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SYNTHESIS AND EMERGING IDEAS

Groundwater nutrient concentrations near an incised midwestern stream: effects of floodplain lithology and land management

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Abstract It has been recognized that subsurface lithology plays an important role in controlling nutrient cycling and transport in riparian zones. In Iowa and adjacent states, the majority of alluvium preserved in small and moderate sized valleys consists of Holocene-age organic-rich, and fine-grained loam. In this paper, we describe and evaluate spatial and temporal patterns of lithology and groundwater nutrient concentrations at a riparian well transect across Walnut Creek at the Neal Smith National Wildlife Refuge in Jasper County, Iowa. Land treatment on one side of the stream reduced the grass cover to bare ground and allowed assessment of the effects of land management on nutrient concentrations. Results indicated that groundwater in Holocene alluvium is very nutrient rich with background concentrations of nitrogen, phosphorus and dissolved organic carbon that exceed many environmentally sensitive criteria. Average concentrations of ammonium exceeded 1 mg/l in several wells under grass cover whereas nitrate concentrations exceeded 20 mg/l in wells under bare ground. Phosphate concentrations ranged from 0.1 to 1.3 mg/l and DOC concentrations exceeded 5 mg/l in many wells. Denitrification, channel incision, land management and geologic age of alluvium were found to contribute to variable nutrient loading patterns at the site. Study results indicated that riparian zones of incised streams downcutting through nutrient-rich Holocene alluvium can potentially be a significant source of nutrient loadings to streams.

Keywords Alluvium · Denitrification · Incised channel · Nutrients · Riparian zone

Introduction

Recent attention has focused on the important role that subsurface lithology and stratigraphy play in controlling nutrient cycling and transport in riparian zones (DeVito et al. 2000; Hill et al. 2004). Subsurface variations in soil texture, organic matter content, denitrification potential, and other physical and chemical properties affect dynamics of dissolved organic carbon cycling (Jacinthe et al. 2003), nitrate removal (Hill et al. 2004; DeVito et al. 2000; Vidon and Hill 2004; Haycock and Burt 1993; Gold et al. 1998) and phosphate concentrations (Carlyle and Hill 2001). Because groundwater flowpaths in valleys are often complex with highly conductive sand and gravel lenses interspersed with less permeable silts, clays

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and peats (Haycock and Burt 1993; Simpkins et al. 2002; Hill et al. 2004), groundwater residence times are strongly affected by the stratigraphy of riparian zones (Cirmo and McDonell 1997). Buried organic-rich layers have been identified as important carbon sources supporting denitrification activity (Hill et al. 2000, 2004; Gold et al. 1998; Jacinthe et al. 1998). Owing to the complexities of subsurface stratigraphy in many riparian zones, Devito et al. (2000) and Hill et al. (2004) recommended that more detailed studies be conducted relating nutrient dynamics to subsurface lithology.

In Iowa, the majority of alluvial fill in valleys is Holocene in age collectively called the DeForest Formation (Bettis 1990; Bettis et al. 1992). The formation is divided into four members based on lithologic properties (texture, color, bedding structures and pedogenic alterations) and landscape associations and includes the Camp Creek, Roberts Creek, Gunder and Corrington members (Bettis 1990; Bettis et al. 1992). These members are mappable lithostratigraphic units across Iowa and in adjacent states (Bettis 1990; Mandel and Bettis 1992; Bettis and Autin 1997). The three alluvial units found in small tributary valleys (Camp Creek, Roberts Creek, Gunder members) were each deposited during a restricted time range during the Holocene, with the Gunder Member deposited between 10,500 and about 5,000 B.P., the Roberts Creek Member from 3,500 to about 500 B.P. and the Camp Creek Member from about 400 B.P. to present (Bettis et al. 1992). While texture of each member varies as source materials change, the fills are dominantly silty loamy and clayey, and buried organic matter is often preserved. The Roberts Creek Member consistently contains a higher content of organic carbon than the Gunder Member (Bettis et al. 1992).

Effects of alluvium lithology on shallow groundwater quality have been recognized in Iowa. Hallberg et al. (1983) observed that groundwater from piezometers completed within the Roberts Creek Member in the Big Spring Basin (northeast Iowa) had significantly lower nitrate concentrations than water sampled from tiles and streams. In the western Iowa Bluegrass Watershed, lowest nitrate concentrations in shallow groundwater over a 4-year period occurred in wells screened in Roberts Creek alluvium where annual concentrations were all <0.2 mg/l (Seigley et al. 1996). In contrast, annual nitrate concentrations in Gunder Member alluvium and upland loess ranged from 0.9 to 9.3 mg/l; and 21.6 to 26.4 mg/l, respectively. Elsewhere in larger river valleys, low nitrate concentrations observed in alluvial aquifers was attributed to denitrification occurring in organic-rich alluvium (Thompson 1984, 1986). Total dissolved phosphorus, though less studied than nitrate, was observed at concentrations as high as 1,030 ug/l in DeForest Formation alluvium in western Iowa (Burkart et al. 2004). Thus groundwater concentrations of N and P in alluvial fills can be quite high and differences in nutrient processing among alluvial members have been detected.

Despite the widespread occurrence of DeForest Formation alluvium across the Upper Midwest, few if any studies have examined nutrient dynamics in riparian groundwater at a site where subsurface lithology and stratigraphy have been described in detail. Lithologic, hydrologic and water quality conditions described herein document an alluvial system likely representative of the midcontinent United States where uplands are mantled by loess and till and the valleys contain loess and till-derived alluvium. Furthermore, in addition to ambient nutrient concentrations in groundwater reported in this study, a fortunate set of circumstances has allowed evaluation of the effect that land cover has on riparian nutrient dynamics near an incised stream. Hill et al. (2004) remarked that the relation between riparian vegetation and nitrate removal is often complex and results from this study provide confirmation.

The objectives of this study were to: (1) describe the subsurface lithology and stratigraphy at the Walnut Creek riparian transect within the lithostratigraphic framework developed for the Upper Midwest; (2) evaluate spatial and temporal patterns of nutrient concentrations observed in various stratigraphic units; and (3) assess the role that floodplain hydrology and land cover play in controlling nutrient concentrations in riparian groundwater. We hypothesized that the DeForest Formation alluvium is nutrient-rich and that management of riparian systems underlain by this alluvium should consider appropriate land use to minimize loss of N and P to streams.

Site description

The 5,218-ha Walnut Creek watershed is located in the Southern Iowa Drift Plain landscape region of

Iowa, an area characterized by steeply rolling hills and a well-developed drainage network (Prior 1991). The study site is situated in the central portion of the Walnut Creek watershed at the Neal Smith National Wildlife Refuge (NSNWR) in Jasper County Iowa (Fig. 1). Since 1995, large portions of the Walnut Creek watershed have been restored from row crop agriculture to native prairie and savanna at the NSNWR by the United States Fish and Wildlife Service. As of 2005, 1,224 ha have been planted in native prairie representing 23.5% of the watershed (Schilling and Spooner 2006). Most of the refuge is located in the lower portion of the basin; land use typical of the region is dominated by row crops (83% in upper Walnut Creek watershed; Schilling and Spooner 2006). Native prairie was planted in upland areas surrounding the study site between 1994 and 1996 whereas floodplain land use has remained in cool season grass, consistent with historical land use as pasture.

Walnut Creek flowing through the study site is incised to a depth (d) of 3 m into the floodplain. The measured channel width (w) was 10 m at the study reach and the width–depth ratio was 3.3. Stream sinuosity near the site was approximately 1.2, suggesting that Walnut Creek was channelized through this area in the past. Like many incised streams, discharge in Walnut Creek tends to be very flashy, responding rapidly to precipitation events and snowmelt. Overall, from 1996 to 2005, stream discharge at the downstream gaging station has ranged from a high of 13.9 m^3/s to a low of 0.002 m^3/s (Schilling et al. 2006a, b).

