Identifying Pathways and Processes Affecting Nitrate and Orthophosphate Inputs to Streams in Agricultural Watersheds

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Understanding nutrient pathways to streams will improve nutrient management strategies and estimates of the time lag between when changes in land use practices occur and when water quality effects that result from these changes are observed. Nitrate and orthophosphate (OP) concentrations in several environmental compartments were examined in watersheds having a range of base flow index (BFI) values across the continental United States to determine the dominant pathways for water and nutrient inputs to streams. Estimates of the proportion of stream nitrate that was derived from groundwater increased as BFI increased. Nitrate concentration gradients between groundwater and surface water further supported the groundwater source of nitrate in these high BFI streams. However, nitrate concentrations in stream-bed pore water in all settings were typically lower than stream or upland groundwater concentrations, suggesting that nitrate discharge to streams was not uniform through the bed. Rather, preferential pathways (e.g., springs, seeps) may allow high nitrate groundwater to bypass sites of high biogeochemical transformation. Rapid pathway compartments (e.g., overland flow, tile drains) had OP concentrations that were typically higher than in streams and were important OP conveyers in most of these watersheds. In contrast to nitrate, the proportion of stream OP that is derived from ground water did not systematically increase as BFI increased. While typically not the dominant source of OP, groundwater discharge was an important pathway of OP transport to streams when BFI values were very high and when geochemical conditions favored OP mobility in groundwater.

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Although the increased production and use of fertilizers since 1960 (Howarth et al., 2002) have resulted in sharp increases in crop yields, adverse effects on aquatic ecosystems have been widespread. For example, more than 40% of the stream length in the United States is in poor biological condition, with nutrient over-enrichment as the most common stressor (USEPA, 2006). The transport of stream nutrients to coastal areas has resulted in eutrophication, hypoxia, and loss of biodiversity in receiving waters and is considered the largest pollution problem in these areas (National Research Council, 2000; Howarth et al., 2000).

The transport of N and P to streams is influenced by watershed geomorphology, hydrology, and biogeochemistry (Burt and Pinay, 2005; Cirmo and McDonnell, 1997). Phosphorus is typically sorbed to soils during infiltration. As a result, in most watersheds terrestrial P exports are greatest where surface waters transport P-rich soils rapidly to streams (Gburek and Sharpley, 1998); however subsurface P transport may be important in some systems (Sims et al., 1998). In contrast, terrestrial N exports are dominated by nitrate, which does not sorb to soil particles or aquifer sediments. Consequently, nitrate imports to streams are influenced by the extent to which flow paths intersect suitable redox conditions for biotic reactions including denitrification; principally found in riparian buffer zones (Spruill, 2000) but also in upland anoxic groundwaters (Tesoriero et al., 2005). As a result of these factors, the dominant hydrologic flow paths (e.g., runoff, groundwater discharge) in a watershed are expected to have a significant influence on nutrient loads delivered to streams (Green et al., 2007). We hypothesize that BFI, the ratio of base flow to total flow volume for a given time period, is a useful indicator of the relative importance of runoff versus base flow in nitrate and OP input.

In this study, we examined the interrelationships between nutrient chemistry, near-stream hydrology, and biogeochemical reactions in these settings to discern the sources and pathways of N and P transport to these streams. Specifically, surface-water nutrient concentrations were compared to stream-bed pore water and upland groundwater concentrations to discern the likely pathways of nutrients in each environment.

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Abbreviations: BFI, base flow index; OP, orthophosphate.

Study Area Descriptions

Five study sites were chosen in small, predominantly agricultural watersheds nested inside of larger study basins that are being investigated by the USGS's National Water Quality Assessment Program. Sites were chosen to include important agricultural systems and to also cover a range of hydrologic settings using the hydrologic landscape concept (Capel et al., 2008). Sites selected were Leary Weber Ditch in the White River Basin, Indiana; Maple Creek in the Eastern Platte River Basin, Nebraska; Morgan Creek in the Delmarva Peninsula, Maryland; Valley Creek in the Upper Mississippi Basin, Minnesota; and DR2 in the Yakima River Basin, Washington (Fig. 1; Table 1).

