are referred to as 'secondary' and 'tertiary' channel. Discharge in these sub-channels was evaluated using a small 'mini-weir' temporarily placed in the sub-channel. A small calibrated cup and stopwatch were used to measure this discharge, as well as discharge from streamside macropores. Samples for chemical analysis were collected at the same time, to obtain contaminant fluxes.

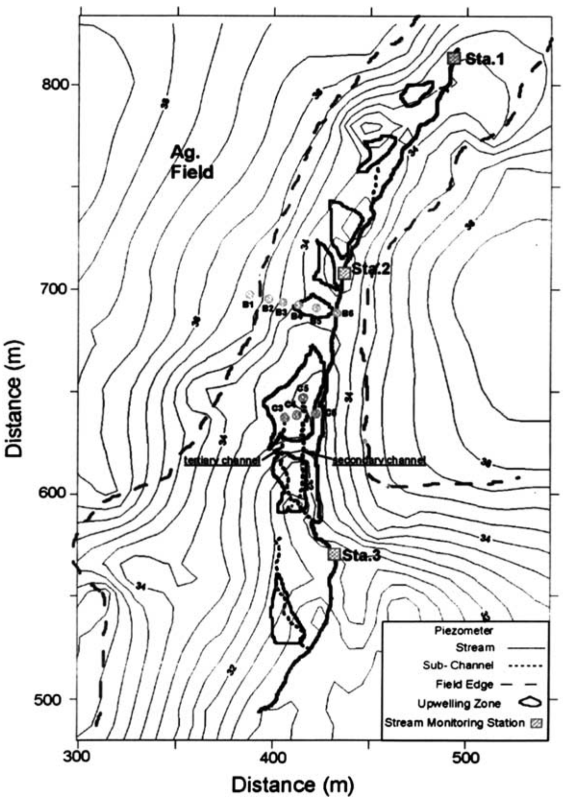

Fig. 2. Plan-view topographic map of upper study site. This map depicts the upper half of the riparian zone, including stations 1–3. Piezometer transects B and C, and secondary and tertiary channels (described in text) are shown.

3.3. Groundwater measurements

The field site was instrumented with approximately 170 piezometers. Most of these were set into nests (series of piezometers placed at different depths in the subsurface) and in transects (series of nests that trended from the field edge to the stream). Nests consisted of two to seven piezometers each. This included wells at different depths within the aquifer, and at different depths in the overlying soil. One inch (2.5 cm) PVC pipes, with 8 in. (20 cm) screened intervals, were used.

Locations for piezometers were originally chosen at regular intervals at the site. Transects of nested piezometers were placed from the field edges to the stream. This allowed for hydrological and geochemical measurements from the upland, along the hillslope, and within the valley. Grouping the piezometers into nests at different depths allowed for vertical as well as horizontal measurements. Nested piezometers were also placed within the stream channel at regular intervals, so that hydrology and water chemistry beneath the channel could be measured.

Water levels were measured in each piezometer with a level indicator. In addition, there were 60 pressure transducers (Global Water WLB14 Water Level Loggers, Geotech, Denver, CO, USA) fitted to piezometers for real-time level measurements. Continuous groundwater levels were automatically logged at 15 min intervals. Hydraulic conductivity (K) values for each piezometer depth were evaluated with the Bouwer and Rice slug test method (from Fetter, 1994).

3.4. Soil and sediment measurements

Soil cores were obtained from the saturated areas of the riparian zone with a core extractor (Eijkelkamp Peat Sampler, Eijkelkamp Agrisearch Equipment, Giesbeek, The Netherlands). The peat sampling instrument extracted 0.5 m increments of low-bulk-density soils intact, with little compression. This permitted detailed examination of soil profiles.

Cores were gathered from each piezometer nest location within the floodplain in the upper half of the site, at intervening zones, and from the stream bottom between sampling stations 2 and 3. Cores were also taken from other parts of the riparian zone with the peat sampler where soft, low-bulk-density material was available. Firmer soils were extracted with a standard hammer/bucket corer. In this way, the extent and continuity of certain subsurface features were evaluated.

The wetland soil was analyzed for several components that affect groundwater hydrology and geochemistry, including water content, percent carbon and nitrogen, and bulk density (Table 1). Sample cores were collected and brought to the lab for analysis. Each core was divided into 20 cm depth intervals. Soil moisture content was determined by drying samples at 105 °C, and were reported on a wet weight basis. Because the soil samples were saturated, pore volume could be estimated by the water content. By this method, the water of hydration of the organic matter in the soil would end up being included in the pore volume estimate. Bulk density was determined by dividing the dry weight of a sample by the volume of water displaced by the wet sample.

3.5. Rainfall measurements

Rainfall data were obtained from an on-site meteorological station, which logged data at 10 min intervals. Snowfall totals were converted to rainfall equivalents.

3.6. Chemical analyses

Stream and groundwater samples were analyzed for NO_3^-, Cl^-, and SO_4^{2-} with an ion chromatograph (Dionex DX-120 IC, Sunnyvale, CA, USA) fitted with an anion exchange column (Dionex IonPac AS9-SC,

Table 1
Soil characteristics

Depth (cm)	Bulk density		% C		% N		% Moisture		K (cm/s)	
	Site A	Site B	Site A	Site B	Site A	Site B	Site A	Site B	Site A	Site B
0–10	0.29	0.51	18	18	0.9	1.1				
10–20	0.46	0.34	10.5	11	0.68	0.68	73.5	78.1		
20–30	0.33	0.29	14	17	0.86	0.92				
30–40	0.28	0.24	15.8	18	0.9	0.96	57.9	77		
40–50	0.26	0.23	18.8	17.5	0.93	0.73			1E-05	2E-05
50–60	0.28	0.47	16	13	0.81	0.55	77.8	68.7		
60–70	0.29	0.3	17.3	15	0.74	0.63				
70–80	0.34	0.49	13.3	10.2	0.61	0.38	71.7	69.7		
80–90	0.41	0.55	11	8.6	0.46	0.3			4E-05	6E-05
90–100	0.58	0.47	8.3	14	0.28	0.5	78.9	59.8		
100–110	0.49	0.29	10.5	18.7	0.4	0.7				
110–120	0.23	0.22	28.2	27	0.95	0.92	67.9	77.2		
120–130	0.22	0.27	29.8	19.3	0.88	0.71			9E-06	8E-06
130–140	0.25	0.41	25.3	11.2	0.82	0.44	63.5	71.1		
140–150	0.3	0.45	17	11.3	0.63	0.4				
150–160	0.42	0.6	4.3	8.3	0.25	0.31	44.9	61.1	4E-06	5E-06
160–170	0.75	1.13	1.3	2.5	0.1	0.11		34.1		
170–180	1.5	–	0.2	–	0.03	–	32.7	–		
Aquifer (210–230)	–	–	–	–	–	–	–	–	1E-03	2E-03

Soil bulk densities, carbon percentages, nitrogen percentages, hydraulic conductivities, and moisture contents with depths for two nest locations along the C piezometer transect. Site A is soil core and piezometer nest 5 m from stream channel (C6), site B is core and nest 15 m from channel (C4).

Sunnyvale, CA, USA). The detection ranges were: 0.1–30 mg/l for NO_3^-, 1–60 mg/l for Cl^-, and 1–40 mg/l for SO_4^{2-}.

