Groundwater Research Report
WR15R003

PREDICTING THE LOCATIONS OF NITRATE REVOVAL HOTSPOTS AT THE GROUNDWATER-SURFACE WATER INTERFACE IN WISCONSIN STREAMS

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Predicting the locations of nitrate removal hotspots at the groundwater-surface water interface in Wisconsin streams **(WRI Project Number WR15R003)**

FINAL REPORT

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Project Period

July 1, 2015 to June 30, 2017

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PROJECT SUMMARY

Title: Predicting the locations of nitrate removal hotspots at the groundwater-surface water interface in Wisconsin streams

Project I.D.: WR15R003

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Principal Investigator: Robert Stelzer, Professor
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Period of Contract: July 1, 2015 to June 30, 2017

Background/Need:
Groundwater nitrate concentrations are elevated in many regions of the world, including central Wisconsin, which can cause human health problems and deleterious ecological impacts on groundwater-dominated ecosystems and coastal areas. Denitrification, the conversion of nitrate to reduced gases (N_2, N_2O) by bacteria, is a mechanism by which nitrate can be permanently removed from groundwater. Denitrification is common where nitrate-laden groundwater comes in contact with anoxic locations in carbon-rich soil or sediment. These conditions frequently occur where oxic groundwater passes through anoxic zones in sediments before discharging to streams. The reaction rate (denitrification) and groundwater discharge rate will both influence how much nitrate removal will occur at the groundwater-surface water interface. However, conditions that favor the highest reaction rates, such as carbon-rich fine sediments, would not be expected to be associated with high groundwater discharge rates, which would in turn not result in maximum nitrate removal. We predicted that groundwater nitrate removal will be optimized at intermediate rates of groundwater discharge, where microbes have suitable redox conditions to reduce nitrate and where groundwater delivers a large supply of nitrate to reaction sites. We also predicted that other environmental variables, such as dissolved oxygen and nitrate availability in groundwater and the organic carbon content of sediments, would play a role in nitrate retention and denitrification in shallow groundwater.

Objectives: The main objective of the research project was to describe and predict spatial variation in nitrate retention and removal in shallow groundwater among and within streams in the central sand plains of Wisconsin. We hypothesized that nitrate transformation rates would be related to the dissolved oxygen availability in pore water, groundwater discharge rate, organic carbon availability and groundwater nitrate concentration.

Methods: The study was conducted at 5 sites on 4 streams in Central Wisconsin. One study site each was selected on Emmons Creek, the West Branch of the White River (WBWR), and Big Roche a Cri Creek (BRC), while two sites were selected on Radley Creek (Suhs and West Roads). Nitrate retention and N_2 production were measured at base flow in June through August of 2016 at WBWR, Radley-West and BRC and nitrate retention was measured at base flow in May and June of 2017 at Emmons Cr. and Radley-Suhs. 25 to 32 piezometers were installed at each site for hydrologic measurements and for adjacent pore water solute sampling. Upwelling was determined at the locations of all of the piezometers used in the study. Pore water was sampled for solutes at 5, 25, and 60 cm sediment depths at each piezometer location. Solute concentrations and fluxes were determined at all 3 sediment depths and differences in nitrate and N_2 fluxes were used to calculate nitrate retention and N_2 production.

Results/Discussion: Grand mean nitrate retention and N_2 production were 0.47 µg NO_3-N/m^2/s and 0.15 µg N_2-N/m^2/s. Nitrate retention differed among the 5 sites and was highest at Radley-Suhs. N_2 production was highest at BRC and Radley-West and lowest at WBWR. N_2 production accounted for 72 and 47% of nitrate retention at Radley-West and BRC but only 14% of nitrate retention at WBWR. A partial least squares regression model based on all 5 sites explained 22% of the variation in nitrate retention ($P < 0.001$). There was no discernable relationship between nitrate retention and groundwater discharge when all 5 sites were considered together. Minimum DO concentration explained 25% of the variation in nitrate retention based on a negative exponential model fitted to the full data set. In general, partial least squares regression models explained much more variation in nitrate retention within sites than at the regional scale; i.e., when all sites were considered together. These models explained 71, 82, 83, and 88% of the variation in nitrate retention at Radley-West, BRC, Emmons, and WBWR ($P < 0.01$). The model coefficients for groundwater discharge were positive and relatively high for Emmons Cr. and WBWR. DO variables were statistically significant predictors of nitrate retention for all sites expect Radley-Suhs based on the initial stepwise multiple regression model ($P < 0.05$). In addition, the 4 statistically significant partial least squares regression models at the site-scale each included 1 to 3 DO variables. Sediment organic matter and chloride concentration at 60 cm were not statistically significant predictors of nitrate retention in any of the multiple regression models.

Conclusions/Implications/Recommendations:

Nitrate retention and denitrification in shallow groundwater associated with streams in the Central Sand Plains of Wisconsin were widespread but highly variable. 5 to 25% of the nitrate flux at 60 cm was retained in the shallow groundwater and retention was less efficient in the high N systems. Preliminary analysis suggests that the rates of nitrate retention and denitrification we measured in shallow groundwater are comparable to the nitrogen transformation rates determined in stream channels throughout the world. We were able to predict nitrate retention using multiple regression models at both regional (Central Sand Plains) and local scales. In general, the statistical models explained a much larger amount of variation in nitrate retention at the local scale than at the regional scale. Consistent predictors of nitrate retention included dissolved oxygen availability and ground water discharge. Strong groundwater-surface water connections are necessary to take advantage of the nitrogen transformation potential in shallow groundwater at the groundwater-surface water interface. We also recommend that conditions are promoted by natural resource managers that will facilitate oxygen removal at this interface, including opportunities for fine sediment deposition and organic carbon (e.g. leaves, wood) accumulation. Groundwater-surface water interactions and the opportunity for groundwater to pass through sediments in which oxygen is low or depleted will provide conditions necessary for nitrate retention and removal.

Related Publications

Stelzer, R.S., E.A. Strauss, M. Coulibaly. 2017. Assessing the importance of seepage and springs to nitrate flux in a stream network in the Wisconsin sand plains. Hydrological Processes 31:2016-2028. DOI: 10.1002/hyp.11161.