Leary Weber Ditch is located in an intensively farmed watershed in the White River Basin in Indiana. This watershed has a humid continental climate and is dominated by poorly drained soils and a nearly flat land surface. The production of corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] is the dominant land use in the watershed and requires extensive subsurface drainage throughout the basin (Baker et al., 2006).

Maple Creek is a natural stream drainage in the Eastern Platte River Basin in eastern Nebraska. Surrounding land use consists of extensive row crop agriculture (corn, soybean, and alfalfa [*Medicago sativa* L.]). The climate is humid continental and precipitation is supplemented with irrigation from groundwater. The surficial geology in the basin consists of loess-mantled till, which has a low hydraulic conductivity (Fredrick et al., 2006). The stream bed consists of sand and fine gravel alluvial deposits with low sediment organic-matter content.

Morgan Creek is located in eastern Maryland on the Delmarva Peninsula. The climate is humid subtropical with the agricultural water demand supplied by rainfall. Corn and soybean are the primary crops grown in the watershed. Numerous surface-water tributaries along both banks originate as groundwater seeps in the adjacent floodplain. An impervious clay layer within the study reach prevents groundwater discharge through the stream bed (Puckett et al., 2008). The stream bed consists largely of silt and clay with high sediment organic-matter content.

DR2 is an incised drainage channel in the Yakima River Basin in south-central Washington. Surrounding land use consists of extensive orchards, vineyards, row crops, and dairies. The climate is arid/semiarid and the irrigation demand during the growing season is supplied by the Yakima River. The stream bed consists of sand and silt with relatively high organic-matter content.

Valley Creek is located in Minnesota just outside the Minneapolis-St. Paul metropolitan area in the St. Croix watershed. Land use in the area is primarily a mix of undeveloped land, row crop agriculture, and rural residential housing (Almendinger, 2003). The climate of this area is humid continental. This setting contains an outwash plain overlying permeable bedrock that promotes infiltration rather than runoff.

Materials and Methods

The design for surface-water, upland groundwater and stream-bed pore-water sampling is briefly described below with detailed methods discussed in Capel et al. (2008) and Duff et al. (2008). Surface-water sampling sites were typically co-located with USGS stream gages. Surface-water samples were collected at fixed intervals (usually every 2 wk) over a 2-yr period (typically October 2002–September 2004) with supplemental samples coinciding with storm-induced runoff. In most settings, 15 to 20 upland groundwater monitoring wells were installed in groundwater recharge areas extending up to several kilometers upgradient of the stream sampling locations and sampled quarterly during 2004. Well screens were 1 m or less in length and were set in the uppermost aquifer. Stream-bed pore-water samples were typically taken at the same time groundwater was sampled using stainless-steel drivepoints (0.64 cm ID) installed 0.1 to 3.0 m below the sediment/water interface. Water was drawn into the drivepoints through three slots ~0.8 cm long and 0.04 cm wide near their pointed base. Stream-bed pore-water samples were collected along stream study reaches ranging from 500 to 1000 m upstream of the surface-water sampling station.

Water samples were collected according to protocols established by the USGS National Water Quality Assessment Program (Koterba et al., 1995). Water samples from all surface water sites were analyzed for ammonia, nitrate, and OP. Samples were collected and analyzed for major ions at all sites except Valley Creek. Water samples for dissolved constituents were filtered with a 0.45-μm filter. Dissolved oxygen and pH were measured while water was being pumped using electrodes placed in a flow cell chamber to minimize atmospheric interactions. Upland groundwater and most stream-bed pore-water samples were analyzed for the same constituents as stream surface water. Descriptions of the analytical methods for nutrients and major ions are provided in Fishman (1993).

The Tukey multiple comparison method was performed on the ranks of nutrient concentrations in each compartment (e.g., upland groundwater, stream water, etc.) to test the null hypothesis that concentrations in these groups were not significantly different ($P < 0.05$). Multiple comparison test and Pearson correlation coefficient calculations were performed using Statistical Analysis Software (SAS Version 9.1.3).

For all sites except DR2, BFI values were calculated using an automated hydrograph separation technique that partitions each value in a time series of measured daily stream flow into slowly varying (base flow) and rapidly varying (quick flow) components. Base flow index calculations were made for the time period 1 Oct. 2002 to 30 Sept. 2004, to coincide with the water quality sampling period (Table 1). Base flow is commonly assumed to originate from groundwater discharge into the stream. A different approach was used for DR2 because this watershed is intensely irrigated. Base flow was estimated for DR2 using stream flow conditions during nonirrigation periods (McCarthy and Johnson, 2009).

