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Vulnerability of Streams to Legacy Nitrate Sources

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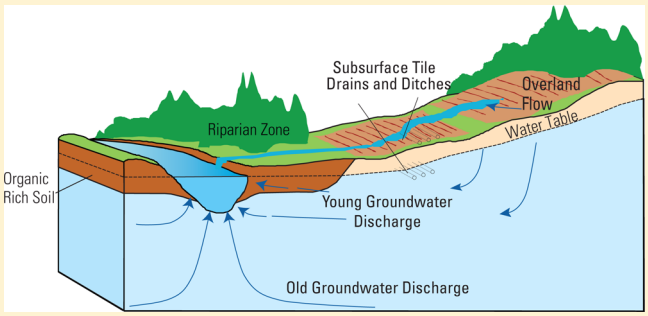
ABSTRACT: The influence of hydrogeologic setting on the susceptibility of streams to legacy nitrate was examined at seven study sites having a wide range of base flow index (BFI) values. BFI is the ratio of base flow to total streamflow volume. The portion of annual stream nitrate loads from base flow was strongly correlated with BFI. Furthermore, dissolved oxygen concentrations in streambed pore water were significantly higher in high BFI watersheds than in low BFI watersheds suggesting that geochemical conditions favor nitrate transport through the bed when BFI is high. Results from a groundwater−surface water interaction study at a high BFI watershed indicate that decades old nitrate-laden water is discharging to this stream. These findings indicate that high nitrate levels in this stream may be sustained for decades to come regardless of current practices. It is hypothesized that a first approximation of stream vulnerability to legacy nutrients may be made by geospatial analysis of watersheds with high nitrogen inputs and a strong connection to groundwater (e.g., high BFI).



INTRODUCTION

Increased nitrogen applications to the land surface have led to a dramatic increase in nitrate concentrations in recharging groundwater over the last 50 years.[1,2] Elevated nitrate concentrations in groundwater also pose a risk to streams; groundwater can be a dominant source of nitrate in base-flow dominated streams in agricultural areas.[3] In addition, the movement of nitrate through aquifers to streams can take decades to occur resulting in decades-long lag times between the time when a land use activity is implemented and when its effects are fully observed in streams.[4] In fact, legacy groundwater sources of nitrate have been suggested as the cause of increasing nitrate concentrations in rivers in the United States,[5] and in the United Kingdom,[6] despite a decline in N inputs.

Hydrogeologic setting has a major influence on both mean base flow transit times in streams and the effectiveness of the riparian zone in removing nitrate from groundwater.[7,8] For example, the presence of a shallow aquitard in upland areas prevents the downward movement of water, restricting groundwater to a local flow system (Figure 1). In this local flow system, recharge in the upland areas of the watershed follows relatively short flow paths and discharges to a nearby stream. These shallow horizontal flow paths are also likely to intercept riparian sediments, potentially rich in electron donors (e.g., organic compounds, sulfide minerals) that may facilitate denitrification.[9] Conversely, when shallow aquitards are not present, thicker surficial aquifers develop resulting in longer groundwater flow paths from recharge areas in the uplands to discharge areas in or near streams. It has been suggested that these longer flow paths are more likely to flow beneath riparian sediments, bypassing zones where denitrification can occur.[10] Similarly, much greater loss of nitrate due to denitrification has occurred in shallow water table environments where hydric soils are more common than at sites having steeper slopes, greater depths to water, and nonhydric soils.[11]

Nitrate loss from groundwater due to denitrification does not occur only in riparian zones but may also occur in upland portions of an aquifer once dissolved oxygen (DO) has been reduced.[12] However, when electron donors are limited, DO reduction rates are low resulting in thick oxic zones and groundwater flow paths that remain oxic for decades.[13] Low DO reduction rates in groundwater and limited stream deposition of organic material may result in oxic streambed conditions providing a potential pathway for nitrate transport to streams.