Key Words

groundwater, hyporheic, groundwater-surface water interactions, stream, sediments, microbes, denitrification, nitrate retention, redox, dissolved oxygen, statistical model, prediction

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INTRODUCTION

Many streams throughout the world, and their associated groundwater, have chronically high nitrate concentrations, which can lead to ecosystem disruption and compromise drinking water quality (Gu et al. 2013, Chaudhuri and Ale 2014, Stets et al. 2015). Healthy lotic ecosystems and intact riparian zones provide opportunities for nitrate retention and removal (denitrification) which can reduce N loading to downstream ecosystems (Hill 1996). The interface between groundwater and surface water in streams is often an active zone of nitrate retention and removal (Hedin et al. 1998). Shallow groundwater associated with streams and hyporheic flow paths that originate from surface water, present excellent opportunities for nitrate removal because the conditions that promote retention and denitrification (nitrate supply, electron donor availability and favorable redox potential) often converge at these locations (Hedin et al. 1998, McClain et al. 2003, Stelzer and Bartsch 2012). However, nitrate supply, electron donor availability and redox potential are frequently spatially and temporally variable in at the groundwater-surface water interface (Heppell et al. 2014) which can lead to hotspots and hot moments of nitrate retention and denitrification (McClain et al. 2003, Lansdown et al. 2015, Peipoch et al. 2016).

The two proximate drivers of nitrate retention and removal rates at the groundwater-surface water interface are reaction rates and groundwater or surface water advection rates (Gu et al. 2007, Flewelling 2012). Relevant reactions include assimilatory and dissimilatory uptake of nitrate by autotrophic and heterotrophic microbes. Because many of the microbes involved in N transformation at the groundwater-surface water interface are heterotrophic, the quantity and quality of organic carbon supply influences N reaction rates (Burgin and Hamilton 2007, Arango et al. 2007, Barnes et al. 2012). Redox conditions, for which oxygen availability is frequently used as a surrogate, influences the type and availability of electron acceptors in sediments, which in turn can influence the prevailing type (assimilatory or dissimilatory) and rates of N uptake. Nitrogen availability also affects N reaction rates in the hyporheic zone and in shallow groundwater (Holmes et al. 1996, Stelzer and Bartsch 2012). Sediment characteristics, hydraulic gradient and recharge rates are among the factors that influence the discharge rates of groundwater at the groundwater-surface water interface.

The dual influences of reaction rate and advection rate on nitrate processing in sediments in upwelling environments can be quantitatively expressed as the Damkohler number, which can be expressed as the ratio of the reaction rate to transport rate. When reaction rates and groundwater discharge rates are both low, nitrate removal rates would be expected to be low. When reaction rates and groundwater discharge rates are high, nitrate removal rates would be expected to be high. However, the conditions that favor high reaction rates (sediments with low porosity that are rich in organic carbon, long water transport times) tend to result in low groundwater discharge rates (Flewelling et al. 2012). At very low groundwater discharge rates, nitrate reaction rates are likely to be high as long as sediments are permeable and conditions for removal (e.g. denitrification) are met. The Damkohler number would be expected to be high in this situation. However, low groundwater discharge rates would minimize the supply of groundwater nitrate that reaches reaction sites in the sediments, resulting in low nitrate removal rates. At high groundwater discharge rates, typical where groundwater upwells through coarse sediment, the groundwater water is likely to remain oxic (Gu et al. 2007) and the Damkohler number low, conditions that would tend to minimize nitrate retention and removal, particularly that due to denitrification (Zarnetske et al. 2012). We predicted that nitrate transformation rates in shallow groundwater will be a Gaussian function of groundwater advection rates, such that nitrate retention and removal peak at intermediate groundwater discharge rates (Mendoza-Lera and Datry 2017). Intermediate groundwater advection rates could occur where relatively fine sediment containing organic carbon promotes oxygen decline (favorable redox conditions for denitrification) and where nitrate delivery is moderate.

Given the benefits of nitrate retention and removal at the groundwater-surface water interface, it is important that the locations of hot spots and hot moments of this activity can be identified for improving understanding of nitrogen transformation and for ecosystem management and restoration (Mclain et al 2003, Sudduth et al. 2011, Refsgaard et al. 2014, Gomez-Velez et al. 2015). Although numerous investigators have documented nitrate retention and denitrification at the groundwater-surface water interface (Tesoriero et al. 2007, Puckett et al. 2008, Duff et al. 2008, Zarnetske et al. 2012, Anderson et al. 2014, Stelzer and Bartsch 2012, Stelzer et al. 2014, Lansdown et al. 2015), there have been fewer attempts to predict where and when nitrate retention and removal occurs at this interface. Barnes et al. (2012) showed that denitrification potentials of stream sediments were strongly related to dissolved organic matter (DOM) quality. Zarnetske et al. (2012) used a multiple Monod kinetics model to demonstrate that water residence time and oxygen uptake in the hyporheic zone predicted whether nitrate was a source or sink to streams. Gomez-Valez et al. (2015) predicted the denitrification reaction potential at the groundwater-surface water interface in large river basins with a hydrogeomorphic model that was sensitive to hyporheic exchange. Many of the predictive models relevant to nitrogen biogeochemistry in groundwater have focused on nitrate removal potential in aquifers. Merz et al. (2009) used a MODEST model to predict regional denitrification potential in groundwater along entire flow paths (recharge to discharge) based on redox potential and Fe concentration. Rosecrans et al. (2017) developed boosted regression trees to predict groundwater dissolved oxygen concentration, a proxy of denitrification potential, at the regional scale in the Central Valley of California, USA. Hinkle and Tesoriero (2014) were able to predict the extent of denitrification in aquifers at the continental scale in the United States from soil water depth, water residence time and other variables. Many of the statistical and analytical models that have been developed for predicting nitrate retention and removal in freshwater ecosystems, including streams and wetlands, have been restricted to surface water environments (Alexander et al. 2000, Fennel et al. 2009, Mulholland et al. 2009, Seldomridge et al. 2012, Aguilera and Sabatar 2013) with less emphasis on the groundwater-surface water interface.