4. Results

4.1. Stream and floodplain configuration and orientation

Fig. 2 is a plan-view topographic map of the upper portion of the riparian zone. One notable aspect of this stream head area (especially near stations 2 and 3) is that the channel itself does not lie directly in the valley axis, but rather on the eastern flank of the valley floodplain. The off-axis orientation of the stream was likely due in part to the lack of soil cohesion within much of the floodplain. The soils around the valley axis, especially in upwelling zones, had high organic matter contents (~25% on average) and were 60–80% water by wet weight (see Table 1), depriving them of significant cohesiveness. Stable channel structures, and specifically channel heads, do not tend to form in non-cohesive material (Dunne, 1980). The left (eastern) bank of the main stream channel consisted of the edge of firmer, more cohesive soils on the eastern hillslope. The upwelling zones and secondary channels, on the other hand, did lie along the valley axis, and as a result, most of the groundwater was discharged into the valley axis rather than under the stream channel, with the stream channel (erosional feature) spatially distinct from the active zones of groundwater discharge to the floodplain surface. The groundwater discharge zones and associated sub-channels were oriented differently from other erosional features (gulleys, hollows, and other runoff-generated surface features) as well, parallel rather than perpendicular to the stream channel. This has seldom been noted in literature that addresses asymmetrical stream flow generation, which typically concentrate on the impact of topography, saturated overland flow and other runoff-related processes (e.g. Anderson and Burt, 1978). Areas that exhibited the greatest flow increase per length under baseflow conditions (station 2–3) were not the same areas that displayed the largest increase during storm events (station 3–4), when surface runoff processes were the dominant mechanisms for stream flow generation.

4.2. Soil/sediment characteristics

4.2.1. Soil characteristics

The basic geomorphological/sedimentary structure of the study site is a relatively permeable agricultural upland adjacent to a wetland valley. The wetland soil taxonomic classification is Typic Haplosaprist. The soil series in the upper part of the riparian zone is classified as Johnston Silt Loam (very poorly drained). In the lower valley section the soil is classified as Bibb Silt Loam (poorly drained). The valley wetland soils are generally less permeable and thus would normally be expected to act as a semi-confining 'cap' to the underlying (highly transmissive) sand and gravel aquifer. In the absence of preferential flow mechanisms, the less-conductive wetland soils should inhibit groundwater from emerging onto the floodplain (Devito et al., 2000).

4.2.2. Hydraulic characteristics

There were continuous sand layers (~5 cm thick) at common depths within the wetland soil, between approximately 80–95 and 120–130 cm below the surface. These layers had higher hydraulic conductivity (K) values than the rest of the wetland soil (see Table 1). K values varied by almost 5 orders of magnitude within this system as a whole, and by as much as 3 orders of magnitude within a single profile (McCarty and Angier, 2001). Similar variations in K values (3 orders of magnitude) were observed in a study by Fraser et al. (2001). However, that study involved a peatland with an unsaturated zone, whereas there was little or no unsaturated zone in the area discussed here. Other studies that have documented large K variations commonly show K decreasing with depth (e.g. Devito et al., 1996). The observed variations in K values at this site indicated that certain portions of the otherwise confining soil cap were far more likely to transmit water through the soil zone (upper 2 m). These layers provided subsurface pathways for preferential flow within a body of relatively non-conductive material, and were most common and continuous (and extensive) within a wide swath (at least 50×100 m) of the wetland, in the area where there was also a preponderance of groundwater upwelling (discharge) zones. Actively discharging macropores were visible on the land surface within some of these upwelling zones, indicating likely connection with the deeper subsurface. This supposition was supported by the presence of fine sand visibly discharged from macropores along the stream channel side; the bulk of the wetland histosol was fairly sand-free, with the nearest source for sand being the shallowest sand layer at least 80 cm below the surface. In addition, numerous continuous macropores (some vertically oriented) were present in many soil cores extracted from this area.

4.3. Stream flow

Stream flow at the site varied substantially, both spatially and temporally. Fig. 3 shows stream flows for stations 2–5 for the three-year period from Dec. 1998 to Dec. 2001. Fig. 4 shows rainfall for the site from 1999 to 2001. 1999 was a dry year, 2000 was more nearly normal, and 2001 became dry in the latter part of the year. There were notable seasonal differences in stream flows (with highest baseflows typically from November to April), but these were not as great as differences between average annual flows (e.g. 1999 vs. 2000). This was especially evident at station 5 (the outflow point for this first-order stream), with resulting implications for contaminant flux out of this system.

Spatial variability in stream flow characteristics was also evident (Fig. 3). Stream flow was usually lowest at station 2. However, this section of the stream had the most consistent flow regime. During drought conditions (Summer 1999), flow ceased in the stream, except between stations 2 and 3. This part of the stream was constantly fed by exfiltrating groundwater, and did not appear to be as strongly affected by (short-term) meteorological variability as the rest of the stream. When the rest of the channel was dry, flow at station 3 remained about 50% of five-year-average summer baseflow for that station. There appeared to be groundwater sources for this part of the stream that were relatively unaffected by meteorological conditions.

The arrangement of stream sampling/monitoring stations allowed independent analyses of stream segments between stations. Correcting for stream length between stations revealed that additions to stream flow were not uniform along the length of

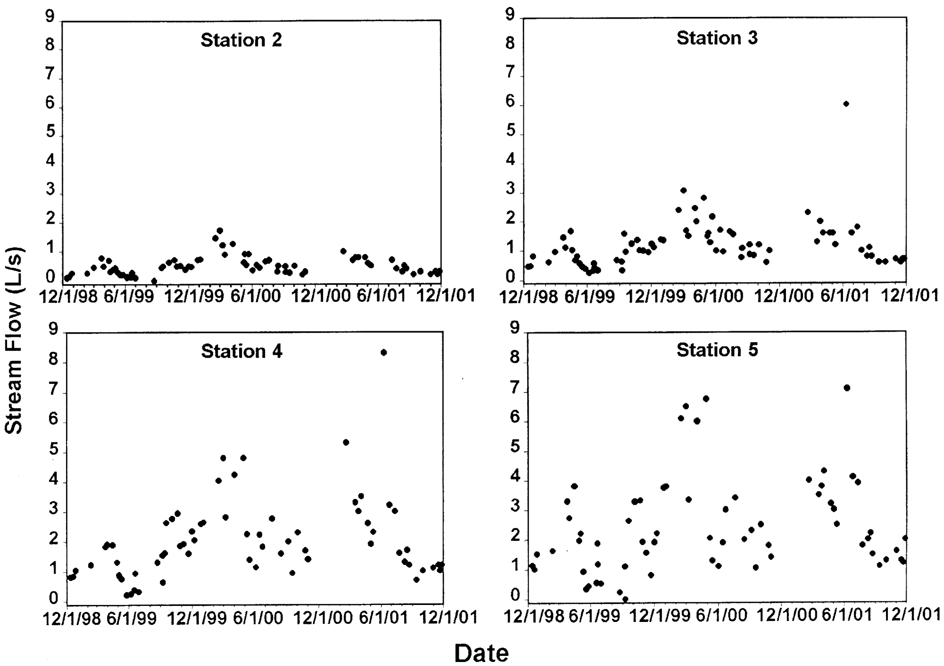

Fig. 3. Stream flows. Stream baseflows at stations 2–5 from December 1998 to December 2001 are shown. Note the seasonal and interannual variations, particularly downstream (stations 4 and 5).