Intensive studies are required to discern nitrate transport along flow paths in a watershed. As a result, it is often not possible to delineate flow paths and associated geochemical reactions at a watershed scale. To assess the vulnerability of streams to legacy nutrients, metrics based on stream hydro-

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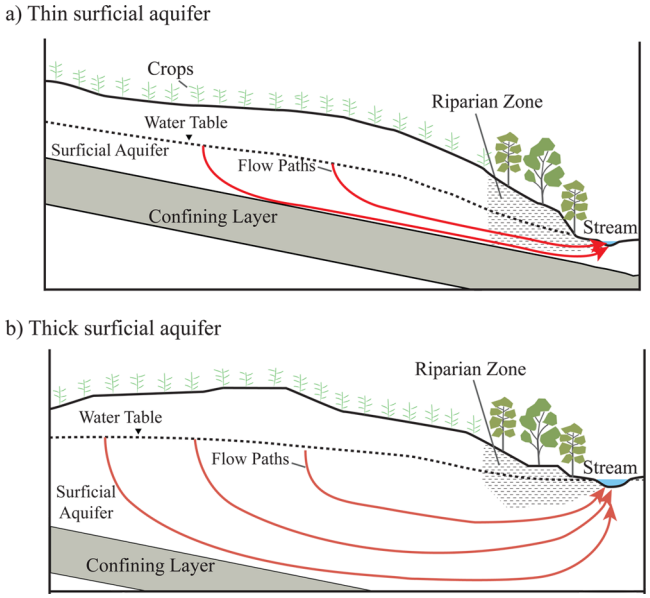

Figure 1. Influence of depth to confining layer on groundwater flow paths to streams. (a) Confining layer at shallow depth results in thin surficial aquifer and flow paths that intersect riparian sediments. (b) Deep confining layer increases likelihood that flow paths pass beneath riparian sediments. Adapted from Böhlke and Denver (1995).[15]

graph characteristics may be useful as an indicator of dominant pathways. Specifically, the base flow index (BFI), which is the percentage of total streamflow that is derived from base flow, may be used to estimate the proportion of nutrients in streams that are derived from groundwater sources.[3,14]

In this study, we examine the influence of hydrogeologic setting on the susceptibility of streams to legacy nitrate. Specifically, using data from seven study sites with a range of hydrogeologic settings we examine the hypothesis that streams with a high BFI are more vulnerable to legacy nitrate compared to low BFI streams due to both the increased portion of streamflow derived from groundwater and the increased likelihood of oxic conditions in the streambed. Streambed samples represent an integration of many flow paths. We hypothesize that flow paths to the streambed in low BFI watersheds are more likely to encounter reduced riparian sediments than are flow paths to the streambed in high BFI watersheds. Second, we examine the age and pathways of nitrate transport to streams in two contrasting hydrogeologic settings − a base flow dominated stream with a thick surficial aquifer and a quick-flow dominated stream with a relatively thin surficial aquifer − to quantify the influence of legacy nitrate on streams and its dependence on hydrogeology. Last, we present results on the legacy that decades of recharge of high-nitrate groundwater has on future trends in stream nitrate concentrations at a high BFI watershed.

■ MATERIALS AND METHODS

Study Areas. Seven study sites were selected to represent a range of hydrogeologic conditions as expressed by the wide range in BFI values (Table 1). Sites were selected from existing USGS studies that had (1) a stream gage with at least one year of continuous discharge data, (2) streambed and upland groundwater samples that were analyzed for at least nitrate and dissolved oxygen, and (3) a sampled reach that was representative of groundwater−surface water interactions for the stream. The seven study sites cover a wide range of hydrologic conditions ranging from systems dominated by quick flow (BFI <0.2) to those dominated by slow flow (BFI >0.8). Study sites were typically in agricultural areas; however, at some sites rural residential or suburban areas were present. Details of each site are provided in previously published reports.[12,15−20]