The main objective of the research described here was to describe and predict spatial variation in nitrate retention and removal in shallow groundwater among and within streams in the central sand plains of Wisconsin, a region in which groundwater and surface water are chronically elevated in nitrate. We hypothesized that nitrate transformation rates would be related to the dissolved oxygen availability in pore water, groundwater discharge rate, organic carbon availability and groundwater nitrate concentration.

PROCEDURES AND METHODS

Study Locations
The study was conducted at 5 sites on 4 streams in Central Wisconsin (Table 1). One study site each was selected on Emmons Creek, the West Branch of the White River (WBWR), and Big Roche a Cri Creek (BRC), while two sites were selected on Radley Creek (Suhs and West Roads). Radley-Suhs was located about 2 km downstream of Radley-West. Emmons Creek, WBWR, and Radley Creek are located in the Lake Michigan Basin and within the Central Sands Ridges ecoregion. BRC is located in the Mississippi River Basin and within the Glacial Lake Wisconsin ecoregion. The watersheds of all the study streams had mixed land use consisting of forest, oak savanna (Emmons and Radley Creek watersheds), wetland, and

Table 1 Descriptive data (means, SD) for the study sites in Central Wisconsin.

Site	Location	Wetted width (m)	Reach length (m)	Piezometers	Groundwater discharge ($cm^3/m^2/s$)	Sediment organic matter (%)	Surface water nitrate (mg NO_3-N/L)	Surface water specific conductance (µS/cm)
Big Roche a Cri Creek	44°10’32.6 N 89°35’45.9 W	5.0 (1.2)	72	24	0.44 (0.32)	1.23 (1.10)	9.74 (0.88)	532
Emmons Creek	44°17’46.8” N 89°14’28.3” W	5.5 (0.8)	52	32	1.02 (1.39)	3.82 (5.68)	2.24 (<0.01)	407
Radley Creek (Suhs Rd)	44°16’34.4” N 89°11’28.1” W	5.4 (0.8)	60	31	1.25 (1.29)	1.87 (1.45)	3.81 (0.06)	407
Radley Creek (West Rd)	44°15’42.5” N 89°12’51.3” W	3.0 (0.4)	84	25	0.41 (0.36)	5.06 (4.43)	4.66 (0.10)	421
West Branch White River	44°04’37.6” N 89°20’40.1” W	5.7 (1.2)	72	21	0.69 (0.72)	1.95 (1.51)	1.48 (0.02)	355

row-crop agriculture. BRC and Radley-Suhs and Radley-West contained a larger proportion of row-crop agriculture in their watersheds than the other three streams, which is reflected in the relatively high groundwater or surface water nitrate concentrations (Table 1, Table 2). The riparian zones were forested at all of the study sites. The soils are sandy in both ecoregions and underlain by an aquifer consisting of sand and gravel (Holt 1965, Summers 1965). Groundwater is the main source of water for streams in these ecoregions and it is generally oxic (Stelzer and Bartsch 2012). Hence, the streams are cold-water ecosystems that support trout populations. The streams were third or fourth order and the study reaches were 52 to 84 m in length with mean wetted widths at base flow of 3 to 5.7 m. The specific conductance of surface water was similar among streams (Table 1). Sand was the predominant surficial sediment at all 5 sites but silt, gravel and cobble were also present in lower quantities. The majority of the stream bed in all of the study reaches contained a 5 to 60-cm (the deepest depth assessed) thick fine sediment (sand, silt) layer which overlaid a coarser layer consisting of gravel and cobble. The thickness of the fine sediment layer varied among the study sites.

Table 2. Mean (SD) solute concentrations and fluxes by sediment depth per study site in Central Wisconsin

Site	Depth (cm)	NO_3-N Concentration (mg/L)	NO_3-N Flux (µg/m2/s)	Cl- (mg/L)	SO_4-S (mg/L)	DO (mg/L)
BRC	60	15.14 (6.11)	6.87 (5.94)	19.63 (8.32)	5.60 (3.12)	4.7 (2.5)
	25	14.36 (7.17)	6.38 (5.58)	19.03 (9.33)	5.28 (2.79)	4.6 (2.2)
	5	13.67 (7.65)	6.20 (5.74)	19.09 (9.07)	5.32 (2.65)	2.1 (1.9)
Emmons	60	1.90 (1.15)	2.01 (2.80)	1.76 (0.68)	2.65 (2.23)	6.3 (1.2)
	25	1.63 (1.22)	1.46 (2.06)	1.77 (1.21)	2.09 (0.71)	4.3 (1.6)
	5	1.45 (1.29)	1.26 (1.79)	1.45 (0.59)	1.96 (0.92)	3.2 (2.3)
Radley-Suhs	60	10.15 (4.84)	14.47 (17.14)	12.95 (5.47)	9.73 (3.39)	3.3 (3.3)
	25	10.51 (4.54)	14.63 (17.34)	12.82 (5.07)	9.41 (3.02)	2.5 (2.5)
	5	9.70 (4.85)	13.61 (16.89)	12.38 (5.34)	9.27 (3.08)	2.0 (2.0)
Radley-West	60	1.63 (1.43)	0.77 (1.01)	1.57 (0.83)	2.55 (0.64)	9.5 (4.7)
	25	1.31 (1.34)	0.68 (0.97)	1.75 (1.37)	2.64 (1.08)	5.7 (5.4)
	5	1.11 (1.24)	0.62 (0.98)	1.71 (0.83)	1.85 (1.23)	4.4 (4.1)
WBWR	60	1.29 (0.49)	0.83 (0.88)	1.78 (1.44)	1.91 (0.65)	5.5 (1.7)
	25	1.20 (0.58)	0.76 (0.83)	2.10 (1.35)	1.92 (0.67)	4.9 (2.0)
	5	0.78 (0.62)	0.56 (0.55)	1.98 (2.33)	1.67 (0.77)	2.4 (2.0)

Study Design

Nitrate retention and N_2 production were measured at base flow in June through August of 2016 at WBWR, Radley-West and BRC and nitrate retention was measured at base flow in May and June of 2017 at Emmons Cr. and Radley-Suhs. 25 to 32 piezometers were installed at each site for hydrologic measurements and for adjacent pore water solute sampling. Piezometers, constructed with CPVC (1.2 cm inner diameter) with the terminal 4.5 cm screened (3 mm holes covered with 100-µm Nitex mesh), were inserted to an average sediment depth of 29 cm throughout the wetted channel, including near the bank and in the thalweg. Upwelling was determined at the locations of all of the piezometers (133 total) used in the study. Downwelling was present at the locations of 6 piezometers initially installed in a cluster at the upstream end of the WBWR study reach. These 6 piezometer locations were not considered further. Pore water was sampled for solutes at 5, 25, and 60 cm sediment depths at each piezometer location. Solute concentrations and fluxes were determined at all 3 sediment depths and differences in nitrate and N_2 fluxes were used to calculate nitrate retention and N_2 production, as described in more detail below.