The computer program used to estimate base flow was developed by the U.S. Bureau of Reclamation (Wahl and Wahl,

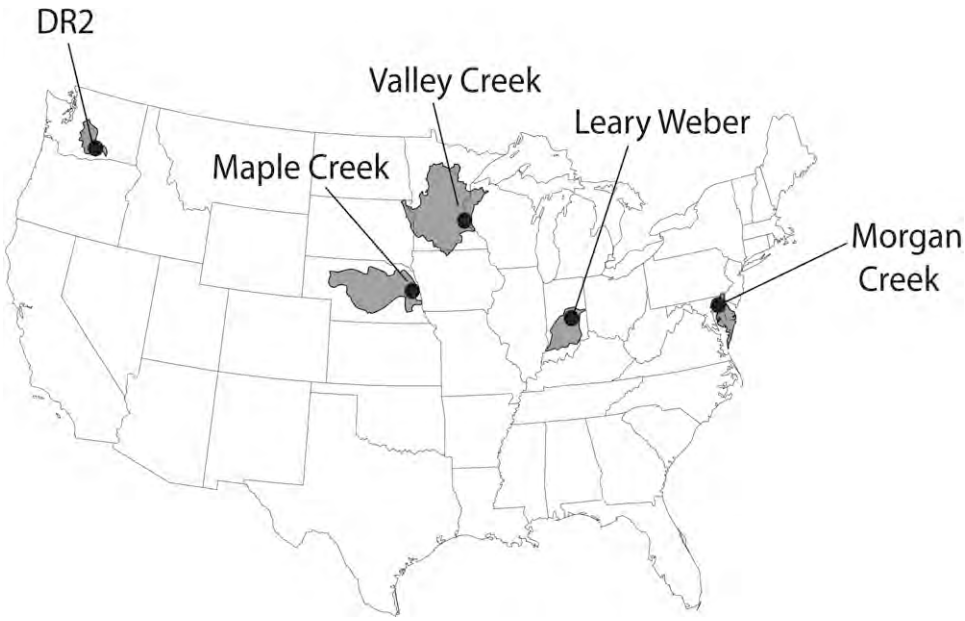

Fig. 1. Locations of the five study areas (dots) within their larger drainage basins (shaded areas): DR2, within the Yakima River Basin; Valley Creek within the Upper Mississippi River Basin; Maple Creek within the Eastern Platte River Basin; Leary Weber within the White River Basin; and Morgan Creek within the Delmarva Peninsula.

Table 1. Basin characteristics, mean annual discharge (for period from October 2003–September 2004) and base flow index (BFI) values for each of the five study areas (adapted from Domagalski et al. (2008) and Capel et al., (2008)).

	Leary Weber Ditch	Maple Creek	Morgan Creek	DR2	Valley Creek
Drainage area (km^2)	7.5	950	31	5.5	31
Mean annual discharge (m^3/s)	0.098	2.0	0.49	0.14	0.28
Base Flow Index†	0.12	0.35	0.45	0.57	0.98
Precipitation (mm)	1109	708	1000	187	762
Climate	Humid continental	Humid continental	Humid subtropical	Arid/semiarid	Humid continental
Soil series	Crosby, Brookston	Nora, Moody	Sassafrass	Warden	Antigo-Chetek-Mahtomedi
Soil texture	Poorly drained glacial till	Aeolian sand, silt, and loess	Fine silt loams	Well drained sand to clays	Well drained glacial outwash
Primary land use	Corn and soybeans	Corn and soybeans	Corn and soybeans	Orchards, vineyards, row crops, dairies	Row crops, rural residential
Percent Agriculture	97	97	74	89	18
Artificial drainage	Yes	No	No	Yes	No
Irrigation for agriculture	Low	Moderate	Low	High	Low

† BFI calculations were based on stream flow data from 2002 to 2004.

1995) and is commonly referred to as the "BFI Program." This program estimates the annual base-flow volume and computes an annual BFI, which is the ratio of base flow to total flow for a given period. While the method is not expected to precisely quantify the amount of base flow in a stream, the BFI has been found to be a reasonable indicator of differences in base flow among different streams (Wahl and Wahl, 1995).