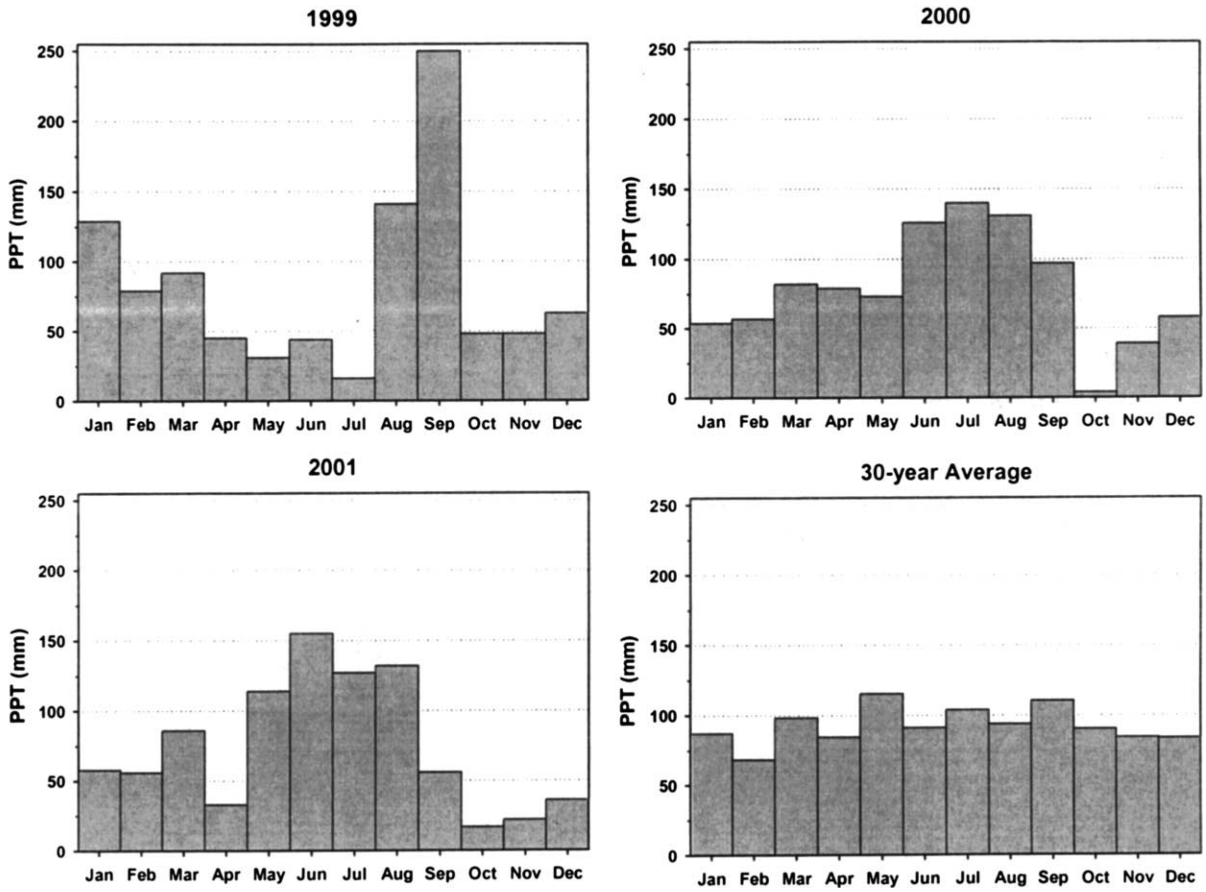

Fig. 4. Rainfall. Monthly precipitation for 1999, 2000, and 2001, recorded at an on-site meteorological station. 30-year (1971–2000) monthly averages for Beltsville, MD also shown.

the stream. Fig. 5 shows the amount of stream flow added between stations (normalized for stream lengths) over time. Except during periods of high flow, the most flow added per unit stream length typically occurred between stations 2 and 3. This coincided with the portion of the riparian zone that exhibited surface-saturated conditions at all times. Unlike the rest of the riparian zone, where surface-saturated areas were few, small and transient, this portion had at least 25% of its surface continuously under standing water. Many of these saturated areas were fed by foci of rapidly exfiltrating groundwater. In some places, groundwater emerged onto the land surface at a rate such that sub-channels formed to drain the water and carry it to the stream channel. These zones of robust groundwater emergence (upwelling zones) typically accounted for a disproportionate amount of total stream flow generated, and were capable of delivering substantial amounts of groundwater contaminants to the surface. One such upwelling zone, the origin point for the secondary channel (Fig. 2), was especially important to stream flow as a whole. This small (4.8 m^2) upwelling area comprised about 0.006% of the total riparian area (or approximately 0.001% of the entire catchment), yet supplied on average 4% of total stream flow. The total volume of groundwater emerging from this point was relatively constant compared to the rest of the system; during low-flow periods this point contributed a greater proportion of total stream flow, under high-flow

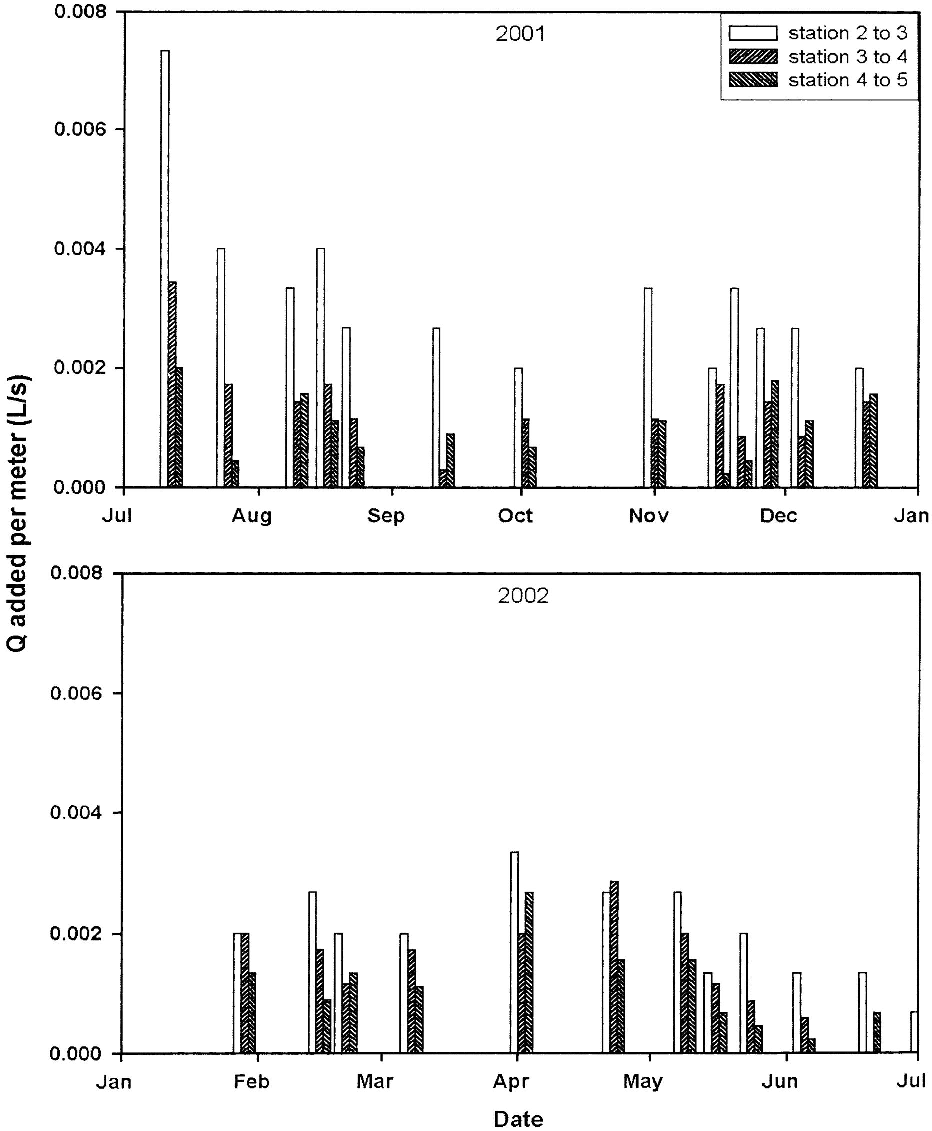

Fig. 5. Flow added per unit meter of stream. Stream discharge (Q) added between stations, per unit meter of stream length. A one year period is shown, from July 2001 to July 2002 (baseflow conditions only). In most cases, the greatest amount of flow increase (per meter of stream length) is between stations 2 and 3.

regimes this point supplied a smaller percentage of total flow. During the Summer drought of 1999, the entire stream channel dried up, except for the section that was fed by this upwelling zone and by other nearby (highly active) groundwater discharge zones. Discharging streamside macropores delivered groundwater directly into the stream channel most abundantly in this section as well.