Groundwater Hydrology

Piezometers were developed immediately after installation with a peristaltic pump.
Groundwater discharge (q, $cm^3/m^2/s$) was estimated based on Darcy's Law using the following equation:

$$q = K_v\ (\Delta h/\Delta l) \qquad \text{Eq. 1}$$

where:
K_v is vertical hydraulic conductivity (cm/s)
Δ h is the difference between the static head and stream surface water level (cm)
Δ l is the depth of the piezometer into the sediment (cm)

We measured horizontal hydraulic conductivity (K_h) using falling-head slug tests (Hvorslev, 1951; Stelzer et al., 2011). The slug tests were performed by adding 200 mL of water to each piezometer, measuring the return time to the static head level, and back-calculating the time lag (T_0) for the water to return to 37% of the initial change in head level (Hvorslev, 1951). Slug tests were performed in duplicate in each piezometer and mean values of T_0 were used to estimate q. We assumed that K_v was 1/10th of K_h (Dahm et al. 2006). Vertical hydraulic gradient (VHG) (Δ h/Δ l) was measured in each piezometer as described in Dahm et al. (2006) and Stelzer et al. (2011). Measurements for VHG were collected on the same day that slug tests were performed.

Pore Water Sampling

Pore water was collected at 5, 25, and 60 cm sediment depths using modified MINIPOINT samplers that consisted of stainless steel tubes (ID) that were perforated with slits and screened (100 um Nitex) along a 1 cm terminal section (Stelzer et al. 2014). Vertical groundwater flow paths were assumed. Thus, pore water collected from the 3 different sediment depths was considered to be on the same flow path. This assumption was assessed based on chloride concentrations as described subsequently. MINIPOINTS were inserted within 5 cm of each piezometer and pushed in by hand where fine sediments (silt, sand) would allow. At locations where surficial or deeper sediments were coarser an installation driver (0.8 cm diameter steel drive point inserted into a 1.1 cm diameter steel pipe) was used to insert the sampler. Thus, we were able to sample throughout the wetted channel and were not restricted to locations only containing fine sediments. Pore water was collected by slowly drawing water with a 60 ml syringe connected to a 3-way fitting which was connected to each MINIPOINT with tubing. Samples for nitrate, chloride, and sulfate were immediately filtered in the field through Whatman GF/F filters, placed on ice in the field, and stored at -20 ºC in the lab. Nitrate, chloride and sulfate concentrations were measured with an ICS-1000 ion chromatograph (Dionex, Waltham, Massachusetts) equipped with an IonPac AS14A column.

At three sites (WBWR, Radley-West and BRC) pore water was also collected for N_2, Ar and O_2 using MINIPOINTS. The pore water was immediately added to 24 mL glass test tubes, preserved with ZnCl, and sealed with a ground glass stopper. To further reduce N_2 contamination from the atmosphere the tubes were wrapped tightly with Parafilm and then submerged in sealed 1 L bottles filled with stream water immediately before placing the samples on ice in the field. The samples were kept cold during storage in the lab and during air-shipment to the University of Arkansas where gases were measured using membrane-inlet mass spectrometry (MIMS) using the methods described in Stelzer et al. (2014).

Nitrate Retention and N_2 Production

Nitrate and N_2 fluxes (µg N/m2/s) at 5, 25 and 60 cm were determined by multiplying solute concentrations by groundwater discharge at each piezometer location. Nitrate retention (µg NO_3-N/m^2/s) was determined as the maximum decline in nitrate flux along an upwelling flow path per piezometer location. In most cases this maximum decline was based on the differences between the nitrate fluxes at 60 and 5 cm. The Damkohler number for nitrate retention was calculated based on equation 5 in Flewelling et al. (2012) for use as an indicator of the relative importance of reaction rate and groundwater advection rate on nitrate retention. At the sites where N_2 was measured N_2 production (µg N_2-N/m^2/s) was determined as the maximum increase in N_2 flux per piezometer location. We assumed that N_2 production was caused by denitrification but other processes, such as Anammox, yield N_2 and could have contributed to the N_2 production rates.

Dissolved Oxygen

At 3 sites (WBWR, Radley-West and BRC) the dissolved oxygen concentration of pore water at 5, 25 and 60 cm was measured using MIMS as described previously. At Emmons Cr. and Radley-Suhs the DO of pore water was measured in the field. Pore water was collected into syringes using MINIPOINTS as described previously and the water was immediately injected into a flow cell that housed a YSI dissolved oxygen probe.

Sediment Organic Matter

Surficial sediment (upper 10 cm) was collected at each piezometer location with a cut-off 60 ml syringe for determination of organic matter content. Sediments were stored at -20 ºC in the lab, dried at 60 ºC and then combusted for 4 hours at 500 ºC. Percent organic matter was determined by dividing the mass loss after combustion by the dry mass.

Data and Statistical Analysis

We were primarily interested in assessing nitrate retention or N_2 production that occurred along continuous flow paths which linked the 5, 25, and 60 cm sampling points. Chloride tends to behave conservatively in sediments. Thus, chloride concentrations were compared among the 5, 25, and 60 cm depths at each piezometer location to assess if flow paths were vertical. In most cases chloride concentrations of pore water did not change in a vertical direction, which suggested that most flow paths were vertical. Cases in which the decline in chloride concentration was equal to or exceeded the decline in nitrate concentration decline were removed from the data set prior to calculating nitrate retention and N_2 production. Cases in which the initial nitrate concentration was very low (<0.1 mg NO_3-N/L) at 60 cm were also not considered when nitrate retention and N_2 production were calculated.