In 2001, hydrologic investigations were initiated at the study site because it is the location of ongoing efforts by the NSNWR to restore a portion of the floodplain from vegetation dominated by reed canary grass (*Phalaris arundinacea*) to native floodplain ecotypes. *P arundinacea* is an aggressive invasive species found throughout temperate North America that has been cultivated as forage grass because it is adapted to wide extremes in soil moisture (Galatowitsch et al. 1999). During the restoration process in 2002 and 2003, the west side of the riparian zone and floodplain of Walnut Creek was periodically (1) burned to weaken the reed canary grass and expose new shoots for herbicide treatment; (2) mowed; and (3) sprayed with herbicide (2% glyphosate) to effectively kill the treated *Phalaris arundinacea.* As a result, much of the overlying vegetation on the west side of the study transect was removed and bare soil was largely present from mid-2002 to fall 2003. In fall and winter 2003–2004, a native seed mix was planted in the management area and native plants were transplanted to the area. In 2004, the west

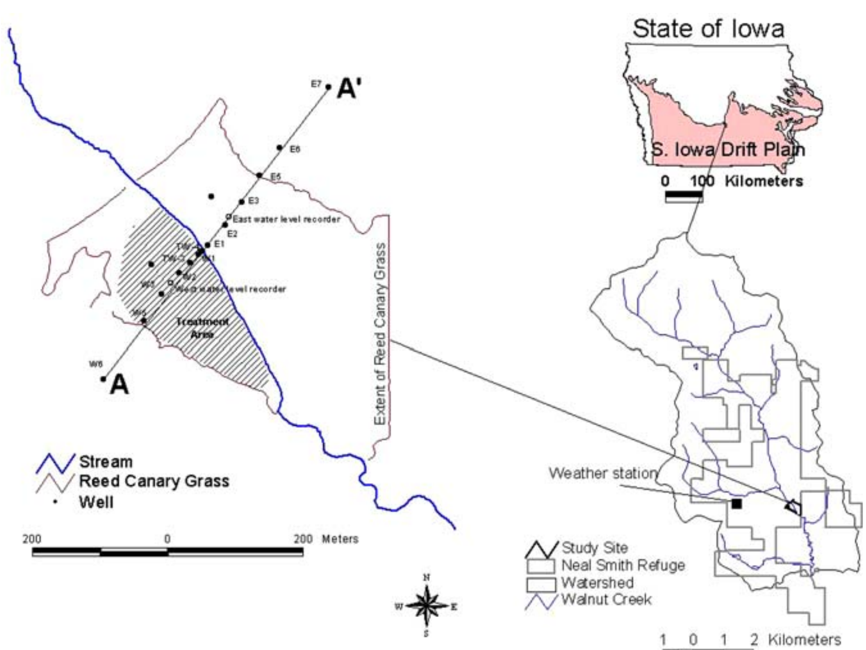

Fig. 1 Location map of study site

portion of the site consisted of a mixture of sedge meadow plants, such as tussock sedge (*Carex stricta*), prairie cord grass (*Spartina pectinata*) and winged loosestrife (*Lythrum alatum*) in addition to remnants of reed canary grass.

Several hydrologic investigations have been conducted at the study site in conjunction with the land treatment activities. Before land treatment began, background hydrologic and water quality conditions were established at the site. A series of 35 shallow, nested groundwater monitoring wells were installed in a transect across the Walnut Creek floodplain. The entire transect of wells spans a distance of 550 m from upland landscape positions on both sides of the floodplain (Fig. 2). Water level monitoring from 2002 reported in Schilling et al. (2004) described how channel incision of Walnut Creek altered the natural riparian hydrology at the site. Channel incision was found to have lowered the water table from the stream edge to a distance of approximately 30 m, thus creating a large unsaturated zone in the near-stream riparian zone compared to more distant floodplain zones. Hydraulic head monitoring during a runoff event in Walnut Creek indicated little potential for interaction of surface water with aquifer materials in riparian zone of the incised channel. Pre-treatment groundwater concentrations were measured in transect wells in fall 2001 and spring 2002. In all well samples collected during these two periods, nitrate concentrations in groundwater were less than 0.5 mg/l on both sides of Walnut Creek (other analytes relevant to this study were not measured; data unpublished).

In spring 2003, concurrent with land treatment on the west side of Walnut Creek, additional hydrologic and water quality monitoring was initiated to investigate groundwater surface water interaction near the incised stream. Continuous water level monitoring was conducted in six west-side wells (TW-4, W1C, W1D, TW-3, W2B and W2D; Fig. 2). During a spring high flow event typical for the region, stream stage rapidly increased in response to precipitation with stream stage rising and falling nearly 2.5 m in less than a day (Schilling et al. 2006a, b). A reversal of flow into the streambank occurred for 8-h, but the hydraulic conductivity of the silty alluvium and the limited time period of flow reversal prevented significant stream water penetration into the alluvium. Analytical and numerical modeling suggested that surface water traveled less than 1.6 m into the aquifer during the high flow event (Schilling et al. 2006a, b). These results along with 2002 data (Schilling et al. 2004) confirmed that surface water interactions with the alluvium were effectively isolated to a narrow zone immediately adjacent to the channel.

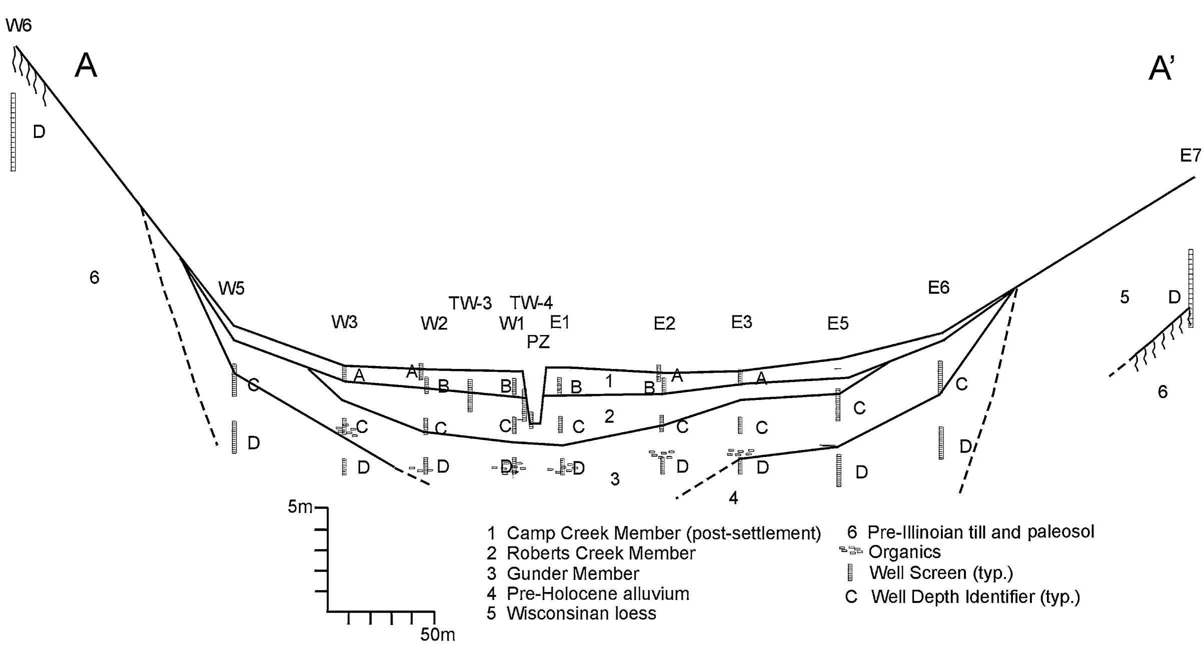

Fig. 2 Cross-section across Walnut Creek floodplain

Groundwater samples collected from the same six wells showed elevated nitrate concentrations (up to 20 mg/l) in riparian groundwater near the incised stream where the unsaturated zone was thickest. Nitrate concentrations were then found to decrease with distance away from the stream as the water table became shallower and perennially wet conditions were maintained (Schilling et al. 2006a, b). Peak nitrate concentrations near the stream channel were also observed to decrease to concentrations typical of pre-event water over the 2-month period that followed the runoff event. Numerical modeling was used to confirm that both dilution and denitrification processes contributed to the nitrate reductions in the riparian zone. While the Schilling et al. (2006b) study concluded that denitrification is an important process in the floodplain sediments of Walnut Creek, no attempt was made to distinguish differences in nitrogen processing among the various alluvial units delineated at the site. Further, the study was conducted on the west side of Walnut Creek when the overlying vegetation was largely bare. Questions remained whether similar nitrate concentration patterns were present on the vegetated east side of the channel.

This present study capitalized on the existing monitoring well network established at the site to expand on the previous work by (1) characterizing spatial and temporal variations in biogeochemical processing in distinct floodplain stratigraphic units; and (2) characterizing additional nutrient concentrations (N, P, and C) on both sides of Walnut Creek—one side undisturbed cool-season grassland, and the other side potentially affected by a legacy of aggressive land management.

Methods

Most shallow wells were installed at the site in 2001 and 2002. Those nearest the stream channel were installed using a 152-mm hand auger whereas upland wells on both sides of the floodplain (5, 6 and 7 well clusters) were installed using a truck mounted hydraulic probing unit. Soil descriptions were based on logging of a continuous 76-mm diameter core collected at the probing locations or soil cuttings collected from the hand auger. Selected representative soil samples were analyzed for particle-size (sand, 0.063–2 mm; coarse silt 0.063–0.02 mm; fine silt, 0.02–0.002 mm and clay, <0.002 mm) using the pipette method at the University of Iowa Department of Geoscience.