Fig. 6 shows secondary channel flow vs. stream flow at station 3 (which is about 30 m downstream of where the secondary channel joins the main stream stem B see Fig. 2). Discharge from the secondary channel varied by only 0.1 L/s between the highest and lowest recorded flows. The secondary channel origin (associated with piezometer nest C5) produced enough groundwater to generate flows of 40–60 ml/s.

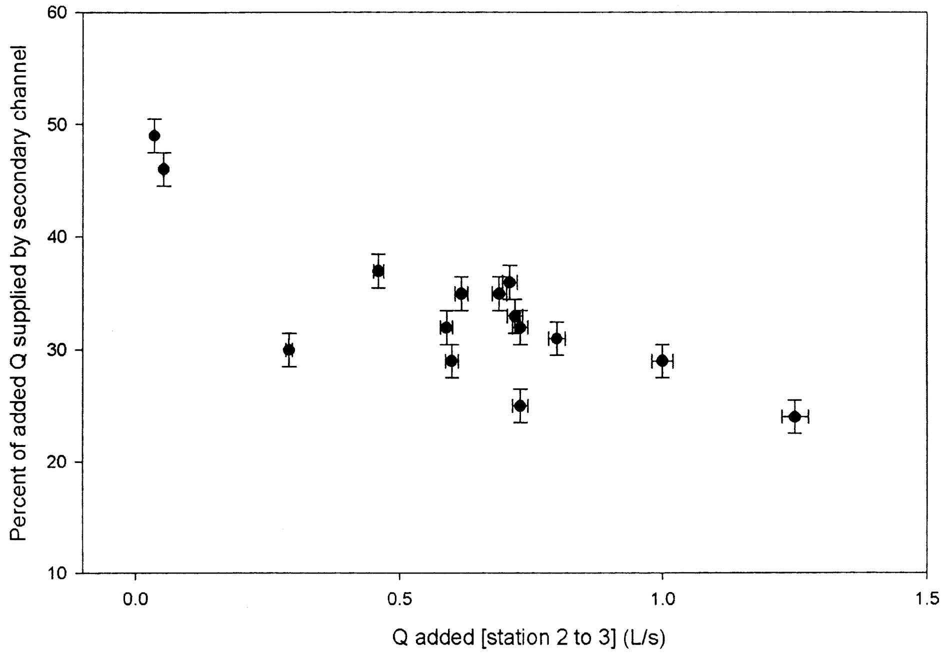

Fig. 6. Percent of flow added between stream stations 2 and 3 contributed by secondary channel. Shows the relationship between the amount of stream flow added between stations 2 and 3 and the percentage of that added flow that is supplied by the secondary channel. The greater the amount of total added stream flow, the smaller the relative contribution of the secondary channel to that flow increase.

The tertiary channel origin (associated with piezometer nest C3) also had measurable discharge to the surface (15–35 ml/s). Flows increased over the lengths of the secondary and tertiary channels as well. Secondary channel outflow was usually about 30–35% of total flow added to the stream between stations 2 and 3, except under very low-flow conditions, when its contributions were as great as 50%.

4.4. Temporal and spatial variations in groundwater behavior

In piezometer transect B (Fig. 2), total hydraulic heads at the same depth (~2.3 m) within the aquifer were higher than the land surface starting about 15 m from the stream. The potential for groundwater exfiltration was especially great at about 5–10 m from the stream, where total head (and water within the piezometers) was typically ~50 cm above ground. This corresponded with a very large active upwelling zone and area of year-round surface saturation.

Fig. 7 shows hydraulic gradients along the B transect from April 1999 to April 2000. The data indicated that the intensity of the vertical gradient for B3 was highly variable. However, most of the time this area was nearly hydrostatic. B4 showed some variability as well. During the Summer drought of 1999 this nest became relatively inactive. However, once normal stream flow resumed, this area recovered and became a groundwater discharge zone. The only time this nest showed recharge characteristics was during flooding caused by hurricane Floyd (September 19, 1999), when gradients reversed strongly; however, recovery here was quick, and the gradient reversal lasted only as long as there was an overburden of standing water on the floodplain. The B5 piezometer nest lies within a large upwelling zone, where vertical gradients were strongly positive all year with relatively little change. This area was a continuous supplier of groundwater to the surface, and much of the pooled water could be seen entering the main stream channel through macropores that connected the saturated area to the stream bank. The horizontal gradient from B2 to the stream channel (B6 nest) was also plotted in Fig. 7. The horizontal

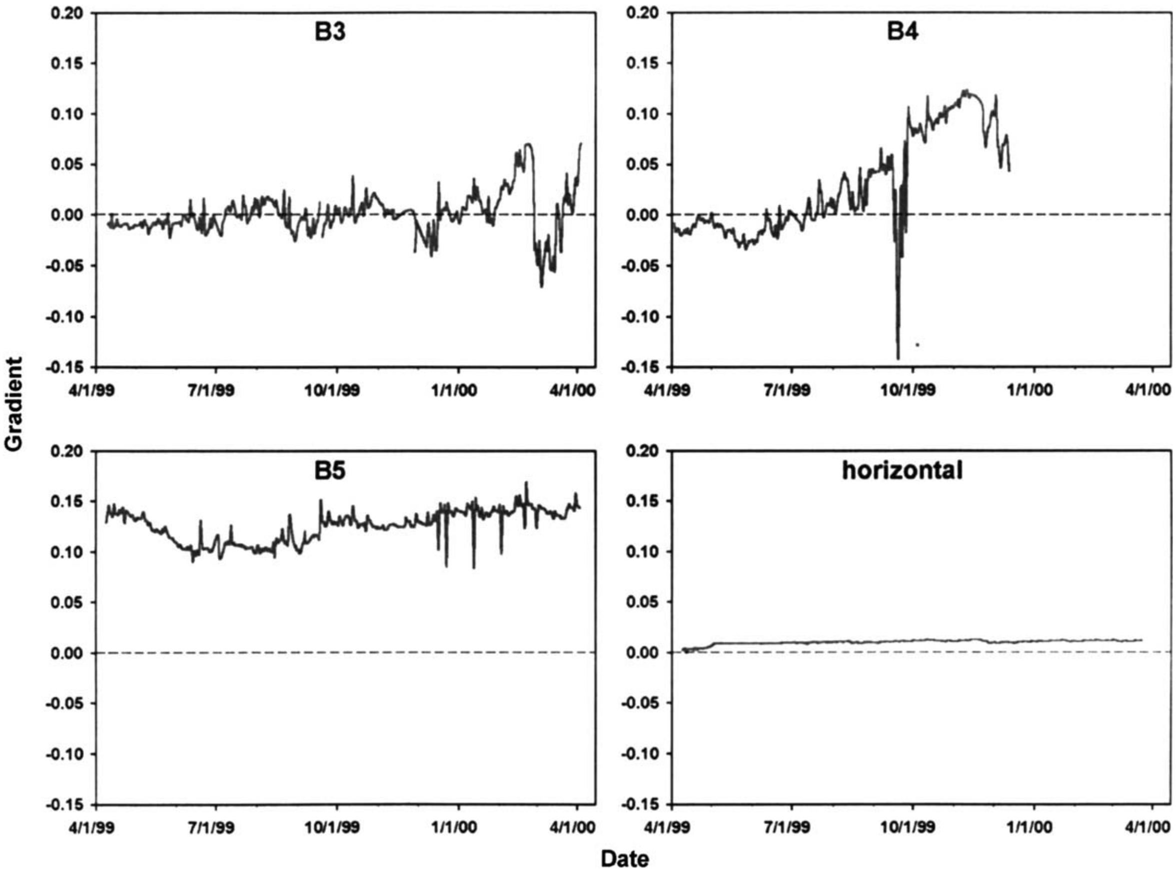

Fig. 7. Hydraulic gradients for B Piezometer transect. Vertical gradients for piezometer nests B3 (hillslope), B4 (base of hill) and B5 (active groundwater upwelling zone) are shown, along with the horizontal gradient from B2 (top of hill) to B6 (stream edge), from April 1999 to April 2000. Gradients within the upwelling zone (where groundwater continuously discharges to the surface) at B5 are consistently high, while horizontal gradients are consistently very low, indicating a likelihood that groundwater will travel upward onto the floodplain rather than horizontally into the stream channel.

gradient was very weakly positive and unchanging, indicating that horizontal groundwater flow was probably not that important in this part of the wetland.