Multiple regression models were used to assess the influence of candidate independent variables on nitrate retention and N_2 production at all 5 sampling sites collectively and within each site. The independent variables included groundwater discharge, pore water nitrate and chloride concentrations at 60 cm, sediment organic matter and three dissolved oxygen variables (minimum DO concentration, the DO concentration at 60 cm, and DO loss, defined as the difference between the maximum and minimum DO concentrations per piezometer location). Stepwise multiple regression was used initially to identify statistically significant models and independent variables. This information was used to develop statistical models using partial least squares regression (Carrascal et al. 2009). One advantage of partial least squares regression is that it is less sensitive to multicollinearity. The statistical significance, amount of variation explained and the size and sign of the standard coefficients associated with each independent variable were used to evaluate the models and the importance of the various explanatory variables. In addition to multiple regression, nonlinear regression was used to develop simple models that described how nitrate retention and N_2 production were related to minimum DO concentration. All statistical analysis was conducted using Systat v. 13.

RESULTS AND DISCUSSION

Hydrology

Vertical hydraulic gradient was positive at 132 of the 133 piezometer locations used to measure nitrate retention (it was zero at one location). The grand mean VHG was 0.130 and means per site ranged from 0.095 to 0.169. Emmons Cr. (0.161) and Radley-Suhs (0.169) had the highest mean VHG. The grand mean of vertical hydraulic conductivity was 5.78 x 10^{-4} cm/s and site means ranged from 5.14 x 10^{-4} (BRC) to 6.91 x 10^{-4} (Radley-Suhs) cm/s. Groundwater discharge had a grand mean of 0.802 $cm^3/m^2/s$ and was highest at Emmons Cr. and Radley-Suhs (Table 1).

Pore water solutes

As mentioned previously pore water nitrate concentrations were 5 to 15-fold higher at BRC (mean of 15.14 mg NO_3-N/L at 60 cm sediment depth) and Radley-Suhs (10.15) than at Radley-West (1.63), Emmons Cr. (1.90) and the WBWR (1.29, Table 2). Chloride and sulfate pore water concentrations were also much higher at BRC and Radley-Suhs than at the other 3 sites. In most cases mean nitrate concentrations declined from 60 to 5 cm (Table 2) with the exception of Radley-Suhs at which the highest mean nitrate concentration occurred at 25 cm and the lowest occurred at 5 cm. Pore water chloride concentration, on average, did either not appreciably differ among sediment depths (Radley-West, WBWR) or declined (BRC, Emmons Cr., Radley-Suhs) by a lower magnitude than the decline in pore water nitrate concentration (Table 2). The sulfate concentration in pore water also tended to decline from 60 to 5 cm sediment depth.

Groundwater nitrate flux was highest at Radley-Suhs and BRC which reflected the relatively high pore water nitrate concentrations at these sites and the relatively high groundwater discharge at Radley-Suhs (Table 1, 2). Groundwater nitrate fluxes were much lower at Emmons Cr., Radley-West and the WBWR.

The pore water at 60 cm was oxic (i.e. > 2 mg DO/L) at 88% of the piezometer locations while pore water at 5 cm was hypoxic (i.e. < 2 mg DO/L) at 52% of the locations. Mean DO concentration at 60 cm was oxic at all of the study sites and ranged from 3.3 (Radley-Suhs) to 9.5 (Radley-West) mg/L. Mean DO concentration declined by a factor of 1.5 to 2 from 60 to 5 cm at all sites. Mean DO concentration at 5 cm approached hypoxia at BRC, Radley-Suhs, and WBWR.

Nitrate retention

Grand mean nitrate retention and N_2 production were 0.47 μg NO_3-N/m^2/s and 0.15 μg N_2-N/m^2/s. Nitrate retention differed among the 5 sites and was highest at Radley-Suhs (Fig. 1). N_2 production was highest at BRC and Radley-West and lowest at WBWR. N_2 production accounted for 72 and 47% of nitrate retention at Radley-West and BRC but only 14% of nitrate retention at WBWR.

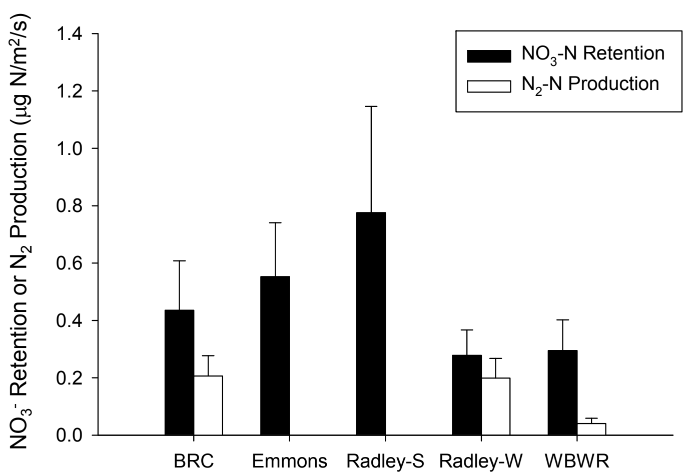

Fig. 1 Nitrate retention and N_2 production (mean, SD) in shallow groundwater at the 5 study sites in Central Wisconsin. BRC = Big Roche a Cri Creek, Emmons = Emmons Creek, Radley-S = Radley-Suhs Creek, Radley-W = Radley-West Creek, WBWR = West Branch of the White River. N_2 production was not measured in Emmons Cr. or at Radley-Suhs.

A partial least squares regression model based on all 5 sites explained 22% of the variation in nitrate retention (Table 3, $P < 0.001$). Based on the coefficient size groundwater discharge was the strongest (positive) predictor of nitrate retention for the full data set. DO loss was a weak positive predictor of nitrate retention and DO concentration at 60 cm sediment depth was a weak negative predictor. There was no discernable relationship between nitrate retention and groundwater discharge when all 5 sites were considered together (Fig. 2A). Minimum DO concentration explained 25% of the variation in nitrate retention based on a negative exponential model fitted to the full data set (Fig. 2B). At most of the locations where nitrate retention occurred minimum DO concentration was less than 2 mg/L.