Groundwater and Stream Sampling. The surface water, upland groundwater, and streambed pore water sampling design is briefly described below with details provided elsewhere.[3,21,22] All surface water sampling sites were located near USGS stream gages, where continuous streamflow measurements were recorded. Surface water chemistry samples were typically collected at fixed intervals (usually every 2 weeks) over a two-year period with supplemental samples coinciding with storm-induced runoff. In most settings, 15−20 upland groundwater monitoring wells were installed in groundwater recharge areas along a single transect extending up to several kilometers upgradient of the stream and sampled quarterly during a single year. Well screens were 1 m or less in length and were set in the uppermost aquifer. Streambed pore water samples were typically taken at the same time groundwater was sampled using stainless-steel drive point piezometers. Streambed pore water samples were collected along stream study reaches ranging from 500 to 1000 m upstream of the surface water sampling station. Although the chemistry of streambed pore water may be influenced by hyporheic exchange, bromide tracer studies indicate that there is little hyporheic exchange in these systems.[22]

Water samples were collected according to established protocols.[23] Water samples from all surface water and most groundwater sites were analyzed for major ions, ammonia, nitrate, and orthophosphate. Nitrate concentrations are reported as nitrogen. Water samples for dissolved constituents were filtered with a 0.45 μm filter. DO and pH in groundwater were measured using electrodes while water was being pumped

Table 1. Basin Characteristics, Mean Annual Discharge, and Base Flow Index Values for Each of the Seven Study Areas

location[a]	stream	drainage area (km^2)	mean annual discharge[b] (m^3/s)	base flow index[b]	upland surficial geology
Crumpton, MD	Chesterville Branch	16	0.21	0.71	sand and gravel
Kennedyville, MD	Morgan Creek	31	0.49	0.45	sand and gravel
Lizzie, NC	Sandy Run	74	0.52	0.17	medium to fine sand
Nelsonville, WI	Tomorrow River	110	0.74	0.84	glacial outwash
Mohawk, IN	Leary Weber Ditch	7.2	0.098	0.12	glacial till
Nickerson, NE	Maple Creek	950	2.0	0.35	loess, till and alluvium
Granger, WA	DR2	5.5	0.14	0.57	alluvial fan and loess deposits

[a]Refers to town that is nearest to stream gage. [b]Mean annual discharge, base flow index values, and streamwater quality samples are for water years 2003 and 2004 except for Chesterville Branch (1997−2002), Sandy Run (2000−2001), and Tomorrow River (1995).

through a flow cell chamber to minimize atmospheric interactions. At the Tomorrow River site, streambed pore water samples were also collected and analyzed for chlorofluorocarbons (CFC11, CFC12, CFC113), with recharge dates estimated using published methods.[24] Descriptions of the analytical methods for nutrients and major ions are provided in Fishman et al.[25]

Statistical Methods. An analysis of variance was performed on the ranks of dissolved oxygen concentrations in streambed pore water at each site to test the null hypothesis that concentrations at these sites were not significantly different ($p < 0.05$). The Tukey multiple comparison test was used to determine which sites were different from others. This approach was also used to determine if nitrate concentrations (or nitrate/chloride ratios) in groundwater and streambed pore water were significantly different at a site. All statistical calculations were performed using *Statistical Analysis Software* (*SAS* Version 9.1.3).

The method used to calculate the base flow contribution of water and nitrate at each site relied on the "BFI Program"[26] to estimate base flow and the LOADEST model[27] to estimate the portion of the nitrate load in each stream that is derived from base flow. Details on these methods are provided elsewhere.[3,14]

Tomorrow River Groundwater−Surface Water Interaction Study. An intensive groundwater−surface water interaction study was conducted using previously published methods[22] at the Tomorrow River. At this site, discharge was measured at 3 locations by tracer injection for 72 h along a 1.3 km stream reach with no tributaries. The injectate consisted of sodium bromide (Br^-) mixed with ~600 L of streamwater in a plastic stock tank. The injectate was pumped into the stream at ~0.1 L min^{-1} using a rotary-drive, positive-displacement piston pump controlled by a data logger. Bromide was sampled at the base of a mixing reach and at 3 downstream locations (reach lengths: 276, 583, 458 m). Groundwater discharge was calculated by tracer dilution between upstream and downstream stations.