4.5. Surface and ground water NO_3^-

Stream NO_3^- concentrations were temporally and spatially variable at this site. Baseflow NO_3^- concentrations were usually highest at stations 2 and 3 (Angier et al., 2001), which was fed by a series of upwelling zones on the adjacent floodplain. This reflected the characteristics of the emergent groundwater in this section. Table 2 shows discharge (flow), NO_3^- concentration, and NO_3^- flux from the secondary channel on the floodplain (see Fig. 2) where it drained into the main stream channel, from a large continuously discharging macropore in the stream channel side (between stations 2 and 3), within the stream channel at station 3 (which includes contributions from the secondary channel and several discharging macropores) and at station 5 (the outflow point for stream flow in this watershed). Discharge, concentration and flux data are also included for the upwelling zone associated with the C5 piezometer nest (Fig. 2), which was the origin point for the secondary channel, and

Table 2
Observed wetland NO_3^- sources

Location	Discharge (L/s)	NO_3^- concentration (mg/L)	NO_3^- flux (mg/s)
Stream (station 3)	0.87	5.3	4.6
Macropore	0.08	7.8	0.6
Secondary channel	0.29	6.3	1.8
C5 (surface)	0.09	8.2	0.7
C5-s (80 cm)	–	11.2	–
C5-m (150 cm)	–	16.8	–
C5-d (240 cm)	–	20.6	–
Outflow (station 5)	1.93	2.7	5.2

Discharge, NO_3^- concentration, and NO_3^- flux (where applicable) are given for major stream flow source contributions in the upstream part of the riparian zone. Stream station 3 includes inputs from the secondary channel and macropore. Data for C5 piezometer nest are included (depths below surface are listed for each piezometer: e.g. C5-s = 80 cm below surface). C5 (surface) is the origin point of the secondary channel. Data for stream outflow from the watershed (station 5) are also given. Sampled 16 Aug. 2000.

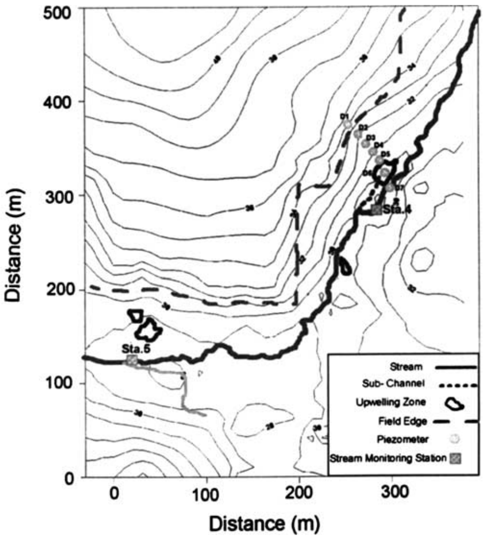

Fig. 8. Plan-view topographic map of lower study site. Depicts the lower half of the riparian zone, including stations 4 and 5. Piezometer transect D is shown. The sole sub-channel here (dotted line, near station 4), unlike upstream, is only active under high moisture conditions.

NO_3^- concentration for each of the three C5 piezometer depths (*s*, *m*, and *d*) are listed.

4.6. Comparison with other portions of riparian zone

The upstream area of extensive groundwater discharge differed from other portions of the riparian zone in physical appearance, percent of total stream flow supplied, and geochemistry. Fig. 8 is a close-up plan-view of the lower (downstream) portion of the site. Note that there are few saturated surface areas. The behavior and geochemistry of the riparian system were markedly different here. Comparison of NO_3^- in the source water (aquifer groundwater) and surface water gave an indication of the degree to which NO_3^- was removed. Although the groundwater beneath the field contained agricultural NO_3^- levels similar to the field upstream (typically about 15–20 mg/l), little of that NO_3^- ended up in the stream channel in this area. In addition, excess dinitrogen (based on dissolved N_2/Ar ratios) was detected in more of these wells, evidence that denitrification was probably taking place (Martin et al., 1995; Blicher-Mathiesen et al., 1998; Mookherji et al., 2003). There were also differences in soil between this portion of the riparian zone and the area further upstream. Although there was still abundant macroporosity, this area lacked the continuous and extensive sand layers found upstream, suggesting that macroporosity alone may not be indicative of circumvention of riparian zone function.

The subsurface hydrology in the lower portion of the watershed was different from that of upstream areas. Here, there were far fewer upwelling zones, and none of the continuously running sub-channels that were found upstream. Consequently, the hydrological characteristics of the groundwater were different as well. This was reflected in the gradient data for the D piezometer transect, which intersected a very small upwelling zone on the riparian floodplain.

Hydraulic gradients for this transect are shown in Fig. 9, including vertical gradients for D4 (base of hillslope), D6 (weakly active upwelling zone), D7 (within the stream channel), and horizontal gradient from D2 (top of hill) to stream (D7 nest). D4 showed substantial variability in response to rain events. D6 exhibited a fairly constant, positive vertical hydraulic gradient, but this decreased during the drought of 1999. However, most of the potential for groundwater discharge appeared to be directly under the stream channel at D7, which displayed the strongest vertical hydraulic gradients. The horizontal gradient along