In general, a partial least squares regression models explained much more variation in nitrate retention within sites than at the regional scale; i.e., when all sites were considered together (Table 3). These models explained 71, 82, 83, and 88 % of the variation in nitrate retention at Radley-West, BRC, Emmons, and WBWR ($P < 0.01$). The partial least squares regression model for nitrate retention at Radley-Suhs was not statistically significant. The model coefficients for groundwater discharge were positive and relatively high for Emmons Cr. and WBWR. DO variables were statistically significant predictors of nitrate retention for all sites expect Radley-Suhs based on the initial stepwise multiple regression model ($P < 0.05$). The 4 statistically significant partial least squares regression models at the site scale each included 1 to 3 DO variables. DO loss was a positive predictor of nitrate retention at BRC and Emmons Cr. and a negative predictor of nitrate retention at Radley-West. DO concentration at 60 cm was a negative predictor of nitrate retention at BRC and WBWR and a positive predictor at Radley-West. DOmin concentration was a negative predictor of nitrate retention at Radley-Suhs, Radley-West and WBWR based on the partial least squares regression models (Table 3). Nitrate concentration at 60 cm was a positive predictor of nitrate retention at WBWR and a negative predictor at BRC. Sediment organic matter and chloride concentration at 60 cm were not statistically significant predictors of nitrate retention in any of the multiple regression models.

Table 3. Partial least square regression model coefficients for nitrate retention, factors used in the regression model, the amount of variation in nitrate retention explained, the number of locations included in the models and their statistical significance. GWQ = ground water discharge, DO_{loss} = decrease in dissolved concentration, DO_{60} and $NO3_{60}$ = dissolved oxygen and nitrates concentrations at 60 cm sediment depth, DO_{min} = minimum dissolved oxygen concentration.

Site	Term	Coefficient	Factors	Variation explained (%)	N	P-Value
All Sites	GWQ	0.452	3	22	98	<0.001
	DO_{loss}	0.132				
	DO_{60}	-0.096				
BRC	DO_{60}	-0.393	3	82	14	<0.001
	DO_{loss}	0.184				
	$NO3_{60}$	-0.086				
Emmons	GWQ	0.883	2	83	27	<0.001
	DO_{loss}	0.128				
Radley-Suhs	DO_{min}	-0.425	1	9	24	0.148
Radley-West	DO_{min}	-0.897	3	71	16	0.002
	DO_{60}	0.857				
	DO_{loss}	-0.855				
WBWR	GWQ	0.691	4	88	19	<0.001
	$NO3_{60}$	0.649				
	DO_{min}	-0.142				
	DO_{60}	-0.093				

DO_{min} concentration tended to be a better predictor of nitrate retention at the individual site scale than when all sites were considered collectively. At Radley-West and BRC 68 and 47% of the variation in nitrate retention was explained by DO_{min} when negative exponential models were fit to the data (Fig. 3). However, at Emmons Cr and Radley-Suhs DO_{min} only explained 25 and 21% of the variation in nitrate retention, a similar amount of variation explained by DO_{min} at the regional scale (Fig. 2B). There was no relationship between nitrate retention and DO_{min} at WBWR.

A pattern emerged when the Damkohler number for nitrate retention was plotted against DO_{min}. In almost all of the locations at which the Damkohler number for nitrate

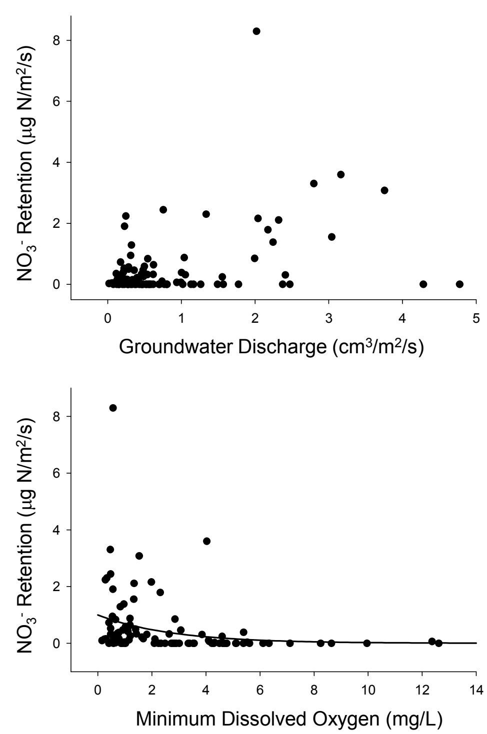

Fig. 2 Nitrate retention plotted against groundwater discharge (A) and minimum dissolved oxygen (DO_{min}) concentration in pore water (B) for all 5 sites. The nonlinear model in B is nitrate retention = exp (-0.369 DO_{min}), $r^2 = 0.245$.

retention was high, DO_{min} was less than 2 mg/L (Fig. 4). Where pore water was oxic throughout the sediment column, Damkohler numbers tended to be at or near zero.

Discussion

Predictors of nitrate retention and N_2 production

Nitrate retention and N_2 production varied among and within the study sites. We lacked the statistical power to assess causes of variation among the 5 sites. When the full data set was considered and when sites were evaluated individually groundwater discharge and DO variables were the most consistent predictors of the magnitude of nitrate retention. The amount of variation in nitrate retention that was explained by predictor variables in multiple regression models was much higher at the site scale than at the regional scale. Thus, our hypothesis that nitrate retention would be related to DO availability, groundwater discharge, nitrate availability and sediment organic carbon quantity was partially supported.