Approximately 60−80 Br^- samples were collected intensively during the rise of the tracer at each location and then every 4 h during the plateau to estimate travel time between stations, stream discharge, groundwater inflow, and transient storage. Water samples were also collected upstream of the injection to correct for background Br^-.

■ RESULTS AND DISCUSSION

Nitrate Pathways to Streams Across Hydrogeologic Settings. In six of the seven streams studied, the portion of annual stream nitrate loads from base flow exceeded the portion of streamflow derived from base flow (i.e., plotted above 1:1 line in Figure 2). These results extend the findings observed earlier[3,14] that groundwater discharge to streams is a preferential pathway for nitrate loadings to these streams. It should be noted that the two watersheds with the lowest BFI values have extensive tile drainage. If streamflow is relatively constant due to sustained periods of tile drainage, this flow will be included as a part of base flow. As a result, nitrate from tile drainage may be a significant portion of the base flow nitrate load in these systems.

Redox conditions in the streambed can have a dramatic effect on the transport and transformation of nitrate. Nitrate is mobile under oxic conditions but often denitrified when suboxic conditions are encountered. It is hypothesized that DO concentrations in streambed pore water will increase as a function of BFI. As BFI increases, streams are more likely to be in watersheds with well drained sediments, have thicker surficial aquifers, and have flow paths that bypass riparian zone sediments (Figure 1).[8,28] To examine this hypothesis, DO concentrations were measured in streambed pore water at each of the seven sites representing a wide range of BFI values. Although DO concentrations are highly variable at individual sites, concentrations tend to be higher when BFI is higher (Figure 3). The sites with the highest BFI (Chesterville Branch and Tomorrow River) had DO concentrations that were statistically similar to each other but higher than those found at sites with lower BFI values (Figure 3).

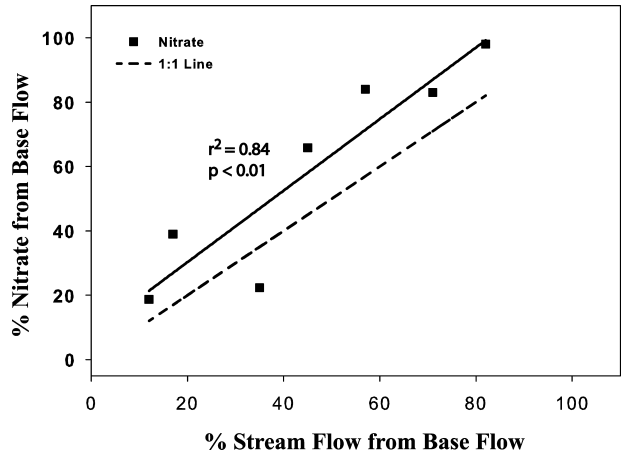

Figure 2. Estimated percentage of stream nitrate load that is derived from base flow versus the percentage of streamflow from base flow (squares). Solid line is linear regression fit to data. See Table 1 for period of record.

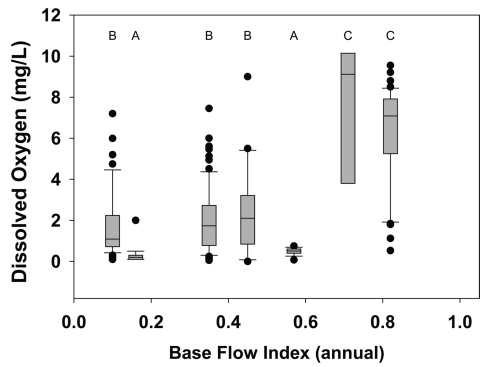

Figure 3. Dissolved oxygen concentration boxplots for streambed pore water versus base flow index. Box plots with different letters above them are statistically different ($p < 0.05$) from each other.