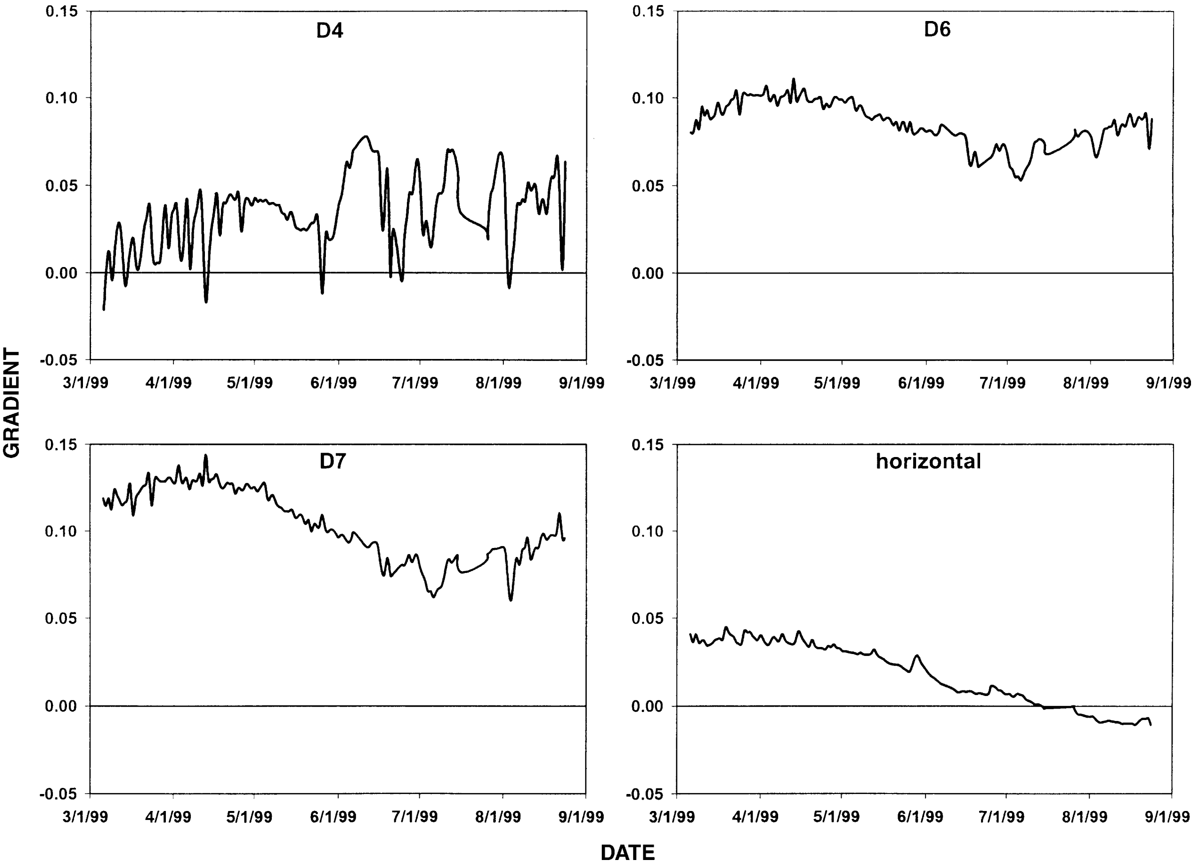

Fig. 9. Hydraulic gradients for D Piezometer Transect. Vertical gradients for piezometer nests D4 (base of hill), D6 (groundwater upwelling zone) and D7 (stream channel) are shown, along with the horizontal gradient from D2 (top of hill) to D7, from April 1999 to September 1999. Gradients are strongest beneath the stream channel, indicating a likelihood for groundwater to emerge directly into the stream in this area.

the D transect was significant in the wetter seasons, but as the drought of Summer 1999 increased in severity, the horizontal gradient steadily decreased. Finally, by mid-July 1999, the horizontal gradient approached zero and even became slightly negative. The stream should have started losing water to the aquifer at this time, but was already dry.

5. Discussion

5.1. Stream configuration and orientation

Examination of Fig. 4 shows the zones of groundwater exfiltration along a line within the valley axis distinct from the (off-axis) stream channel. This provides evidence that a surface erosional feature (stream channel) need not correspond spatially with groundwater discharge locations. Vertical hydraulic gradients were higher beneath the exfiltration (upwelling) zones (0.16–0.23) than under the stream channel (0.05–0.09) in this area. These upwelling zones contributed disproportionately to total stream flow, and were responsible for much of the stream flow added between stations 2 and 3. Under baseflow conditions, about 50% of total stream flow generated between stations 2 and 3 was contributed by upwelling zones arrayed parallel to the stream within the floodplain; 35–40% of flow added by a secondary/ tertiary sub-channel system draining an upwelling area (see Fig. 2), 10–15% contributed by two large macropores draining a nearby upwelling zone. These same upwelling zones, and associated secondary channels, contributed disproportionately to total stream NO_3^- loads (∼50%) as well. However, average soil *K* values (3.2E-04, derived from Table 1) for the wetland sediments could not account for the amount of groundwater exfiltration and stream flow increase in this area. Preferential flow, particularly through macropores (many of which have been observed actively discharging groundwater onto the floodplain surface within upwelling zones) and subsurface macropore systems, was responsible for most of the extra water (and NO_3^-) added to the stream along this reach.

This indicates conditions under which disproportionate amounts of total stream water flow and groundwater contaminant fluxes can be supplied to a stream by a small area. The constant high vertical hydraulic heads beneath the wetland soil may help give rise to the low soil bulk densities and high water contents found here, and enhance preferential bypass flow from the subsurface to the surface (due to the constant high underlying water pressure). The off-axis stream orientation, resulting from lack of cohesion and inability to sustain channel structure, would then be symptomatic of these conditions. The preponderance of subsurface preferential flow as a means of stream flow generation increases the likelihood that these areas will contribute disproportionately to stream contaminant load (Angier et al., 2001, 2002).

5.2. Soil/sediment characteristics

The hydrologic setting and hydrologic properties of the soil were very important for groundwater delivery within the wetland. Strong upward hydraulic pressure within the aquifer created conditions wherein heterogeneities and preferential flow paths within the wetland soils permitted intense, focused discharge of groundwater onto the surface (Hill and Siegel, 1991; Angier et al., 2001). The more transmisive layers in the subsurface (Table 1) probably acted as large-scale preferential groundwater transport sites. Calver (1990) suggested that subsurface features may direct groundwater to certain stream areas, and explain why some stream sections in his study exhibited greater rates of flow increase per contributing catchment area. These areas of efficient stream flow generation can have an impact on the remediation capability of the entire ecosystem. Many previous studies have focused on the bulk properties of a riparian ecosystem, whereas more attention may need to be given to zones of preferential flow and areas of enhanced stream flow generation.

5.3. Stream flow

Surface-groundwater interactions are crucial to stream flow generation, and to contaminant transport (Herczeg et al., 1992; Emmett et al., 1994). Once groundwater has emerged onto the land surface, focusing and channeling this emergent water is the most effective means of delivering water and contaminants to a stream (Ashby et al., 1998; Devito et al., 2000). This was observed at the study site. Evidence of focused groundwater exfiltration to the floodplain surface as a major supplier of total stream flow at this site is similar to the phenomenon of 'springing' or seepage faces at hillslope bases (Devito et al., 1996; Ashby et al., 1998) seen in higher-relief ecotones. However, this phenomenon is less widely appreciated in low-relief areas, and the location of upwelling zones along a line roughly corresponding to the valley axis (but not beneath the stream channel) has been less often noted. Devito et al. (2000) and others have observed similar phenomena, but have neither explicitly documented the orientation of such, nor recorded quantitative contributions from these areas. The location of focused upwelling zones, which provided a disproportionate amount of stream flow per wetland area, at or near the stream head for this first-order stream was probably not coincidental; just as hillslope springs are often the ultimate origin points for first-order streams in higher-relief regions (Dunne, 1980), so extensive and highly active upwelling (groundwater discharge) zones are likely indicative of origin points for first-order streams in low-relief environments. Documentation of the preponderance of groundwater-fed wetlands associated with first-order stream head areas in Maryland (Haas, 1999) lends support to this hypothesis.

5.4. Temporal and spatial variations in groundwater behavior

Spatial uneveness in stream flow generation caused by variabitity in surface runoff contributions to stream flow has long been appreciated (Anderson and Burt, 1978; Calver, 1990), but a similar phenomena under baseflow conditions resulting from spatially consistent zones of focused groundwater exfiltration to a floodplain surface has been less thoroughly documented. The relationship between groundwater discharge zones and wetland habitat maintenance has also been often noted (e.g. Siegel, 1988), but assumption of a relatively simple uniform hydrology in these settings (Devito et al., 1996) may be incorrect. Groundwater discharge to the surface in this study site was focused and localized within the permanently saturated area, and rather than temporal variablity in saturation being reduced by relatively diffuse discharge across the area (Devito et al., 1996), discharging groundwater pooled out onto the floodplain surface (when it was not channelized) from discrete sources, helping to sustain saturated conditions throughout this area. Small hummocks and microtopographic features typically projected above the saturated land surface.

To better understand how exfiltration rates related to hydraulic gradients, it was useful to examine conditions where a specific site generated surface flow and compare measured vertical gradients at that point with measured surface flow. This was done at the origin of the secondary channel, the C5 piezometer nest (see Fig. 2). Here the zone of intensive upwelling was fairly small and well-defined, and the exfiltrating groundwater was immediately channelized. Fig. 10 shows the relationship between vertical gradients at the C5 nest and flow generated from that point. There was a positive correlation between vertical gradient and amount of flow generated at the surface. A linear regression line was passed through the data points and extrapolated back to the *Y*-axis. The point of intersection was approximately a gradient of 0.14. This indicated the critical gradient below which upwelling groundwater would not be expected to emerge rapidly enough to generate surface flow.