The LOADEST model (Runkel et al., 2004) was used to estimate the portion of nitrate and OP loads in each stream that is derived from base flow at each site. Using available concentration data, the LOADEST model was used to develop regression models that best describe the relationship between loads and explanatory variables (e.g., flow, time). Regression models were developed first for all flow regimes. These regression equations were then applied to daily flow data to predict loads for the period of October 2002 to September 2004. Regression models were then developed using only data from time periods having the highest BFI values to describe the relation between loads and explanatory variables during the base-flow period. These regression models were then applied to daily base-flow data for the same time period as the calculation for the total load. The portion of stream flow nutrient load that is derived from base flow was then calculated by dividing the base-flow load by the total load for both nitrate and OP.

Results

Base-flow Index Values

The BFI values estimated at the study areas ranged from 0.12 to 0.98. Leary Weber Ditch and Maple Creek had the lowest BFI values (0.12 and 0.35, respectively; Table 1), suggesting that most flow was derived from rapid-flow events. Leary Weber Ditch is a tile drain dominated system with only negligible water and chemical inputs from groundwater (Baker

et al., 2006). We conclude that the BFI value of 0.12 for Leary Weber Ditch largely represents steady periods of flow from tile drains; only a small portion of this amount is from direct groundwater discharge. The intermediate BFI at Morgan Creek (0.45) suggested that both base flow and quick flow contribute roughly equal portions of stream flow. Nonirrigation periods were used to establish base flow at DR2, resulting in a BFI value of 0.57, with the remaining water largely derived from irrigation water diverted from the Yakima River, which has very low nutrient concentrations (McCarthy and Johnson, 2009). Valley Creek had the highest BFI value (0.98) indicating that most of the stream flow was derived from base flow, as might be expected due to the occurrence of high hydraulic conductivity surficial deposits in most of the basin. However, snow melt in the spring may also contribute to base flow in this watershed.

Identifying Nutrient Sources from Concentration Gradients

Nitrate concentrations measured in groundwater wells, stream-bed drivepoints, and stream surface water suggested that ground water is potentially a major source of N to streams with moderate to high BFI values. At sites with moderate to high BFI values (i.e., Morgan Creek, DR2 and Valley Creek), nitrate concentrations in groundwater were similar to or higher than concentrations in surface water (Fig. 2, Table 2). Low BFI systems (Leary Weber Ditch and Maple Creek) had upland ground-water nitrate concentrations that were lower than stream surface water (Fig. 2, Table 2), suggesting that excess land-applied N was transported to the streams along other pathways. Denitrification may be responsible for low nitrate concentrations in groundwater in these low BFI watersheds (Green et al., 2008). Conversely fast pathways (i.e., tile drains, overland flow) in low BFI systems had nitrate concentrations that were often greater than those found in surface water and are the likely pathway for nitrate transport to these streams (Fig. 2 and Baker et al., 2006).

In all watersheds except Maple Creek, median concentrations of OP in stream-bed pore water and groundwater were less than those measured in stream water, however differences were not always significant (Fig. 3). At Maple Creek, concentrations of OP were not significantly different in groundwater, stream-bed pore water, and in the stream which is consistent with groundwater transport of OP through the bed. In watersheds where quick flow pathways (i.e., overland flow) were measured, OP concentrations were similar to or exceeded stream OP concentrations.

Nutrient Loading from Base Flow

Estimates of the portion of the total nitrate and OP loads that were derived from base flow were made using the computer program LOADEST (Runkel et al., 2004) and BFI values determined from the BFI program (Wahl and Wahl, 1995). Base flow loads were not calculated for Leary Weber Ditch because BFI values likely do not represent direct groundwater discharge in this tile drain dominated watershed (Baker et al., 2006). The estimated fraction of total nitrate and OP load derived from base flow was related to BFI values for the 2-yr sampling period (Fig. 4). These simulations suggest that the fraction of the nitrate load in streams derived from base flow increased systematically as BFI increased and was typically greater than the BFI (Fig. 4). In contrast to nitrate, the fraction of the OP load in streams that is derived from base flow did not increase systematically as BFI increases and was always less than the BFI.