At the hand-augered boreholes, three 25-mm PVC standpipes were installed in the alluvium to depths of 1.0, 3.0 and 4.8 m below ground surface. At TW-3 and TW-4 locations, single wells were installed in the borehole (Fig. 2). A 0.6 m long factory-slotted PVC well screen (0.025-cm) was used for the 1, 2, 3 and 4 well clusters. The 0.6 m screen was less than the thickness of the individual geologic units targeted for investigation and allowed for collection of sufficient water for analysis representative of the formation. At the hydraulic probe locations, a 1.5 m long factory slotted PVC well screen (0.025-cm) was installed. A silica sand filter pack was poured around the screen, bentonite chips were added to provide a seal and drill cuttings were backfilled in the rest of the borehole. In the channel of Walnut Creek, a well point was driven to a depth of approximately 1 m into the streambed for measurement of stream stage and vertical gradients across the streambed. Ground surface and top-of-casing elevations at well locations and streambed piezometer were surveyed to the nearest 0.25-mm and referenced to a local United States Geological Survey (USGS) benchmark. A GPS unit was used to establish horizontal control to the nearest 0.3 m. Hydraulic heads were measured in the wells to an accuracy of 0.25-mm using an electronic water level probe. Falling head tests in the wells were used to assess hydraulic conductivity (K) in stratigraphic units. K was lowest in upland glacial drift deposits (2.0×10^{-7} m/s) and highest in the Camp Creek Member (5.6×10^{-5} m/s). The average K of the Gunder Member was greater than the Roberts Creek Member (4.9 compared to 1.7×10^{-5} m/s) (Schilling et al. 2004).

Water levels in wells were measured on a weekly to biweekly basis from May 2001 to November 2004. In July 2003, two shallow wells (2 m) were installed at a distance of 40 m from the creek edge on both sides of Walnut Creek for purposes of recording continuous water level fluctuations (Fig. 1). The water levels in these two wells were automatically recorded with an In-Situ transducer and datalogger at 30 min intervals for a period of 122 days from July 21 to November 20, 2003. The wells were monitored again in 2004 at 60-min intervals for a period of 215 days from May 1 to December 1, 2004. Accuracy of the transducer was within 1 mm and checked by manual measurements on a bimonthly basis. Stream stage during this monitoring period was measured at 15-min intervals at a USGS stream gage located at the mouth of the Walnut Creek watershed (Fig. 1). Precipitation was monitored at hourly intervals at a weather station located at the Prairie Learning Center of the NSNWR (Fig. 1).

Water samples were collected from site monitoring wells, the streambed piezometer and Walnut Creek on four occasions in 2004 (May 25, June 22, September 17 and November 17) corresponding to early to mid growing season, late growing season and after senescence of reed canary grass. Water samples from wells were collected using a peristaltic pump and analyzed in the field for temperature, specific conductance, pH, dissolved oxygen and reduction–oxidation (redox) potential using a Hydrolab H20 water quality meter. Accuracy of the measurements was ±0.10°C for temperature, ±0.2 pH units for pH, ±0.1% for SC, ±0.2 mg/l for DO and ±20 mv for ORP.

Water samples for laboratory analysis were field filtered through a 0.45 micron glass-fiber filter. Dissolved organic carbon was measured via Pt-catalyzed, high temperature oxidation (TOC-V Total Organic Carbon Analyzer, Shimadzu Scientific Instruments, Inc., for total non-purgeable organic content from acidified water samples, APHA 1995) at Grinnell College. Water samples were analyzed for ammonium (NH_4^+-N; phenol-hypochlorite spectrophotometric analysis, Solorzano 1969), nitrate (cadmium reduction, APHA 1995) and soluble reactive phosphorus (SRP; modified molybdenum blue ascorbic acid method, APHA 1995) by flow injection analysis (QuickChem 8000, Lachat Instruments).

Analysis of variance was used to examine differences in geochemical parameters among wells. Pairwise comparisons were made using the Holm–Sidak test. In cases of unequal variance, Kruskal–Wallis One-Way Analysis of Variance on Ranks, followed by Dunn's Test for pairwise comparisons, was used. Pearson correlation analysis was used to examine relationships among geochemical parameters across sample wells.

Results

Lithology

The alluvial stratigraphy found in the Walnut Creek riparian corridor is similar to other third- and fourth-order valleys in the Southern Iowa Drift Plain. Three alluvial units comprise members of the DeForest Formation at the Walnut Creek riparian site (Camp Creek, Roberts Creek and Gunder members), a fourth alluvial unit was considered older than the oldest member of the DeForest Formation (termed "pre-Gunder"; Bettis et al. 1992), and two units occupy hillslope locations (Wisconsin loess and pre-Illinoian till).

The Camp Creek Member is the youngest unit at the site and consists of post-settlement alluvium mantling the entire floodplain (Fig. 2). The unit is stratified and very dark grayish brown to yellowish brown (10YR3/2-5/4) silt loam. The unit was thickest near the current stream channel (1.2 m) and thinned toward the floodplain margins. Surface soils are Entisols (A–C profiles). The Roberts Creek Member consists of very dark gray to dark gray (2.5YR3/0, 10YR3/1-4/1) silty clay loam with a relatively thick A–C soil profile (Mollisol) developed into its upper part corresponding to the pre-settlement soil surface. The Roberts Creek Member was thickest in the central portion of the floodplain (about 2 m) and laterally pinched out near the floodplain boundary. The Gunder Member was brown to yellowish brown to grayish brown (10YR5/3 to 2.5YR5/2) silt loam with common strong brown to yellow brown mottles (7.5YR5/8 to 5YR5/8). Abundant organic-rich muck, wood, and preserved plant material were common in the Gunder Member, particularly concentrated in a zone 4–4.5 m below ground surface (Fig. 2). The thickness of the Gunder Member exceeded 4 m in the central portion of the floodplain but was less than 2 m along the valley walls. An undifferentiated, Late Wisconsin to Early Holocene age, silt loam underlies the Gunder Member at depth in the floodplain. The unit was dark gray (10YR4/4), reduced, unmottled and unleached, and contained small white carbonate concretions and few to occasionally prominent organic-rich zones. The silt loam was occasionally interbedded with sandy loam and small gravel. The unit appeared in some locations to be reworked loess, and in other locations appeared part of an alluvial point bar complex.

The alluvial units were all silt and clay dominated with fine and coarse silt comprising 60–81% of the matrix (Table 1). Total carbon and nitrogen were highest in the Camp Creek member and decreased with depth through the Roberts Creek and Gunder members (Table 1).

Table 1 Summary of texture and carbon–nitrogen content in various geologic units

Lithologic unit	*n*	Sand (%)	Coarse silt (%)	Fine silt (%)	Clay (%)	Carbon (%)	Nitrogen (%)	C–N ratio
Camp Creek	6	3.2 ± 2.3	36.2 ± 6.8	36.8 ± 11.1	24.1 ± 10.7	1.70 ± 0.83	0.17 ± 0.06	9.74 ± 2.29
Roberts Creek	8	4.7 ± 3.1	31.75 ± 10.1	48.8 ± 21.3	14.7 ± 12.5	1.30 ± 0.93	0.10 ± 0.07	12.98 ± 4.09
Gunder and pre-Gunder	11	12.3 ± 13.5	35.51 ± 13.6	25.1 ± 10.8	26.9 ± 11.7	0.49 ± 0.31	0.06 ± 0.02	6.10 ± 2.61
Pre-Illinoian till	3	41.8 ± 3.0	20.3 ± 5.2	20.5 ± 9.4	17.4 ± 10.5	0.61 ± 0.41	0.06 ± 0.02	10.36 ± 6.79

In the uplands (W6 and E7 well locations), undifferentiated Wisconsin loess overlies weathered pre-Illinoian till (Fig. 2). Soil development that occurred on the pre-loess landscape, which was subsequently buried by Wisconsin loesses, is referred to as the Sangamon Soil. The Sangamon Soil is yellowish-red (5YR5/6) medium subangular blocky, with some sand and pebbles, and commonly contains iron and manganese accumulations along roots and joints. Oxidized pre-Illinoian till was dark yellowish brown (10YR4/6) with common grayish brown mottles (10YR5/2), variably leached of carbonates, and contained abundant joints and roots coated with Fe and Mn. Pre-Illinoian till was coarser than the alluvial fills (61% sand and coarse silt) and contained little total carbon (0.6%) and nitrogen (0.06%) (Table 1).

Hydrology

A total of 726 mm of precipitation occurred from April to December 2004 (Fig. 3) with the months of May, July and August contributing 178, 136 and 166 mm, respectively. A rainy period in mid-May delivered 110 mm of precipitation within a 1-week period and caused a noticeable water table rise at the site (Fig. 3). Major rainfall periods also occurred on July10–11 (39.6 mm), July 22 (26.4 mm), August 3–4 (79.5 mm) and August 25–28 (100.9 mm), with less intense rainfall during the fall period (October–December) adding an additional 95.5 mm of precipitation. Maximum surface water discharge occurred on May 26 and July 12 when streamflow peaked at 6.4 and 3.9 m^3/s, respectively. These events resulted in less than a 1 m rise in stream stage with no overbank flooding. Overall average discharge for the April to November study period was 0.4 m^3/s.