The origin point of the tertiary channel (C3 nest) was also suitable for this type of analysis. There was a limited area of upwelling here as well, and it was also

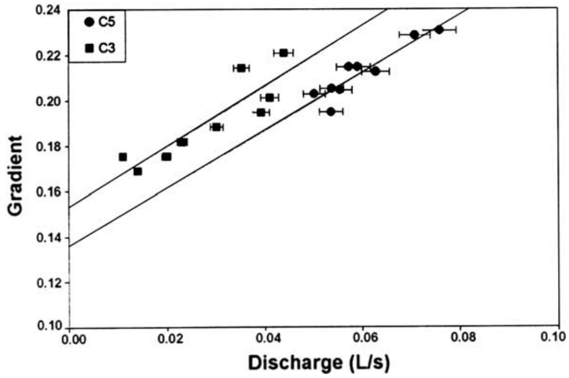

Fig. 10. Discharge vs. Gradient for Groundwater Upwelling Points. Hydraulic gradients are plotted against discharge (*Q*) for the origin points of the secondary channel (C5 piezometer nest) and tertiary channel (C3 piezometer nest). These origin points are small areas of intense, channelized groundwater exfiltration. Higher gradients in the subsurface correspond with increased discharge to the surface. Trends in both nests are similar.

channelized. As with the secondary channel, there was a positive correlation between vertical gradient and amount of flow generated at the surface (Fig. 10), and the slope was very similar. In this case the *Y*-intercept for the regression line was 0.15. Thus there was good agreement on the critical gradient above which channelized surface flow was initiated.

Direct measurement of the amount of groundwater discharged to the surface and delivered to a stream channel, and the quantity of NO_3^- exported as a result of this process, had often been considered implausible because of the assumption that groundwater discharge from a wetland to a stream was relatively insignificant and too difficult to measure (Siegel, 1988).

Reviews of studies involving hydrologic controls on NO_3^- transport indicate a growing appreciation of the importance of near-stream areas in NO_3^- delivery, but typically focus on behavior in response to storms events (especially the role of saturated overland flow) and the impact of topographic controls on subsurface flow (e.g. Cirmo and McDonnell, 1997). Incorporating piezometric groundwater data with stream and sub-channel flow data and NO_3^- flux information under baseflow conditions gives a better understanding of the impact of preferential flow and focused groundwater exfiltration on riparian zone NO_3^- removal function.

5.5. Surface and ground water NO_3^-

The upwelling zones on the floodplain, and discharging macropores within the stream channel, were responsible for much of the total NO_3^- load conveyed by the stream (and exported from the watershed). Under most baseflow conditions, it was the region between stations 2 and 3 that usually displayed the highest surface water NO_3^- contents, and provided a disproportionate amount of total NO_3^- flux to the stream (Angier et al., 2001). Table 2 shows that NO_3^- fluxes contributed by two preferential flow paths, the secondary channel on the floodplain and a copiously discharging macropore in the stream channel, together accounted for nearly half (2.4 mg N/s) of the total flux exported (5.2 mg N/s) on this sampling date. This was a typical range and distribution for baseflow conditions in this watershed. These focused zones of groundwater contribution to stream flow were significant not only for total stream flow generated (~ 19% of total stream flow supplied by two preferential flow paths—the secondary channel and a single macropore), but also for total stream NO_3^- flux (~ 46%).

Within the secondary channel, most of the sub-channel flow and NO_3^- flux was generated at the site of the C5 piezometer nest. This area of intense groundwater exfiltration supplied a disproportionate amount of total stream flow and NO_3^- flux, with about 31% of secondary channel flow (4% of total stream outflow) and approximately 39% of the secondary channel NO_3^- flux (13.5% of total stream NO_3^- flux) emerging onto the floodplain surface and conveyed to the main stream channel (along the secondary channel) from this point. The groundwater beneath this upwelling point showed evidence of enhanced NO_3^- delivery (Table 2). Groundwater within the underlying aquifer (C5-d) was relatively high in NO_3^- (20.6 mg N/L), as was the case throughout most of the riparian zone subsurface at this depth (240 cm below surface). However, there was substantial penetration of N-bearing groundwater up through the soil profile at this point, with emergent groundwater displaying the highest NO_3^- concentrations (8.2 mg N/l) usually seen in surface water at this study site. Nearby areas on the floodplain that displayed little or no visible groundwater delivery to the surface showed 100% removal of NO_3^- within the first 60 cm above the aquifer/wetland soil interface (~120 cm below the surface) (Angier et al., 2002).

Discharge of (N-bearing) groundwater onto the land surface (and into the stream channel) via preferential flow sustained the riparian wetland conditions in this area and accounted for much of the total stream flow in this watershed. This upstream area had many discharging macropores within the stream channel (other than the one sampled) and other (unchannelized) upwelling zones, which likely supplied additional NO_3^- to the stream along this reach. Thus, preferential subsurface flow (macropores and groundwater upwelling zones) provided a substantial portion of total stream flow and NO_3^- flux.

6. Conclusions

The typical model for lateral subsurface flow leading to denitrification posits that NO_3^- enters the groundwater from upland agricultural areas and flows laterally through the shallow subsurface of a riparian zone (Jordan et al., 1993; Lowrance et al., 1995). The shallow subsurface is under the influence of riparian vegetation, and often includes organic-rich soil and reducing conditions, all of which present a high potential for NO_3^- removal. Although these organic-rich soils are often characterized as poorly-drained, extensive biological (and hydrological) activity in the riparian corridor tends to generate a network of macropores. These macropores create preferential flowpaths through the soil, and may increase infiltration and exfiltration within the riparian zone. Macropores are typically considered in terms of enhancing infiltration (recharge) into the subsurface, yet they can also serve as foci for discharging groundwater (which has been less thoroughly examined). This can lead to heterogeneous, asymmetric groundwater contributions to the surface, and have significant effects on the overall denitrification potential of the ecosystem. It is therefore necessary to better understand hydrological processes in riparian zones before specific land management regulations (to enhance remediation function) can be successfully formulated and applied.

A simplified hydrologic model of horizontal flow was inadequate for describing groundwater behavior in this riparian wetland. The first indication of deviation from this model was exhibited by the surface water hydrology. Disproportionate stream flow generation between stations 2 and 3 led to a closer examination of extensive zones of groundwater exfiltration onto the floodplain surface in this area. Erosional features (stream channel structure) did not correspond to zones of groundwater exfiltration. The lack of linkage between areas of groundwater discharge and the stream channel indicated that these two phenomena could behave independently, and that channel morphology (created by relatively infrequent large storm runoff events) could be uninfluenced by the more common stream baseflow conditions (sustained primarily by subsurface preferential flow) that accounted for most of the total annual stream flow (and NO_3^- load). Examination of soil cores revealed the presence of significant stratigraphic features and macroporosity, indicating preferential subsurface flow potential. Piezometers instrumented in this area confirmed that hydraulic heads and gradients favored vertical groundwater exfiltration over horizontal flow. Sand pods and layers within the ($\sim$2 m deep) soil profile likely acted as the principal preferential flow mechanisms in the deeper portion of the wetland soil. Specific macropores or macropore systems probably acted as the primary conduits for groundwater flow from the subsoil to the surface (and had been explicitly observed in soil cores extracted from the site). This combination of factors led to the conclusion that a uniformly distributed horizontal groundwater flow regime should not be assumed for riparian zone studies. Preferential flow, especially in the upper (headward) portion of the catchment, played an important role in streamflow generation, and explained differences between expected and observed NO_3^- removal. In wetlands with very low bulk density soils, preferential flow may dominate the groundwater-surface flow regime. The appearance of large continually saturated zones and extremely soft soils seemed to be the most distinguishing visual surface feature of areas that contributed disproportionately to total stream flow (and NO_3^- flux). Considerable deviation from a valley axis-oriented stream configuration may also be a visually identifiable indicator of such areas.