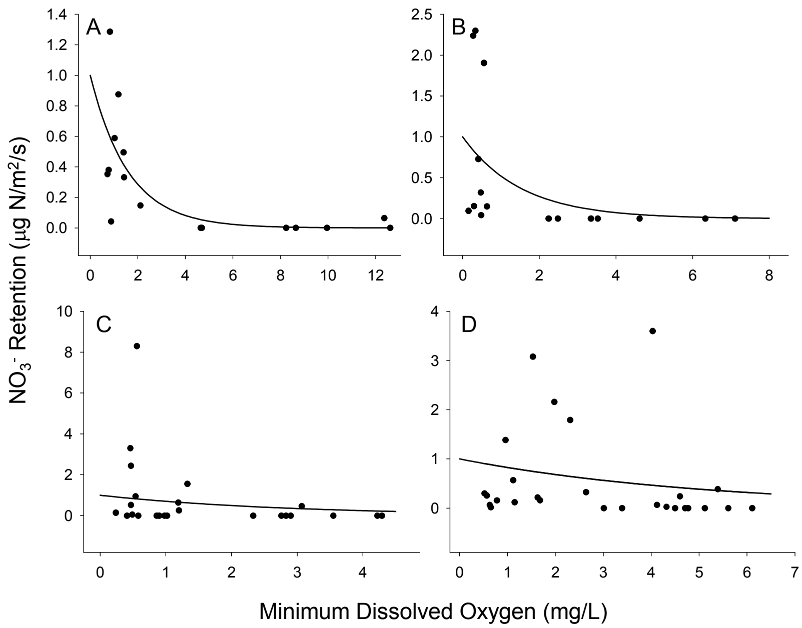

Fig. 3 Nitrate retention plotted against DO_{min} at Radley-West (A), Big Roche a Cri (B), Radley-Suhs (C) and Emmons Cr. (D). The general form of the nonlinear model is nitrate retention = exp (-x DO_{min}). The coefficients and r^2 are 0.626, 0.677 (A), 0.653, 0.465 (B), 0.349, 0.21 (C), 0.190, 0.254 (D).

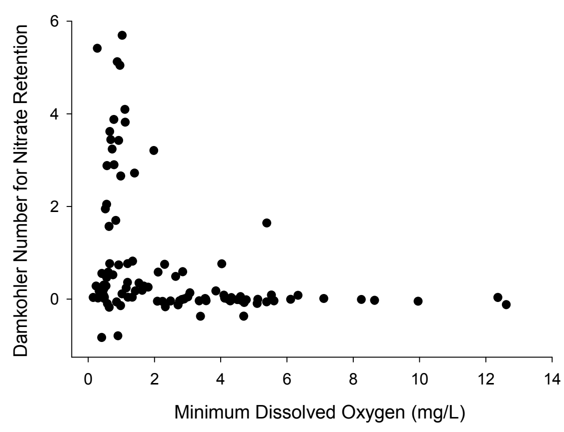

Fig. 4 The Damkohler number for nitrate retention plotted against minimum dissolved oxygen concentration for all 5 sites.

We predicted that nitrate retention would peak at intermediate rates of groundwater discharge. Nitrate retention exceeded 1µg NO_3-N/m^2/s at many locations (Fig. 2). However, groundwater discharge ranged from low (0.3 cm^3/m^2/s) to high (3.8) at these locations and there was no evidence that nitrate retention peaked at intermediate rates of discharge. On the contrary, groundwater discharge was positively related to nitrate retention in the partial least squares regression model at the regional scale and for two individual sites (Emmons Cr. and WBWR). Our prediction may have not been supported because groundwater discharge varied by less than 2 orders of magnitude at the vast majority of piezometer locations. At 84% of the piezometer locations the DO concentration of pore water decreased along the nominal upwelling groundwater flow paths. In addition, there was no correlation between DO loss and groundwater discharge rate (Pearson Correlation, P = 0.107). These results suggest that groundwater advection was sufficiently slow to allow biological activity to affect the solute concentrations. Several authors have reported that the magnitude or type of nitrogen transformation was limited at high advection rates, or maximized at low advection rates, at the groundwater-surface water interface (Flewelling et al. 2012, Zarnetske et al. 2011, Krause et al. 2013) but our results were not consistent with these previous findings, perhaps because the range of groundwater discharge among our sampling locations was not large enough to detect an impact on N transformation.

The partial least square regression model based on the full data set and the individual sites consistently showed that nitrate retention was related to DO variables. In all cases where DO_{min} was a significant predictor of nitrate retention the regression coefficient was negative which is consistent with redox potential influencing nitrate retention. In addition, the biplots of nitrate retention and DO_{min} (Fig 3) showed that for most locations nitrate retention was negligible or zero when DO_{min} was greater than 2 mg/L. 2 mg O_2/L has been widely considered a threshold for denitrification (Tesoriero et al. 2015). At two of the three sites considered N_2 production accounted for at least 47% of the nitrate retention, which suggests that denitrification was important at these sites. In most cases (Table 3) DO loss was a positive predictor (i.e. positive regression coefficient) of nitrate retention which is consistent with the role of denitrification in nitrate retention. Aerobic bacteria probably played an important role in consuming DO in the sediments, which likely facilitated denitrification after redox potential declined. However, our results suggest that a considerable amount of nitrate retention was due to assimilatory uptake by bacteria which is well known to occur in sediments (Bunch and Bernot 2012). The DO concentration at 60 cm frequently was a statistically significant predictor of nitrate retention in the multiple regression models and in most cases, including when the full data set was considered, was a negative predictor. One possible explanation for this result is that the DO concentration at 60 cm reflected the microbial activity over a longer flow path than which we characterized with the MINIPOINT samplers. For example, low DO concentrations at 60 cm might indicate favorable zones for oxygen consumption and by extension nitrate retention or removal, in the sediments. Several other investigators have found relationships between nitrogen transformation, including denitrification, and DO availability in groundwater, sediments and soils (Piña-Ochoa and Álvarez-Cobelas 2006, Tesoriero and Puckett 2011, Burgin and Groffman 2012).

Progress and challenges in predicting of nitrogen transformation hotspots

We were able to predict 71to 88% of the variation in nitrate retention at 4 of the 5 study sites, when considered separately, but our predictive power was much lower at the regional scale. Although the study sites shared several similarities (surficial fine sediments, gaining stream reaches) differences among sites, such as nitrate availability and the magnitude of groundwater discharge, may have contributed to the decreased ability to predict nitrate retention at the regional scale. One limitation of our study was the lack of quantitative data on sediment grain size, structure, and organic matter quantity and quality, particularly below 10 cm. The lack of data on abundance, community structure and function of the microbial community may have also influenced our ability to predict nitrate retention at the regional scale, particularly if these components varied among the study sites. DO_{min} predicted nitrate retention reasonably well at two of the sites, but DO_{min} and other variables were weaker predictors of nitrate retention at the regional scale. Although hypoxic to anoxic conditions in sediments favor dissimilatory uptake of nitrate, electron donors and nitrate supply are also necessary for dissimilatory N transformation processes such as denitrification. Low or zero nitrate retention at some of the locations with favorable redox potential for denitrification may have been due to unmeasured variables such as organic carbon quantity and quality in deeper sediments (> 10 cm).