Water table elevations fluctuated in 2004 with highest levels occurring in mid-May following a series of rainfall events. The water table was at or near the land surface during this period with standing water occasionally observed between sites 2 and 3 on

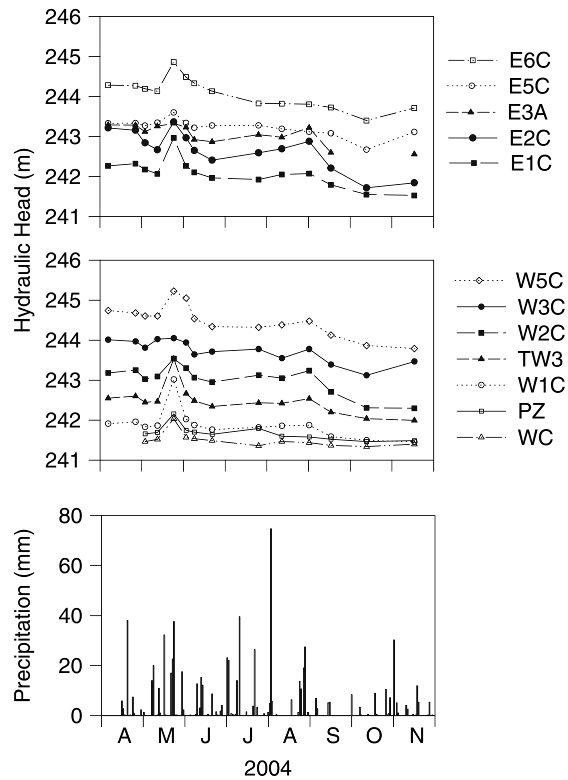

Fig. 3 Hydrograph of hydraulic heads measured at various wells

both sides of the transect. Through the summer and early fall, lateral flow to Walnut Creek and evapotranspiration lowered the water table in the floodplain by as much as 1 m (Fig. 3). With the exception of the near-stream wells (W1 and E1 wells, TW-3 and TW-4), the water table depth remained at or above the Roberts Creek Member and fluctuated through the Camp Creek Member. Near incised Walnut Creek, the water table depth increased and the water table primarily fluctuated in response to Walnut Creek stage. Greatest water table fluctuations were observed in upland well E7D, where the depth to the water table ranged from approximately <1 m in May to more than 5 m in November 2004. The water table declined sufficiently deep in November to prevent groundwater sample collection from this well. Overall, water level fluctuations encountered in 2004 were similar to those observed in 2001 prior to land treatment (Schilling et al. 2004).

Groundwater flows from higher landscape positions towards Walnut Creek under hydraulic gradients that were steepest near the upland/floodplain contact and in the near-stream riparian zone. Average vertical gradients were steeply downward at the valley margins (>0.1 at W5, E5 and E6) and upward near Walnut Creek (approximately 0.03 at E1C/E1D and W1C/W1D). An upward hydraulic gradient measured at the streambed piezometer (0.1) indicated that Walnut Creek is a discharge zone for local groundwater flow (Fig. 3). Between the valley margins and Walnut Creek, groundwater flow was largely horizontal under flat hydraulic gradients (<0.01).

Continuous water level measurements indicated relative consistency in water table depth on the east and west sides of Walnut Creek in 2004 (Fig. 4). The water table depth was shallow in the central portion of the floodplain, ranging from near the ground surface to a depth less than 1.5 m. A wet period in mid-May resulted in water table rise to near the land surface on both sides of the creek, with several other rainfall events through August 2004 causing similar water table responses (Fig. 4). The water table on the west side was often lower than the east side during dry periods but overall, water table fluctuations in 2004 showed no statistical difference ($p > 0.1$).

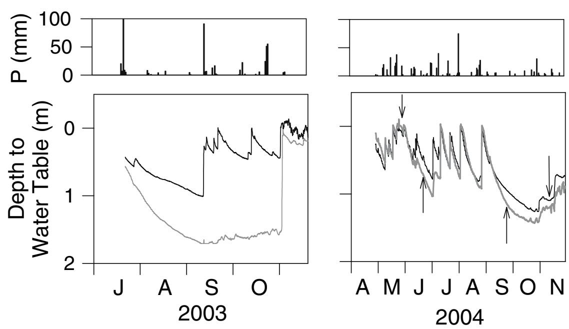

Fig. 4 Hydrograph of hourly water table depths measured in west well (dark line) and east well (light gray line) in 2003 and 2004. In 2003, riparian land cover was bare soil on west side of Walnut Creek and dense grass cover on the east side. In 2004, land cover consisted of grasses and sedges on both sides of Walnut Creek riparian zone. Arrows shown in 2004 plot indicate day of groundwater sampling

In contrast to 2004 water table behavior, water table fluctuations in summer and fall 2003 showed substantial variation between the east and west sides of Walnut Creek (Fig. 4). Land treatment conducted in 2003 to eradicate reed canary grass on west side of the Walnut Creek floodplain resulted in the area largely consisting of bare ground. In contrast, the untreated east side was covered with reed canary grass. Over the course of continuous monitoring, the water level in the east side well was lower and had much less response to rainfall events than the bare ground west-side well. Similar differences in water table depth were noted in 2002. Over a 120-day period in 2002, hydraulic heads were as much as 1.2 m lower on the untreated east side compared to the treated west side (Schilling et al. 2004). Hence, considering that lateral flow and groundwater conditions were similar prior to land cover change, land cover had a significant effect on water table depth in 2002 and 2003. Differences in water table behavior were attributed to differences in antecedent soil moisture conditions under grass and bare ground as evapotranspiration (ET) demands by the grass resulted in a soil moisture deficit that increased the capacity of the soil to retain infiltrating precipitation (Zhang and Schilling 2006).

Water quality

Water quality conditions and concentrations of nutrients measured in individual wells (Table 2) and classified by geologic unit (Table 3) indicate substantial variability in groundwater chemistry at the Walnut Creek floodplain. Geologic units were divided into alluvial units, upland locations, and surface water and piezometer samples. A separate classification was developed for near-stream wells located on the west side of Walnut Creek (TW-4, W1B, C, D, TW-3) to capture the effects of land cover differences on nutrient concentrations, particularly nitrate (Table 3).

Groundwater temperatures were generally highest in shallow wells (Camp Creek Member), surface water and in the streambed piezometer and lowest in deeper pre-Gunder and upland wells (Table 3). Water pH was within a relatively narrow range in all wells, ranging from 5.9 in near stream Roberts Creek well TW-4 to 6.8 in upland well E7D (Table 2). Surface water pH in Walnut Creek was significantly higher ($x = 7.1$) than groundwater samples. Specific

Table 2 Summary of water quality conditions measured in monitoring wells, a streambed piezometer and Walnut Creek