Identifying Nutrient Sources from Nutrient-Base Flow Relations

In watersheds where base flow was the major source of nitrate, nitrate concentrations were positively correlated with BFI values determined for the day of sampling (r = 0.63, 0.83, 0.69 for Morgan, DR2, and Valley Creek, respectively; $P < 0.05$ in all cases). Significant correlations between stream nitrate concentrations and BFI were not observed in the remaining watersheds. To evaluate nitrate pathways during base flow conditions, nitrate concentrations were plotted as a function of BFI for streams where base flow is the major contributor to nutrient loads (i.e., Morgan, DR2, and Valley Creek). Nitrate concentrations increased as base flow increased in each of these streams (Fig. 5). Nitrate concentrations in streams during base flow conditions (i.e., BFI values approaching 1) were typically much greater than stream-bed pore-water concentrations but similar to concentrations found in upland groundwater (Fig. 5).

Stream OP concentrations were significantly ($P < 0.05$) and negatively correlated with BFI values determined for the day of sampling in Leary Weber Ditch, Morgan Creek, DR2, and Valley Creek (r = –0.40, –0.56, –0.40 and –0.66, respectively). Negative correlations at these sites are consistent with the fact that quick pathways often have higher concentrations of OP than groundwater in these watersheds (Fig. 3). In contrast, stream OP concentrations were weakly, and not significantly, correlated with BFI in Maple Creek (r = –0.19; P = 0.15), as might be expected in a watershed where OP concentrations in groundwater are similar to those found in overland flow (Fig. 3).

Discussion

Nutrient Pathways to Streams in Agricultural Watersheds

Nutrient chemistry data from a range of environmental compartments covering different hydrologic settings have provided new insights into how nutrients move from fields to streams in agricultural watersheds. Most conceptual models of nutrient transport consider dominant pathways to be comprised of quick flow paths such as overland flow and tile drains and slow flow paths consisting primarily of groundwater discharge to streams (Heathwaite et al., 2000). Intuitively, one may infer that the relative importance of the "slow" flow paths will be related to the portion of stream flow that is derived from this source as expressed by the BFI. However, biogeochemical processes, particularly in the near-stream environment, will also affect which pathways are dominant for N and P transport to streams (Cirmo and McDonnell, 1997). If hydrologic processes are dominant, the fraction of the total load that is derived from