Several investigators have used mechanistic or statistical models to predict nitrate retention, denitrification, or its potential at regional to continental scales (Boyer et al. 2006, Tesoreiro et al. 2015). Mulholland et al. (2009) found that surface water discharge, nitrate concentration, and ecosystem respiration and transient storage predicted denitrification rate in stream channels based on a continental-scale study (LINX II). Fennel et al. (2009) used mechanistic models and correlations to predict denitrification occurring in sediments using a large global data set from freshwater, brackish and marine ecosystems. A multiple regression model that included several independent variables (sediment oxygen consumption, nutrient fluxes, and nitrate and DO concentrations) successfully predicted denitrification rates. Sediment oxygen consumption was the strongest predictor of denitrification based on the magnitude of its standardized partial regression coefficient. Duncan et al. (2013) determined that microtopography within the riparian zone was a strong predictor of soil O_2 and denitrification rates. Liao et al. (2012) determined that modeled zero-order rates of DO reduction and denitrification were correlated in groundwater. Tesoreiro et al. (2015) used data on surficial geology and hydrologic variables to predict redox conditions, an indicator of denitrification potential, in groundwater at the regional scale. Although several variables have been used to predict nitrate retention and denitrification in ecosystems DO concentration and loss have been shown to be some of the most powerful and consistent predictors of these rates in sediments and soils, which is consistent with the results of our study.

CONCLUSIONS/IMPLICATIONS/RECOMMENDATIONS

Nitrate retention and denitrification in shallow groundwater associated with streams in the Central Sand Plains of Wisconsin were widespread but highly variable. 5 to 25% of the nitrate flux at 60 cm was retained in the shallow groundwater and retention was less efficient in the high N systems. Preliminary analysis suggests that the rates of nitrate retention and denitrification we measured in shallow groundwater are comparable to the nitrogen transformation rates determined in stream channels throughout the world. We were able to predict nitrate retention using multiple regression models at both regional (Central Sand Plains) and local scales. In general, the statistical models explained a much larger amount of variation in nitrate retention at the local scale than at the regional scale. Consistent predictors of nitrate retention included dissolved oxygen availability and ground water discharge. Strong groundwater-surface water connections are necessary to take advantage of the nitrogen transformation potential in shallow groundwater at the groundwater-surface water interface. We also recommend that conditions are promoted by natural resource managers that will facilitate oxygen removal at this interface, including opportunities for fine sediment deposition and organic carbon (e.g. leaves, wood) accumulation. Groundwater-surface water interactions and the opportunity for groundwater to pass through sediments in which oxygen is low or depleted will provide conditions necessary for nitrate retention and removal.

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Appendix A

Published papers and manuscripts

Stelzer, R.S., E.A. Strauss, M. Coulibaly. 2017. Assessing the importance of seepage and springs to nitrate flux in a stream network in the Wisconsin sand plains. Hydrological Processes 31:2016-2028. DOI: 10.1002/hyp.11161.

In Prep (Fall 2017 submission target):
Stelzer, R.S., Scott, T. Predicting hotspots of nitrate retention at the groundwater- surface water interface in sandplain streams. Target journal: Journal of Geophysical Research-Biogeosciences

Presentations

Stelzer, R.S. and T. Scott. 2017. Towards predicting spatial variation in nitrate retention and denitrification at the groundwater-surface water interface in sandy streams. Abstract of oral presentation at the Society for Freshwater Science Annual Meeting, June 4-8, Raleigh, NC. About 1000 attendees at meeting.

Kasten, R and R.S. Stelzer 2017. The effects of flow rate and organic matter on nitrate retention in laboratory sediment columns. Abstract of poster presentation at University of Wisconsin Oshkosh Celebration of Scholarship. April 27, Oshkosh, WI. About 100 attendees at meeting.

Stelzer, R.S. and T. Scott. 2017. Identifying nitrate retention and denitrification hot spots at the groundwater-surface water interface in streams of the Central Sands. Abstract of a poster presentation at American Water Resources Association (Wisconsin Section) Annual Meeting, March 9-10, Elkhart Lake, WI. About 200 attendees at meeting.

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Impact of work to layman

Nitrogen is essential for all forms of life, including humans. However, excess nitrogen in water can make people sick and can cause algae blooms which can lead to fish kills and associated problems. Our research showed that shallow groundwater associated with streams in Wisconsin is an important location for nitrogen removal. These streams provide the ecosystem service of water quality improvement. However, in some of the ecosystems with high amounts of nitrogen the supply of nitrogen overwhelmed the ability of shallow groundwater to remove the nitrogen. We determined that the amount of groundwater discharge and the supply of oxygen in the groundwater were good predictors of the amount of nitrogen that streams could remove. Maintaining good connections between groundwater and surface water in streams and providing opportunities for low oxygen underneath the stream bed are important for nitrogen removal. One way to promote oxygen removal in stream beds is to allow leaves and wood to accumulate in streams. In addition to providing important habitat for water bugs and fish, leaves and wood tend to decrease the amount of oxygen underneath the stream bed, which is important for nitrogen removal.

We think our work has implications for aquatic resource management and monitoring. Our research successfully identified variables, including a suite of dissolved oxygen variables, that could predict nitrate retention. Monitoring programs in streams that include evaluations of groundwater quantity and quality (including dissolved oxygen availability and nitrate concentration) could be used to more fully characterize the risks of nitrate pollution to streams and the opportunities for nitrate retention and removal. We were able to better predict nitrate retention at the local scale than at the regional (Central Wisconsin) scale. We advocate that researchers gain further understanding about the drivers of nitrate retention at the surface water-groundwater interface in order to choose the appropriate variables that could be successful in predictive models of nitrate retention and denitrification at regional and continental scales.