Well ID	Lithology	Temp (°C)	pH	Cond (μS)	DO (mg l^{-1})	Redox (mV)	NH_4^+–N (mg l^{-1})	NO_3^-–N (mg l^{-1})	SRP (mg l^{-1})	DOC (mg l^{-1})
E7D	p-I till	12.1 ± 1.0	6.79 ± 0.4	563 ± 3	4.26 ± 0.71	216 ± 42	0.030	0.13 ± 0.02	0.019 ± 0.001	0.95 ± 0.33
E6C	G	14.8 ± 1.4	6.57 ± 0.2	263 ± 98	2.05 ± 1.00	184 ± 46	0.073 ± 0.017	0.14 ± 0.10	0.215 ± 0.067	5.71 ± 0.081
E6D	p-G	12.3 ± 1.3	6.67 ± 0.3	481 ± 39	1.76 ± 0.26	182 ± 39	0.095 ± 0.113	0.64 ± 0.29	0.063 ± 0.015	1.07 ± 0.14
E5C	G	14.3 ± 1.5	6.48 ± 0.3	250 ± 14	2.03 ± 0.87	186 ± 35	0.099 ± 0.120	0.21 ± 0.14	0.121 ± 0.015	3.38 ± 1.12
E5D	p-G	12.2 ± 1.5	6.49 ± 0.2	351 ± 16	1.36 ± 0.11	131 ± 10	0.168 ± 0.087	0.31	0.266 ± 0.127	2.27 ± 1.40
E3A	CC	15.8 ± 1.1	6.04 ± 0.2	516 ± 74	1.95 ± 0.04	205 ± 16	0.161 ± 0.041	ND	0.234 ± 0.156	8.45 ± 0.03
E3C	G	12.3 ± 2.3	6.29 ± 0.3	558 ± 20	1.63 ± 0.69	203 ± 24	0.062 ± 0.013	0.10	0.132 ± 0.023	2.52 ± 0.30
E3D	p-G	11.4 ± 1.7	6.63 ± 0.2	518 ± 25	1.22 ± 0.24	114 ± 18	1.913 ± 0.904	ND	0.351 ± 0.248	3.50 ± 0.42
E2A	CC	15.1	6.26	457	2.28	29	0.082	ND	0.192	7.67
E2B	RC	15.0 ± 1.9	6.32 ± 0.3	672 ± 146	1.71 ± 76	200 ± 76	0.196 ± 0.175	ND	0.174 ± 0.028	5.93 ± 0.62
E2C	RC	13.0 ± 1.4	6.47 ± 0.23	942 ± 269	1.41 ± 0.47	141 ± 41	5.248 ± 3.242	0.16 ± 0.15	0.059 ± 0.017	10.89 ± 2.25
E2D	G	11.6 ± 1.7	6.38 ± 0.2	1,298 ± 17	1.43 ± 0.20	109 ± 12	17.500 ± 3.77	0.15	0.122 ± 0.069	15.83 ± 5.45
E1B	CC	12.6	6.15	298	5.12	201	0.017	4.89	0.113	5.45
E1C	RC	13.2 ± 2.5	6.48 ± 0.3	659 ± 130	2.59 ± 0.50	172 ± 39	1.227 ± 0.476	0.75 ± 0.30	0.177 ± 0.165	6.65 ± 1.05
E1D	G	11.6 ± 1.8	6.34 ± 0.3	567 ± 5	1.85 ± 0.73	199 ± 17	0.261 ± 0.061	0.18 ± 0.13	1.264 ± 0.217	6.29 ± 0.78
W6D	p-I	12.1 ± 2.4	6.62 ± 0.2	859 ± 10	2.33 ± 0.39	201 ± 110	0.117 ± 0.031	ND	0.051 ± 0.015	2.03 ± 0.14
W5C	G	14.3 ± 1.9	6.54 ± 0.3	145 ± 21	2.35 ± 1.05	267 ± 117	0.206 ± 0.184	0.37 ± 0.27	0.208 ± 0.074	7.92 ± 3.04
W5D	p-G	11.8 ± 1.5	6.78 ± 0.4	320 ± 93	1.99 ± 0.61	237 ± 125	0.137 ± 0.063	0.14	0.065 ± 0.040	3.16 ± 3.21
W3A	CC	16.7	6.68	152	3.78	282	0.182	0.11	0.254	13.24
W3C	G	14.1 ± 1.8	6.48 ± 0.2	331 ± 24	1.49 ± 0.20	125 ± 56	0.162 ± 0.160	0.07 ± 0.05	0.266 ± 0.203	2.69 ± 0.69
W3D	p-G	12.5 ± 2.4	6.39 ± 0.2	264 ± 7	1.64 ± 0.17	136 ± 11	0.070 ± 0.013	0.01	0.040 ± 0.012	1.78 ± 0.16
W2A	CC	16.0	6.25	149	4.17	236	0.080	ND	0.382	19.03
W2B	RC	16.5 ± 2.0	6.44 ± 0.2	580 ± 191	1.42 ± 0.75	154 ± 77	2.308 ± 1.887	0.60 ± 0.74	0.561 ± 0.448	12.83 ± 12.6
W2C	RC	13.7 ± 2.4	6.25 ± 0.2	252 ± 43	1.65 ± 0.60	215 ± 67	0.178 ± 0.088	1.37 ± 1.89	0.142 ± 0.023	7.04 ± 3.29
W2D	G	12.6 ± 1.9	6.33 ± 0.1	436 ± 9	2.19 ± 0.76	177 ± 43	0.066 ± 0.059	0.19 ± 0.13	0.028 ± 0.014	2.56 ± 0.23
TW-3	RC	14.0 ± 2.8	6.17 ± 0.24	289 ± 12	2.22 ± 0.98	252 ± 52	0.002	2.29 ± 2.16	0.080 ± 0.012	3.47 ± 0.46
W1B	CC	13.1	5.96	294	6.46	408	0.033	21.44	0.273	5.81
W1C	RC	14.2 ± 3.3	5.97 ± 0.4	420 ± 87	2.78 ± 0.69	333 ± 82	0.150	27.98 ± 14.42	0.069 ± 0.038	3.80 ± 0.32
W1D	G	12.4 ± 2.3	6.29 ± 0.31	406 ± 7	1.86 ± 0.48	293 ± 85	0.151 ± 0.035	0.32 ± 0.26	0.099 ± 0.011	2.51 ± 0.25
TW-4	RC	13.5 ± 2.2	5.91 ± 0.3	393 ± 82	2.38 ± 0.68	340 ± 61	0.159	22.56 ± 13.59	0.085 ± 0.035	4.48 ± 2.14
PZ	RC	15.5 ± 3.0	6.49 ± 0.2	350 ± 75	2.92 ± 1.66	293 ± 108	0.110 ± 0.085	1.39 ± 2.07	0.262 ± 0.297	4.40 ± 0.098
WC		15.7 ± 2.2	7.11 ± 0.2	516 ± 54	7.70 ± 0.18	301 ± 87	0.068 ± 0.059	10.38 ± 2.67	0.103 ± 0.055	2.86 ± 1.13

p-I, pre-Illinoian till; G, Gunder Member; p-G, pre Gunder; RC, Roberts Creek Member; CC, Camp Creek Member
ND, not detected above instrument detection limits; ±, standard deviation; no SD value indicates single sample collected or only single sample above detection limit

Table 3 Summary of water quality conditions measured in various geologic units, west side wells (near stream), and Walnut Creek

Lithology	Temp (°C)	pH	Cond (μS)	DO (mg l^{-1})	Redox (mV)	NH_4^+–N (mg l^{-1})	NO_3^-–N (mg l^{-1})	SRP (mg l^{-1})	DOC (mg l^{-1})
Camp Creek	15.9 ± 0.8 b	6.25 ± 0.3 ab	358 ± 194 ab	2.83 ± 1.07 ab	244 ± 42 ab	0.13 ± 0.05 a	0.03 ± 0.04 a	0.26 ± 0.11 b	11.4 ± 4.82 b
Roberts Creek	14.1 ± 2.2 ab	6.40 ± 0.2 b	617 ± 289 ab	1.78 ± 0.68 a	174 ± 58 a	2.00 ± 2.55 a	0.35 ± 0.70 a	0.21 ± 0.25 ab	8.74 ± 5.50 b
Gunder	13.0 ± 2.0 ab	6.40 ± 0.2 b	495 ± 330 ab	1.87 ± 0.73 a	195 ± 78 a	2.29 ± 5.96 a	0.19 ± 0.14 a	0.29 ± 0.40 ab	5.56 ± 4.64 ab
Pre-Gunder	12.0 ± 1.6 a	6.59 ± 0.3 b	386 ± 108 a	1.59 ± 0.41 a	160 ± 70 a	0.52 ± 0.86 a	0.43 ± 0.34 a	0.16 ± 0.17 ab	2.35 ± 1.70 a
Upland	12.1 ± 1.8 a	6.69 ± 0.3 bc	732 ± 158 b	3.16 ± 1.14 b	207 ± 82 ab	0.07 ± 0.06 a	0.13 ± 0.02 a	0.04 ± 0.02 a	1.57 ± 0.62 a
Near Stream[a]	13.8 ± 2.4 ab	6.02 ± 0.3 a	356 ± 83 a	2.93 ± 1.42 b	307 ± 78 b	0.03 ± 0.05 a	16.8 ± 14.9 b	0.09 ± 0.06 ab	4.16 ± 1.30 ab
Piezometer	15.5 ± 3.0 ab	6.49 ± 0.2 b	350 ± 75 a	2.92 ± 1.66 ab	293 ± 108 b	0.11 ± 0.09 a	1.39 ± 2.07 a	0.26 ± 0.30 ab	4.40 ± 0.10 ab
Walnut Creek	15.7 ± 2.2 b	7.11 ± 0.2 c	516 ± 54 ab	7.70 ± 0.18 c	301 ± 87 b	0.07 ± 0.06 a	10.38 ± 2.67 b	0.10 ± 0.06 ab	2.86 ± 1.13 ab

Results were combined from four sampling periods

[a] Near stream includes wells on west side of Walnut Creek only; letters denote significant differences ($p < 0.05$)

conductance values showed variability in groundwater, with some values exceeding 700 umhos/cm and others less than 300 umhos/cm. Overall, upland groundwater with longer groundwater residence times had significantly higher SC than alluvial groundwater recently recharged with low SC rainfall, with Walnut Creek surface water more intermediate (516 umhos/cm). Groundwater discharging to Walnut Creek through the stream bottom was much lower in specific conductance than Walnut Creek itself, suggesting that Walnut Creek integrates groundwater contributions from both upland and alluvium sources.

Dissolved oxygen (DO) was highest in surface water (7.7 mg/l) and in upland well E7D (4.3 mg/l) compared to alluvial groundwater that had DO concentrations less than 3 mg/l (Table 2). Concentrations less than 2 mg/l were common in alluvial groundwater, with lowest average concentrations found in deeper pre-Gunder alluvium (1.59 mg/l; Table 2). DO levels generally decreased with depth from shallow Camp Creek Member to pre-Gunder alluvium. Higher groundwater DO concentrations were detected in near-stream wells on the west side of Walnut Creek despite these wells being screened in Roberts Creek Member alluvium. Average DO levels were about 1 mg/l higher in the Roberts Creek Member on the west side of Walnut Creek compared to more distal west side locations and similar locations on the east side (Table 3). Similar to DO, redox decreased with depth through the alluvium, with significantly lower average redox values in Roberts Creek, Gunder and pre-Gunder alluvium ($p < 0.05$).