Differences in nitrate concentrations and nitrate/chloride ratios between upland groundwater and streambed pore water were examined at each site to evaluate the influence of hydrogeologic setting on nitrate transport in these agricultural watersheds. Nitrate concentrations are typically low in upland groundwater at two of the three low BFI sites (Leary Weber and Maple Creek) suggesting that denitrification occurred in the unsaturated zone or in the shallow portion of the saturated zone upgradient of our sample locations (left panel of part a of Figure 4). Denitrification in the saturated zone rather than the unsaturated zone is indicated based on vertical profiles of nitrogen species, dissolved gases, and stable isotopes in the

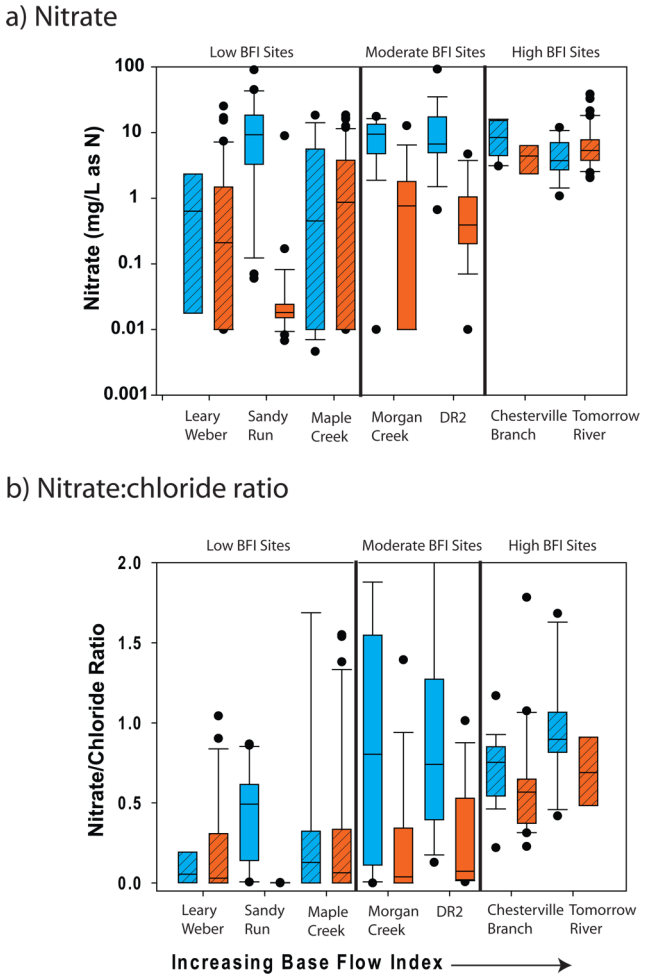

Figure 4. Nitrate (a) and nitrate/chloride mass ratio (b) boxplots for upland groundwater (blue boxplots) and streambed pore water (red boxplots). Hatched boxes indicate sites where groundwater and streambed values are not significantly different ($p < 0.05$).

unsaturated zone at these sites.[29] Although Sandy Run had higher nitrate concentrations than the other low BFI sites, denitrification in upland groundwater was also indicated at the Sandy Run site.[12] In contrast, at the moderate BFI sites (Morgan Creek and DR2), high nitrate concentrations occur in the upland but decrease dramatically in streambed pore water suggesting that conditions are suitable for nitrate transport in upland groundwater but not as groundwater approaches the stream. Denitrification and/or uptake in the riparian zone and/or the streambed is indicated at these moderate BFI sites (middle panel in part a of Figure 4). At the high BFI sites, nitrate concentrations are high in upland groundwater and in streambed pore water suggesting denitrification in the riparian area and streambed has little impact on nitrate concentrations in these systems (right panel in part a of Figure 4). These findings suggest that riparian zone denitrification at these sites is nitrate limited in the low BFI watersheds and electron donor limited in the high BFI watersheds with the moderate BFI watersheds more likely to have an adequate supply of both electron donors and nitrate to facilitate denitrification.