Assuming uniform horizontal groundwater flow through the riparian ecosystem, conditions at this study site should have allowed most of the groundwater NO_3^- to be removed prior to discharge to the stream. Nevertheless, significant amounts of NO_3^- did reach the stream channel. This site was selected because it represented what appeared to be a fairly typical first-order agricultural watershed in this region. However, horizontal matrix flow through the riparian zone was the weakest element of flow in the subsurface, at least in those areas of enhanced stream flow generation and NO_3^- delivery. Research has shown that the denitrification capabilities of the riparian zone are closely linked to the hydrology of the system, and are not merely determined by the biogeochemical characteristics of the wetland soil. The vertical flow of groundwater observed in this riparian wetland indicates that simple parameters, such as riparian buffer width, are not sufficient for ascertaining the probable functionality of a riparian ecosystem. It is the interplay of hydrology and biogeochemistry that ultimately determines the effectiveness of a riparian zone as a natural groundwater remediation site. Since this study site appears to have many similarities to other such sites, it is likely that conditions here are not unique. Further detailed study of other sites should reveal whether this situation is common.

References

Anderson, M.G., Burt, T.P., 1978. Toward more detailed field monitoring of variable source areas. Water Resour. Res. 14, 1123–1131.

Angier, J.T., McCarty, G.W., Gish, T.J., Daughtry, C.S.T., 2001. Impact of a first-order riparian zone on nitrogen removal and export from an agricultural ecosystem. The Sci. World 1 (S2), 642–651.

Angier, J.T., McCarty, G.W., Rice, C.P., Bialek, K., 2002. Influence of a riparian wetland on nitrate and herbicides exported from a field applied with agrochemicals. J. Agricultural Food Chem. 50, 4424–4429.

Ashby, J.A., Bowden, W.B., Murdoch, P.S., 1998. Controls on denitrification in riparian soils in headwater catchments of a hardwood forest in the Catskill Mountains, U.S.A. Soil Biol. Biochem. 30, 853–864.

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

Bohlke, J.K., Denver, J.M., 1995. Combined use of groundwater dating, chemical, and isotopic analysis to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plain, Maryland. Water Resour. Res. 31, 2319–2339.

Bosch, D.D., Hubbard, R.K., West, L.T., Lowrance, R.R., 1994. Subsurface flow patterns in a riparian buffer system. Trans ASAE 37, 1783–1790.

Brinson, M.M., 1988. Strategies for assessing the cumulative effects of wetland alteration on water quality. Environ Manage 12, 655–662.

Calver, A., 1990. Stream head migration: an indicator of runoff processes on chalklands. Catena 17, 399–408.

Cirmo, C.P., McDonnell, J.J., 1997. Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: a review. J. Hydrol. 199, 88–120.

Cooper, A.B., 1990. Nitrate depletion in the riparian zone and stream channel of a small headwater catchment. Hydrobiologia 202, 13–26.

Crownover, S.H., Comerford, N.B., Neary, D.G., Montgomery, J., 1995. Horizontal groundwater flow patterns through a cypress swamp-pine flatwoods landscape. Soil Sci. Soc. Am. J. 59, 1199–1206.

Crum, J.R., Pierce, F.J., Vitosh, M.L., Knezek, B.D., 1990. Potential nitrogen contamination of groundwater as affected by soil, water, and land use relationships. Institute of Water Research, Michigan State University, East Lansing, MI. Report No. 89-G1569-04.

Devito, K.J., Hill, A.R., Roulet, N., 1996. Groundwater–surface water interactions in headwater forested wetlands of the Canadian shield. J. Hydrol. 181, 127–147.

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

Dunne, T., 1980. Formation and controls of channel networks. Prog. Phys. Geogr. 4, 211–239.

Emmett, B.A., Hudson, J.A., Coward, P.A., Reynolds, B., 1994. The impact of a riparian wetland on streamwater quality in a recently afforested upland catchment. J. Hydrol. 162, 337–353.

Fetter, C.W., 1994. Appl. Hydrogeology. Prentice Hall p. 691.

Fraser, C.J.D., Roulet, N.T., Lafleur, M., 2001. Groundwater flow patterns in a large peatland. J. Hydrol. 162, 142–154.

Haas, J.C.,. (1999) Prevalence of headwater wetlands and hydrologic flow paths in a headwater wetland. Masters Thesis, University of Maryland, College Park.

Herczeg, A.L., Barnes, C.J., Macumber, P.G., Olley, J.M., 1992. A stable isotope investigation of groundwater–surface water interactions at Lake Tyrell, Victoria, Australia. Chem. Geol. 96, 19–32.

Hill, A.R., Devito, K.J., Campagnola, S., Sanmugadas, K., 2000. Subsurface denitrification in a forest riparian zone: interaction between hydrology and supplies of nitrate and organic carbon. Biogeochemistry 51, 193–223.

Hill, B.M., Siegel, D.I., 1991. Groundwater flow and the metal content of peat. J. Hydrol. 123, 211–215.

Jordan, T.E., Correll, D.L., Weller, D.E., 1993. Nutrient interception by a riparian forest receiving inputs from adjacent cropland. J. Environ. Qual. 22, 467–473.

Lowrance, R., Altier, L.S., Newbold, J.D., Schnabel, R.R., Groffman, P.M., Denver, J.M., Correll, D.L., Gilliam, J.W., Robinson, J.L., Brinsfield, R.B., Staver, K.W., Lucas, W., Todd, A.H., 1995. Water Quality Functions of Riparian Forest Buffer Systems in the Chesapeake Bay Watershed, Chesapeake Bay Program, Technology Transfer Report 1995 p. 67.

Martin, G.E., Snow, D.D., Kim, E., Spalding, R.F., 1995. Simultaneous determination of argon and nitrogen. Ground Water 33, 781–785.

Martin, T.L., Kaushik, N.K., Trevors, J.T., Whiteley, H.R., 1999. Review: denitrification in temperate climate riparian zones. Water, Air, Soil Pollut. 111, 171–186.

McCarty, G.W., Angier, J.T., 2001. Impact of preferential flow pathways on ability of riparian wetlands to mitigate agricultural pollution. Proc. 2nd International Preferential Flow Symposium. Am. Soc. Ag Eng. 2001;, 53–56. Honolulu, HI.

Mitsch, W.J., Gosselink, J.G., 1993 Wetlands. Van Nostrand Reinhold, New York, NY (Publishers) 722 pp.

Mookherji, S., McCarty, G.W., Angier, J.T., 2003. Dissolved gas analysis for assessing the fate of nitrate in wetlands. J. Am. Water Resour. Assoc. 39, 381–387.

O'Connell, M., 1998. Combined hydrologic and geochemical study of storm and seasonal delivery of solutes to streamflows. PhD. Thesis, University of Maryland, College Park.

Peterson, B.J., Wollheim, W.M., Mulholland, P.J., Webster, J.R., Meyer, J.L., Tank, J.L., Marti, E., Bowden, W.B., Valett, H.M., Hershey, A.E., McDowell, W.H., Dodds, W.K., Hamilton, S.K., Gregory, S., Morrall, D.D., 2001. Control of nitrogen export from watersheds by headwater streams. Science 292, 86–90.

Pionke, H.B., Gburek, W.J., Sharpley, A.N., Schnabel, R.R., 1996. Flow and nutrient export patterns for an agricultural hill-land watershed. Water Resour. Res. 32, 1795–1804.

Sharpley, A.N., Meisinger, J.J., Breeusma, A., Sims, J.T., Daniel, T.C., Schepers, J.S., 1998. Impacts of animal manure management on ground and surface water quality, in: Hatfield, J.L. (Ed.), Animal Waste Utilization: Effective Use of Manure as a Soil Resource. Ann Arbor Press, Chelsea, MI, pp. 173–242.

Sharratt, B.S., 2001. Groundwater recharge during spring thaw in the prairie pothole region via large, unfrozen preferential pathways. Proc. 2nd International Preferential Flow Symposium. Am. Soc. Ag Eng. 2001;, 49–52. Honolulu, HI.

Siegel, D.I., 1988. The recharge–discharge function of wetlands near Juneau, Alaska: part I. Hydrogeological investigations. Ground Water 26, 427–434.

Sims, J.T., 1993. Environmental soil testing for phosphorus. J. Prod. Agric. 6, 501–507.

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