Ammonium concentrations in groundwater were highly variable (Tables 2 and 3) and thus comparisons among geologic units were not statistically significant. However, exceptionally high concentrations were measured in several wells, with the highest single concentration of 22.6 mg/l found in E2D (Gunder) in September 2004. Average ammonium concentrations were nearly 2 mg/l in Roberts Creek and Gunder member alluvium (Table 3). Average concentrations were lower in pre-Gunder alluvium, but samples with high values were occasionally noted in E3D (up to 3.2 mg/l). A common range of ammonium concentrations in alluvium was between 0.05 and 0.2 mg/l. Average ammonium concentrations in west side near-stream wells was less than this range, averaging 0.29 mg/l and often not detectable above 0.001 mg/l. Walnut Creek surface water had detectable levels of ammonium during all four sampling events (0.02–0.146 mg/l) but were lower than values measured in the streambed piezometer (0.110 mg/l; Table 3).

Nitrate concentrations showed the most variability of all nutrient concentrations monitored during this study, ranging from less than 0.1 to a high of 36.9 mg/l detected in W1C in May 2004 (Fig. 5). Highest concentrations were found in shallow west side wells located near Walnut Creek (TW-4, W1C) where average concentrations exceeded 20 mg/l during 2004 (Table 2). A single nitrate sample from W1B in May 2004 also showed nitrate concentration greater than 20 mg/l, whereas average concentrations were greater than 1 mg/l in TW-3, W2C and the streambed piezometer. Walnut Creek averaged 10.4 mg/l during the study period. Nitrate concentrations in near-stream west-side wells and in Walnut Creek were significantly higher than concentrations measured in alluvial groundwater. In contrast, nitrate concentrations measured in east side alluvium were generally less than 0.5 mg/l and many wells showed non-detectable concentrations less than 0.1 mg/l (Table 2). Similarly, in west side wells located more distal to Walnut Creek concentrations were also less than 0.4 mg/l.

Nitrate concentration remained elevated in TW-4 and W1C from May to September before substantially declining in November (Fig. 5). Assuming a linear rate over the 61-day period between September and November sampling events, nitrate concentrations decreased approximately 0.43 and 0.32 mg/l/day in wells W1C and TW-4, respectively. In contrast to the magnitude and fluctuation of nitrate concentration in near-stream west side wells, low concentrations were maintained in east side well E1C during the same period (average of 0.75 mg/l) (Fig. 5).

In 2003, similar nitrate concentration patterns were detected in three east side wells (TW-4; W1C, TW-3; Fig. 5). In May 2003, concentrations in the three wells peaked at 20, 16 and 14 mg/l, respectively, and then declined to pre-study levels (1.2, 3.8 and 1.2 mg/l) by July 1, 2003 (Schilling et al. 2006b). A similar rate of nitrate concentration decrease was observed in 2003 ranging from approximately 0.2 to 0.4 mg/l/day over a 55-day period from late May to July. However, between July 1, 2003 and the first sampling event for this study (May 25, 2004) nitrate concentrations in the three west side wells were observed to have rebounded to levels that compared to or exceeded 2003 levels. The nitrate rebound occurred despite the return of overlying vegetation on the west side of Walnut Creek and the return of similar water table fluctuations (Fig. 4).

Soluble reactive phosphorus (SRP) concentrations in alluvium ranged from less than 0.1 mg/l in upland wells to as high as 1.42 mg/l in riparian wells, although most concentrations were less than 0.3 mg/l (Table 2). Less systematic variation in SRP concentrations was noted, as several wells installed in Roberts

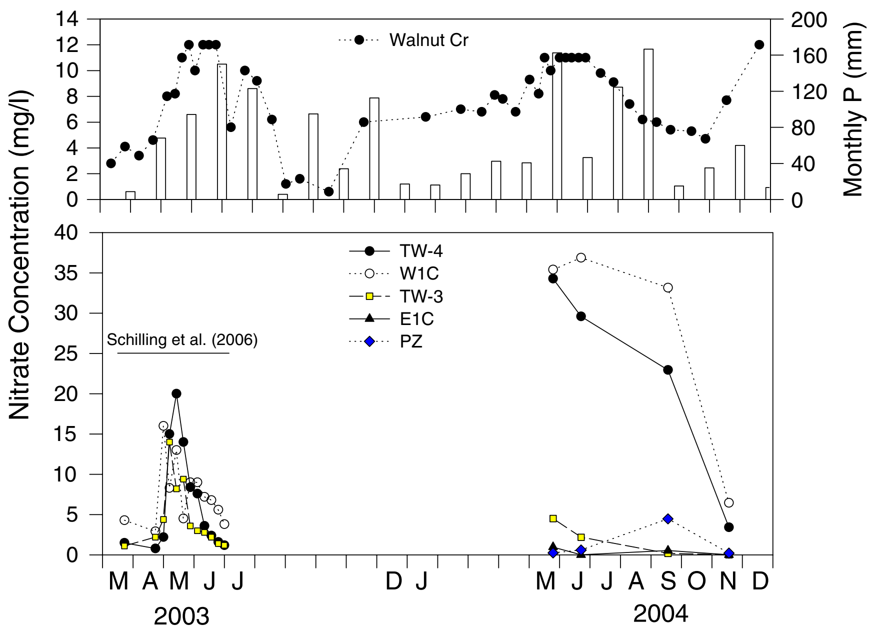

Fig. 5 Upper graph: Nitrate concentrations in Walnut Creek surface water in 2003 and 2004. Total monthly precipitation also shown. Lower graph: Nitrate concentration patterns measured in near-stream west side wells (TW-4, W1C, TW-3), east side well (E1C) and Walnut piezometer (PZ) in 2003 (west-side wells only; data from Schilling et al. (2006a, b study) and 2004

Creek, Gunder and pre-Gunder alluvium occasionally exhibited SRP concentrations greater than 0.4 mg/l. Overall, average SRP levels in alluvial units ranged from 0.16 to 0.29 mg/l and were significantly higher than concentrations measured in upland wells (0.04 mg/l) ($p < 0.05$; Table 3).

Average dissolved organic carbon (DOC) concentrations across all wells ranged from 0.95 mg/l in upland well E7D to 15.8 mg/l in Gunder Member well E2D (Table 2). Like ammonium, DOC concentrations were highly variable making statistical comparisons difficult. Average DOC levels also exceeded 10 mg/l in two Roberts Creek Member wells (E2C and W2B) and several Camp Creek wells. Overall, average DOC concentrations were observed to decrease with depth, with highest concentrations detected in Camp Creek wells (11.37 mg/l), followed by average concentrations in Roberts Creek Member wells (8.74 mg/l) and Gunder Member wells (5.56 mg/l). Significantly lower DOC values were measured in the oldest alluvium (2.35 mg/l in pre-Gunder) and in upland loess and till (1.57 mg/l) compared to younger Holocene alluvium ($p < 0.05$; Table 3). Walnut Creek DOC levels averaged 2.86 mg/l.

Relationships among water quality variables

Correlation was used to identify significant relations among nutrient concentrations and geochemical parameters (Table 4). Ammonium was found to be significantly positively correlated with specific conductance and DOC and negatively correlated with DO and redox (Table 4). Correlations involving nitrate concentrations were generally inverse to ammonium, being positively correlated with DO and redox and negatively correlated with pH. SRP was only weakly correlated with DOC ($p = 0.058$) and not significantly correlated with other geochemical parameters. DOC was positively correlated with specific conductance, ammonium and SRP (Table 4).

Discussion

Study results indicate that alluvium at Walnut Creek is very nutrient rich, contributing high concentrations of N, SRP and DOC to alluvial groundwater. Average concentrations of ammonium exceeded 1 mg/l in several wells and peaked at 17.5 mg/l in well W2D, whereas nitrate concentrations, generally low in east side areas, exceeded 20 mg/l in several west side wells. Hence, nitrogen, whether in the form of ammonium or nitrate, was prevalent at elevated concentrations throughout the alluvial groundwater system. SRP concentrations were similarly high in several riparian wells ranging up to 1.3 mg/l, with most wells showing groundwater SRP concentrations between 0.1 and 0.3 mg/l. Concentrations of SRP were generally higher than those reported for other unconsolidated

Table 4 Pearson correlation coefficients and *p*-values determined using all well samples ($n = 99$)

	Temp	pH	SC	DO	Redox	NH_4	NO_3–N	SRP
pH	0.241							
	0.017							
SC	−0.202	0.079						
	0.046	0.440						
DO	−0.100	−0.171	−0.190					
	0.325	0.091	0.060					
Redox	−0.122	−0.516	−0.329	0.546				
	0.230	0.000	0.001	0.000				
NH_4	−0.094	0.046	0.753	−0.222	−0.327			
	0.358	0.652	0.000	0.028	0.001			
NO_3–N	0.035	−0.473	−0.062	0.309	0.557	−0.099		
	0.729	0.000	0.542	0.002	0.000	0.330		
SRP	0.008	−0.023	−0.011	−0.117	−0.123	−0.015	−0.126	
	0.940	0.819	0.915	0.250	0.228	0.886	0.217	
DOC	0.225	−0.069	0.384	−0.010	−0.078	0.598	−0.086	0.192
	0.026	0.499	0.000	0.919	0.447	0.000	0.401	0.058

SC, specific conductance; DO, dissolved oxygen; Redox, reduction–oxidation potential aquifers and aquitards in Iowa (Burkart et al. 2004). Although nutrient standards for streams are subject to debate, one criterion recommends that total N and P standards be set at 0.9 and 0.04 mg/l, respectively (Dodds and Welch 2000). It can be seen that background concentrations of N and P from Holocene alluvium exceed this recommended limit.