Although changes in nitrate gradients between upland groundwater and streambed pore water may suggest denitrification, dilution may also be responsible for decreases in nitrate concentrations along flow paths. Decreasing nitrate concentrations along a flow path can occur by dilution with water that recharged the aquifer beneath a less agriculturally intense area or with water that recharged during a less agriculturally intense time period. Because both nitrate and chloride are often elevated in agricultural areas, nitrate/chloride ratios help to elucidate whether denitrification or dilution has occurred along groundwater flow paths.[30−32] Lower nitrate concentrations along flow paths are likely caused by dilution if nitrate/chloride ratios remain constant. Conversely, if nitrate/chloride ratios decrease then denitrification is indicated.

Nitrate/chloride ratios are similarly low in upland groundwater and streambed pore water in two of the three low BFI sites indicating little retention along flow paths to the stream because nitrate has already been denitrified prior to reaching sample locations in the upland (left panel in part b of Figure 4). The steepest decline in the nitrate/chloride ratio is observed at the moderate BFI sites indicating a large loss in nitrate as groundwater moves from the upland to the streambed (middle panel in part b of Figure 4). In contrast, only small, statistically insignificant declines in nitrate/chloride ratios are seen at the high BFI sites suggesting denitrification does not remove a large portion of the nitrate from this system (right panel in part b of Figure 4). The finding that nitrate loss due to denitrification in the riparian zone and streambed occurs at moderate BFI sites (DR2 and Morgan Creek) but not at high BFI sites (Chesterville Branch and Tomorrow River) is supported by detailed flow path studies conducted at these locations.[15,16,33]

Comparison between a Quick-Flow and Groundwater-Dominated Watersheds. Two watersheds with contrasting hydrology and geochemistry are examined in greater detail to illustrate the influence these factors have on the timing and pathways of nutrient inputs to streams. Sandy Run, which is in the coastal plain of North Carolina, is an example of a low BFI watershed where water and nutrients move rapidly from fields to streams primarily as overland flow and through tile drains. In contrast, the Tomorrow River in central Wisconsin is a high BFI site where streamflow and nitrate are derived primarily from groundwater discharge.

Stream vulnerability to legacy nitrate is dependent upon the age distribution and pathways of nitrate discharging to streams. Streams receiving groundwater from long, oxic flow paths in watersheds with a long history of N loadings to the land surface are most vulnerable to legacy nitrate. Redox conditions at the Sandy Run and Tomorrow River sites were examined to assess the susceptibility of these streams to legacy nitrate. Oxic conditions (DO >0.5 mg/L) are prevalent throughout the 20 m thickness of the surficial aquifer at Tomorrow River watershed but comprise less than 5 m of the surficial aquifer at the Sandy Run site.[12,16] These differences can be attributed to differences in recharge rates and DO reduction rates between these two sites. Recharge rates at the high BFI site are more than double those at the low BFI site (210 vs 100 mm/yr).[34] Recharge is the only source of DO to aquifers so higher recharge rates result in a higher DO supply to the high BFI aquifer. Furthermore, the rate of DO reduction in the high BFI watershed is only about half of the rate found in the low BFI watershed (5.6 and 10 μmol/L yr, respectively) likely due to a higher amount of electron donors in the low BFI aquifer.[13] The faster recharge rates and slower DO reduction rates at the high BFI site result in a thick oxic zone allowing for the migration of nitrate from the upland through the streambed and into the stream.[16] In contrast, at the low BFI site suboxic conditions occur both in shallow upland groundwater and streambed sediments.[12]

Denitrification in these suboxic conditions prevents nitrate discharge through the streambed. As a result, stream nitrate derived from groundwater in Sandy Run is likely very young water delivered to streams along shallow flow paths because only these flow paths have suitable conditions (sufficient concentrations of DO to limit denitrification) for nitrate transport.