With the exception of the near-stream riparian zone affected by channel incision (discussed later) the water table in the Walnut Creek floodplain was typically very shallow and usually less than 1.5 m deep (Fig. 4). Water tables less than 1 m deep keep nitrogen-rich groundwater in close contact with surface soils rich in organic carbon and in close proximity to plant roots and microbes (Gold et al. 2001). Moreover, high water tables in fine-grained, organic-rich alluvium encourage denitrification by providing the requisite organic carbon supply, anaerobic soil conditions and nitrogen supply (e.g., Lowrance 1992; Starr and Gillham 1993; Burt et al. 1999; Cey et al. 1999; Clement et al. 2002, 2003). These conditions favorable for denitrification were met in the Walnut Creek floodplain. Anaerobic soil conditions were identified by soil hydromorphic features (mottles, iron and manganese concretions) and low concentrations of dissolved oxygen and low redox conditions in groundwater. DO and redox values in alluvial groundwater were significantly correlated with reduced ammonium and inversely correlated with nitrate concentrations (Table 4). Co-occurrence of ammonium and nitrate in some wells and DO concentrations above 1 mg/l imply that dentrification may be occurring primarily in small microenvironments where DO has been depleted and reducing conditions are maintained (Jacinthe et al. 1998). Others have observed denitrification occurring in settings with DO concentrations less than 2 mg/l (Gillham 1991; Cey et al. 1999). Redox conditions less than 200 mv observed in alluvial groundwater at Walnut Creek further favor nitrate removal via denitrification (Anderson 2004).

It was evident that organic carbon was present throughout the alluvial sequence at Walnut Creek, whether as fine-grained disseminated carbon or as organic-rich wood layers. DOC concentrations in groundwater were greater than 5 mg/l in Gunder, Roberts Creek and Camp Creek member alluvium and many concentrations exceeded 10 mg/l. These concentrations are generally higher than those reported for groundwater flowing through peat (Hill et al. 2000). While denitrification of groundwater nitrate by microbial activity may be limited by the availability of organic carbon in some riparian zones (Bradley et al. 1992; Jacinthe et al. 2003), in the case of Walnut Creek alluvium, there would appear to be a large reserve of DOC to support microbial denitrification.

Denitrification in Walnut Creek alluvium is probably occurring to the greatest degree in Roberts Creek Member alluvium. A fluctuating water table through the Camp Creek Member alluvium probably limits denitrification activity in this unit despite abundant organic carbon. Furthermore, the Camp Creek Member is relatively coarse-grained with higher saturated K and when measured, showed elevated DO and redox conditions. On the other hand, the Roberts Creek Member maintained saturated conditions throughout the year. The unit consisted of primarily silt and had the lowest K measured in any alluvial units ensuring long residence times for groundwater. The organic carbon content of Roberts Creek alluvium was also quite high (C:N ratio of 13) and DOC concentrations exceeded 8.7 mg/l. Less organic carbon content and higher K in Gunder and pre-Gunder Member alluvium suggests that these older alluvial units offer less denitrification potential than the Robert Creek Member. Results from this study provide evidence for substantial denitrification in Roberts Creek Member alluvium consistent with other Iowa studies (Hallberg et al. 1983; Seigley et al. 1996).

Monitoring of near-stream west side wells in both 2003 and 2004 provides field evidence supporting denitrification as a contributing factor in decreasing nitrate concentrations in riparian groundwater. During both years, groundwater nitrate concentrations were observed to rapidly decrease in TW-4, W1C and TW-3 wells (Fig. 5) despite the fact that the land cover in 2003 was bare ground and vegetated grass in 2004. The rate of nitrate decrease was similar for both measurement periods (approximately 0.4 mg/l/day). While nitrate decay occurred primarily during May–June in 2003, and during September–October in 2004, both measurement periods showed nitrate concentrations declining over 15 mg/l in about 60 days. Schilling et al. (2006b) used a numerical model to evaluate whether dilution or denitrification was responsible for the nitrate decrease in 2003 and concluded that both factors contributed equally to the observed decrease. Nitrate decay in the transport model was best simulated with a denitrification rate of 0.02 1/day. Given the similarity in observed nitrate decrease between 2003 and 2004, the modeled denitrification rate appears appropriate for describing the alluvial sediments of Walnut Creek.

High organic carbon content of Holocene alluvium may also be responsible for elevated groundwater P concentrations. Carlyle and Hill (2001) suggested that organic P mineralization may influence P concentrations in organic-rich riparian zones. Devito and Dillon (1993) similarly reported that anaerobic mineralization and diffusive flux from deeper peats could be an important source of SRP to surface waters. High concentrations of SRP in riparian zone groundwater may also result from mobilization of phosphorus as iron and manganese oxides are reduced under anoxic conditions. At Walnut Creek, highest average SRP concentrations were observed in Camp Creek, Roberts Creek and Gunder Member alluvium that also contain highest DOC concentrations. The lowest average DOC was measured in upland wells (1.57 mg/l) where the lowest average SRP concentration was also observed (0.035 mg/l). Although SRP and DOC were only weakly correlated in analyses across all wells (Table 4), average SRP and DOC concentrations were significantly related across geologic units (Fig. 6).

It is clear from the sampling data that while the Holocene alluvial groundwater can be considered nutrient rich, concentrations varied considerably across the site, both spatially from east side to west side, and with depth. Factors that contributed to this variability include the geologic age and depositional history of the alluvial members, the effect of channel incision of Walnut Creek into its floodplain, and the role of vegetation cover and hydrology.

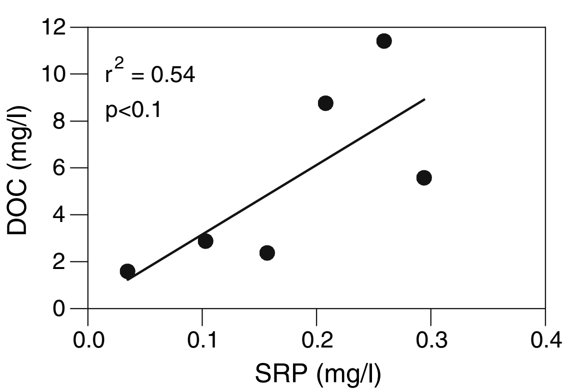

Fig. 6 Relation of average SRP to DOC concentrations in groundwater collected from various geologic units. Data from near-stream west side wells were not included

Effect of geologic age of alluvium

Greater organic carbon and nitrogen content in more recent Holocene alluvium (Camp Creek and Roberts Creek) compared to older Holocene and pre-Holocene units suggests a link between nutrient source material and the geologic history of alluvium deposition. Pre-Gunder and Gunder units were deposited during a time of high suspended sediment loads of silt derived from erosion of loess deposited following the last glacial maximum (Bettis and Autin 1997). Local vegetation during this period was predominantly deciduous forest (Baker et al. 1992) and abundant wood and organic fragments were deposited in Gunder Member alluvium during floodplain aggradation. At Walnut Creek and elsewhere, Gunder Member alluvium is coarser textured than pre-Gunder alluvium and shows a typical fining upward sequence (Bettis and Autin 1997; Bettis 1992). During a period of reduced long-term precipitation in the late middle Holocene (ca. 5,500 yr B.P.) water tables were lower and Gunder Member deposits were oxidized to a much greater degree than later Roberts Creek Member deposits (Bettis et al. 1992; Baker et al. 1992, 1996). The presence of mottling and iron staining in the Gunder Member and the absence of plant macrofossils in the upper oxidized zone indicates substantial post-deposition weathering during a prolonged lower water table period. Labile C and N in the Gunder matrix may have been leached during this period, although larger, less labile, wood and organic fragments remained in the lower reduced zone. Later cooler and wetter conditions in the late Holocene (Denniston et al. 1999) maintained high water tables in floodplains that preserved labile C and N in the Roberts Creek Member. Changing climatic changes during the middle to late Holocene also marked a shift from a forested landscape to one dominated by tall grass prairie (Bettis 1992). Deposition of recent Camp Creek Member alluvium from overbank deposition and upland soil erosion during the last 150 years delivered abundant C and N to the floodplain. Studies suggest that most of the Camp Creek Member was deposited between about 1890 and 1930 as the stream channel adjusted to runoff and sediment load changes brought on by agricultural land use change (Baker et al. 1992; Bettis et al. 1992). In sum, variations in nutrient concentrations measured in Holocene alluvium may be due, in part, to lithologic differences manifested during original sediment deposition and subsequent weathering histories.