Effects of Legacy Nitrate on Streams. Decades of recharge of high-nitrate groundwater are likely to have significant implications for trends in nitrate concentrations in the high BFI watersheds in this study. A groundwater−surface water interaction study employing both a stream tracer injection experiment and water chemistry sampling of multiple environmental compartments was conducted at the high BFI Tomorrow River site to evaluate the impacts of legacy nitrate sources on trends in stream chemistry. Mass balance calculations using data from the stream tracer experiment indicate that nitrate concentrations in discharging groundwater were 8.0, 3.6, and 5.5 mg/L for the three subreaches (red line in part a of Figure 5) and 4.8 mg/L for the entire reach. Nitrate concentrations in streambed pore water were also high (black triangles in part a of Figure 5, median values of 10.9, 5.2, and 6.6 mg/L) in each of the sub-reaches confirming the presence of a strong groundwater nitrate source in this watershed.

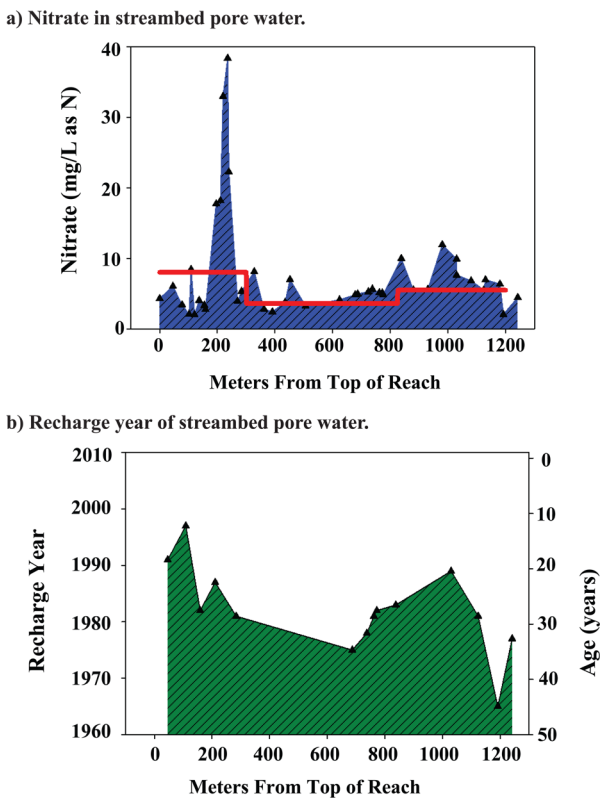

Figure 5. (a) Nitrate concentrations in streambed pore water along the study reach at the Tomorrow River are indicated by triangles and blue hatched area. Red line indicates nitrate concentration of discharging groundwater needed to close stream mass balance during tracer injection study. (b) Recharge year of streambed pore water at the Tomorrow River based on chlorofluorocarbon concentrations are indicated by triangles and green hatched area.

The age distribution of groundwater discharging to the Tomorrow River lends insight into the lag time between land application of N and its effect on streamwater quality. Selected drive point piezometers were sampled and analyzed for chlorofluorocarbons to estimate the apparent ages of these samples. Apparent ages of most streambed pore water ranged from 18 to 32 years with an average age of 27 years (black triangles in part b of Figure 5). This would suggest that decades may pass before changes in land use implemented today will noticeably affect stream chemistry. This finding is consistent with observations in a nearby stream.[35]

To understand how stream chemistry may change in a system with long lag times, it is necessary to estimate how nitrate concentrations vary as a function of recharge date. In the next decade, concentrations of nitrate in the Tomorrow River are likely to increase, not because of recent applications of fertilizer, but because the average recharge date of groundwater discharging to the stream will be from a period with higher nitrate concentrations in recharging groundwater (1990s) than the recharge period that currently discharges to this stream (1980s).[16] A leveling off of N applications to the land surface in recent decades in this area[16] should result in stable, but high, nitrate concentrations in groundwater recharged from mid-1990s to present. As a result, base flow nitrate concentrations in this stream are likely to remain high for decades even if N applications to the land surface are reduced.

Implications for Surface Water Trends. Recently, researchers are finding nitrate trends in streams and rivers do not match expectations based on recent nitrogen source loadings to the land surface and have suggested groundwater discharge with long travel times as the likely factor responsible for these observations.[6] Furthermore, in the Mississippi and Missouri Rivers, nitrate concentrations were found to increase more at low and moderate flows than at higher flows indicating that groundwater is having a substantial effect on river nitrate concentrations.[5] Observations presented in this article establish that lag times on the order of decades occur in some streams and that legacy nitrate sources can result in increases in nitrate concentrations over time regardless of changes in current land use practices.

Although the focus of this article has been on nitrate, other contaminants that are stored in aquifers can affect stream chemistry long after their application to the land surface. For example, elevated chloride concentrations in groundwater where deicing compounds are used may pose a risk to aquatic ecosystems when this chloride-laden water discharges to surface water.[36] Delineating areas with potential legacy issues in streams would help environmental managers establish management strategies and better define the time period in which results from these strategies may be expected. Unfortunately, the intensity of the sampling and analysis required to conduct the above assessment of the effect of legacy nutrients at the Tomorrow River precludes this approach from being widely applied. Rather, a better approach to provide a broad assessment of stream vulnerability to legacy nutrients would be to use geospatial data. Here, and in previous studies,[3,14] we have suggested that BFI is a good first approximation of the expected groundwater contributions to nitrate loads. It is hypothesized that a first approximation of stream vulnerability to legacy nutrients may be made by geospatial analysis of watersheds with high nitrogen inputs and a strong connection to groundwater (e.g., high BFI). For example, watersheds with a BFI greater than 0.4 and a range of nitrogen loadings are shown in Figure 6 to illustrate areas where nitrogen legacy issues may be more likely to occur (darker colors in Figure 6). Estimates of the vulnerability of streams to legacy contaminants would be

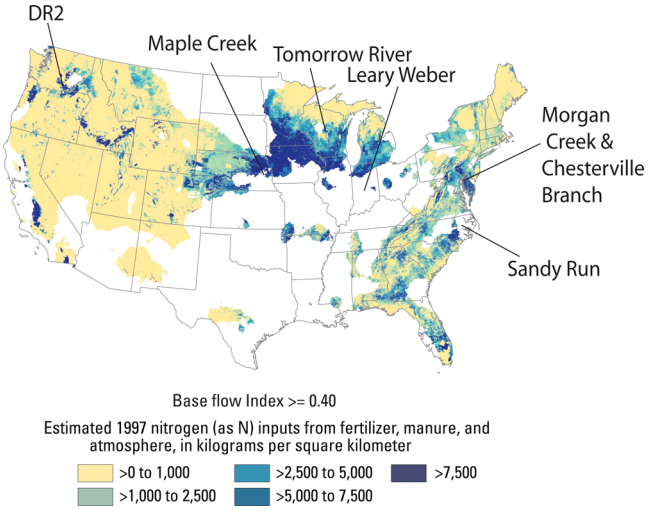

Figure 6. Map depicting nitrogen inputs to agricultural areas of the United States that have base flow index values greater than 0.4. Base flow index values and nitrogen inputs are based on previously published data.[37,38] Study area locations are also shown.

improved by refining estimates of base flow and transformation rates and by determining the relative influence of pathway, transformation, and loading factors on vulnerability.

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Notes

The authors declare no competing financial interest.

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