Effect of channel incision on groundwater nutrient concentrations

At the study transect, Walnut Creek is incised into its floodplain approximately 3 m from historical channel straightening and upstream land use change. Riparian water tables were severely lowered in the vicinity of the channel compared to more distal floodplain areas, which is consistent with results from Schilling et al. (2004). In transect wells, groundwater in well nests E1 and W1, TW-4 and TW-3 appeared to be most affected by channel incision. Elevated DO concentrations were observed in wells nearest the stream channel (E1B, C, W1B, C) where DO concentrations ranged from 2.59 to 6.46 mg/l (Table 2). Compared to "C" wells at E2 and W2 located 40 m into the floodplain, DO concentrations in near-stream "C" wells had levels more than 1 mg/l higher. Redox conditions were also higher in near-stream wells on the west side of Walnut Creek ranging from 333 to 408 mv at W1B and C.

Deeper water tables near incised Walnut Creek result in a more aerobic soil profile conducive for mineralization of soil N, similar to conditions observed by Groffman et al. (2002). On both sides of Walnut Creek, elevated nitrate concentrations were detected in groundwater from shallow wells located nearest the stream channel. On the east side, a single sample from well E1B in May showed the highest concentration of nitrate found in any east side wells (4.89 mg/l). However, this well was dry during subsequent sampling events, so while nitrate concentrations on the east side appear highest near the stream, insufficient data exist to conclusively document this effect under grass cover. On the west side of Walnut Creek where land treatment was conducted, nitrate concentrations in riparian wells were substantially higher, exceeding 30 mg/l in some wells. However, in the case of west side wells, it is difficult to separate the effects of channel incision from the effects of land treatment since both factors would contribute to elevated nitrate losses to shallow groundwater. Despite gaps in the data, results are consistent with hypothesized effects and other research (Groffman et al. 2002) showing that near-stream riparian groundwater on both untreated and treated sides of incised Walnut Creek had higher DO and nitrate concentrations than more distal floodplain areas. However, more work is needed to conclusively document this effect, especially under typical vegetated land cover conditions like those observed on the east side of Walnut Creek.

Channel incision and its effect of lowering near-stream water table levels appeared to have less effect on groundwater phosphate and DOC dynamics. Concentrations of SRP and DOC did not vary systematically with distance away from the stream channel.

Effect of vegetation cover on groundwater nutrient concentrations

The history of land treatment had by far the largest effect on groundwater nutrient concentrations at the site, particularly with respect to nitrate. Because the present study is, in some ways, a continuation of monitoring that has occurred at the site, it is important to follow the history of the site to fully capture the effects of land cover on groundwater nitrate concentrations.

Prior to land treatment, groundwater nitrate concentrations on both sides of Walnut Creek were less than 0.5 mg/l. Following land treatment in 2002 and 2003 on the west side of the floodplain, nitrate concentrations in near-stream west side wells increased to levels above 20 mg/l in May 2003 and then decreased substantially by July 2003 at the conclusion of monitoring (Fig. 5). In 2004, nitrate concentrations measured in near-stream west-side wells appeared to rebound to previous high concentrations despite the fact that vegetation returned to the riparian zone and the water tables fluctuated similarly on both sides of the creek (Fig. 4). Thus, during the time between July 2003 and May 2004, substantial nitrate losses to riparian groundwater evidently occurred again. Although the timing of when additional nitrate losses occurred is unknown, the data suggest that the nitrate concentrations in near-stream wells retained legacy effects from past land management activities.

Continuous groundwater level monitoring that commenced at the site from July to December in 2003 (Fig. 4) in between the chemical monitoring periods provides some insights regarding how land cover differences affected groundwater recharge through the floodplain soils and possible contributed to greater nitrate losses on unvegetated west side soils. Greater groundwater recharge occurred on the bare, west side of Walnut Creek compared to the vegetated ground cover conditions on the east side (Zhang and Schilling 2006). It was hypothesized that the grass cover on the east side reduced soil moisture through ET and resulted in greater capture of infiltrating rainfall by the unsaturated soil profile and less recharge to the water table. From July to mid-October in 2003, more than 100 mm of additional groundwater recharge occurred through the bare west-side soils compared to the vegetated east-side soils (Zhang and Schilling 2006). Following a groundwater recharge event in mid-October 2003, the water table depth on both sides of Walnut Creek was approximately the same through the dormant winter season.

Although vegetation returned to the west side in 2004 with newly planted wet meadow perennials and remnant reed canary grass, the floodplain soils were disturbed during fall and winter planting and the density of vegetation was considerably less than the well-established reed canary grass on the east side. Without a well-established vegetative cover on the west side in spring 2004, it is hypothesized that high rates of soil nitrogen mineralization occurred again in organic rich west-side soils that included highly labile C and N from decaying roots and organic detritus from earlier land treatment. The accumulation of nitrate was then flushed to the water table with recharging precipitation prior to sampling on May 25, 2004. More than 160 mm of precipitation occurred in May 2004 when sampling occurred (Fig. 5). Nitrate concentrations remained elevated in the west-side wells through much of 2004 and began to substantially decrease only in the fall following a summer growing season of cover vegetation. While emerging vegetation cover on the west-side was evidently sufficient for producing normal groundwater level fluctuations (compared to the east side), it was not sufficient for removal of excess nitrate mineralized from floodplain soils and organic detritus.

In this discussion, it is important to note that high groundwater nitrate concentrations measured in 2004 were mainly observed in near-stream wells where subsurface hydrology was strongly affected by channel incision. High rates of soil nitrogen mineralization were concentrated in the thick unsaturated zone near the incised stream channel. Beyond the range of influence of channel incision on water table depths, nitrate concentrations in shallow groundwater remained at or below the level of detection on the west side of Walnut Creek despite the land treatment activities (wells W2A, 2B, W3A). Thus, distinguishing the effects of land treatment from the effect of channel incision on riparian groundwater nitrate concentrations remains problematic when both factors contributed to the observed patterns. However, data from near-stream east side wells clearly indicated that a riparian vegetation cover of cool-season grass greatly reduced losses of nitrate from the unsaturated zone of incised Walnut Creek.

It is unknown whether vegetative assimilation of soil N was responsible for maintaining low nitrate concentrations on the east side of Walnut Creek, or whether the vegetation cover simply reduced groundwater recharge and leaching of soil N. Near Walnut Creek at the E1 well nest, reed canary grass with a rooting depth less than 0.2 m would not intercept the water table. In this case, assimilation of soil nitrogen by the cool season grass may be occurring from the unsaturated zone and capillary fringe rather than directly from the water table. Capillary rise in silt may extend 2 m (Gillham 1984) and place groundwater within the root zone of the cool season grass. However, identification of specific denitrification or plant uptake processes responsible for groundwater nitrate loss may require isotopic investigation (Clement et al. 2003).

Conclusions

Groundwater nutrient concentrations evaluated in this study of the Walnut Creek floodplain are likely representative of groundwater conditions in Holocene and pre-Holocene alluvium found throughout the loess-mantled glaciated Midwest. Unlike many studies where elevated nutrient concentrations in groundwater have resulted from agricultural inputs (e.g., fertilizer, livestock manure, etc.), concentrations measured during this study represent typical background conditions since the land has been owned by the Neal Smith National Wildlife Refuge since 1991. The floodplain remained fallow since that time, whereas the east upland was planted in prairie in 1996. Furthermore, aerial photographs of the riparian zone dating to the 1940s indicates that historical land use on both sides of the floodplain was primarily pasture suggesting that farmers have consistently maintained tolerant reed canary grass in the seasonally wet floodplain.

Results indicated that groundwater in Holocene alluvium is very nutrient rich with background concentrations of N, SRP and DOC that exceed many environmentally sensitive criteria. Average concentrations of ammonium exceeded 1 mg/l in several wells whereas nitrate concentrations exceeded 20 mg/l in wells under bare ground. Phosphate concentrations ranged from 0.1 to 1.3 mg/l and DOC concentrations exceeded 5 mg/l in many wells. Overall, nutrient concentrations tended to be highest in more recently deposited alluvium compared to older Holocene deposits. Several lines of evidence suggested that conditions are conducive for denitrification of groundwater flowing through the alluvium, with greatest potential for denitrification hypothesized for the Roberts Creek Member consistent with other Iowa studies (Hallberg et al. 1983; Seigley et al. 1996).

Removing the vegetation cover on the west side of the floodplain, in combination with effects of channel incision, served to drastically change nutrient concentration patterns in several near-stream wells, particularly with respect to nitrogen. While this combination of land treatment and channel degradation may appear unique at first glance, incised stream channels are common features in the Midwest and their floodplains are often cropped to the channel edge. Hence, row-cropped floodplains of incised channels are bare for long periods of time, analogous to the west-side conditions monitored in this study. Study results indicate that riparian zones of incised streams downcutting through nutrient-rich Holocene alluvium can potentially be a significant source of nutrient losses to streams.

Our results argue for planting perennial riparian buffers near incised streams to provide vegetation cover for the unsaturated zone near the channel. The type of perennial vegetation may not be as important as the buffer itself, since reduced nutrient losses to riparian groundwater were still apparent even when the roots of shallow-rooted cool season grass (reed canary grass) did not extend to the water table. Perennial vegetation cover will capture more infiltrating water and reduce the accumulation of nutrients in the vadose zone available for leaching.

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