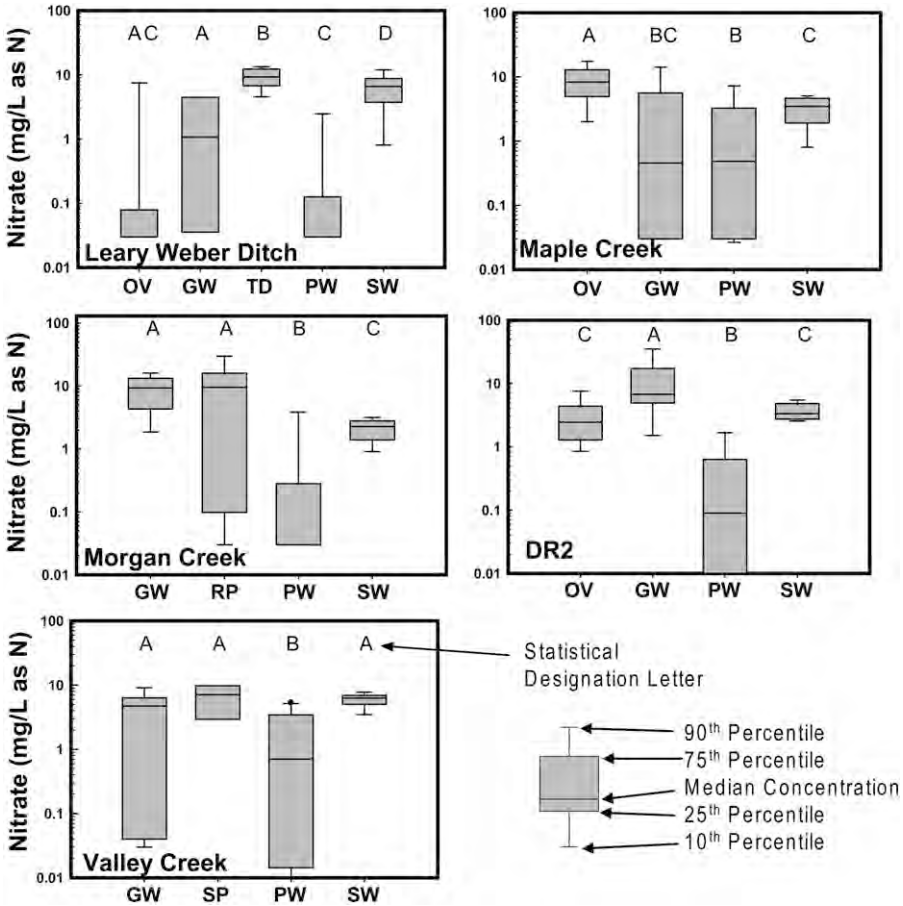

Fig. 2. Nitrate concentration (mg/L as N) box plots for streams (SW) and upland groundwater (GW) for each study area. Overland flow (OV), stream-bed pore water (PW), riparian (RP), springs (SP), and tile drain (TD) data are given for selected study areas. Samples were collected from 2002 to 2004. Boxplots with different statistical designation letters have mean ranks that are significantly different ($P < 0.05$). All concentrations are dissolved.

Table 2. Median concentrations (in mg/L) of selected constituents in stream-bed pore water, upland groundwater, tile drains, overland flow, and streams in the five study areas. Most samples were collected from 2002 to 2004. Value in parenthesis indicates the number of observations used to calculate the median.

Site	Location†	NO_3^- (as N)		Ortho-P (as P)		pH		Dissolved oxygen		SiO_2		SO_4^{2-}	
Leary Weber Ditch, Indiana	OV	0.03	(18)	0.28	(18)	7.5	(18)			3.5	(18)	3.1	(18)
	GW	1.1	(8)	0.006	(8)	7.2	(8)	5.0	(6)	12	(8)	24	(8)
	TD	9.3	(34)	0.006	(29)	7.6	(32)			8.2	(33)	10	(33)
	PW	<0.04	(51)	<0.006	(16)	7.3	(51)	0.8	(48)	13	(16)	32	(16)
	SW	6.6	(76)	0.022	(54)	7.7	(68)	9.8	(39)	8.5	(59)	13	(58)
Maple Creek, Nebraska	OV	8.3	(30)	0.16	(30)	7.7	(12)	7.8	(4)	9.8	(30)	22	(30)
	GW	0.46	(16)	0.25	(16)	6.8	(16)	0.3	(16)	27	(16)	38	(16)
	PW	0.48	(49)	0.26	(19)	7.0	(19)	1.9	(19)	29	(19)	37	(19)
	SW	3.5	(60)	0.21	(59)	8.2	(58)	9.5	(57)	15	(54)	52	(58)
Morgan Creek, Maryland	GW	9.3	(15)	<0.006	(15)	4.8	(15)	7.5	(14)	11	(15)	1.1	(15)
	RP	9.5	(22)	<0.006	(22)	5.0	(22)	4.1	(22)	14	(22)	7.9	(22)
	PW	<0.04	(34)										
	SW	2.3	(53)	0.023	(51)	6.7	(50)	6.6	(40)	8.0	(48)	6.8	(52)
DR2, Washington State	OV	2.5	(9)	0.097	(9)	7.9	(9)	8.0	(9)	19	(9)	7.6	(9)
	GW	6.8	(18)	0.050	(18)	7.4	(18)	2.1	(18)	47	(18)	49	(18)
	PW	0.09	(33)	0.057	(33)	8.0	(16)	0.3	(16)	50	(16)	60	(16)
	SW	3.3	(57)	0.10	(57)	8.0	(56)	8.4	(56)	34	(57)	41	(57)
Valley Creek, Minnesota	GW	5.1	(16)	0.017	(16)					9.2	(6)		
	SP	7.1	(5)	0.019	(5)								
	PW	0.70	(38)	0.013	(38)								
	SW	6.3	(13)	0.032	(13)					7.6	(4)		

† GW, upland groundwater; OV, overland flow; PW, stream-bed pore water; RP, riparian zone piezometers; SP, springs or seeps; SW, surface water; TD, tile drain.

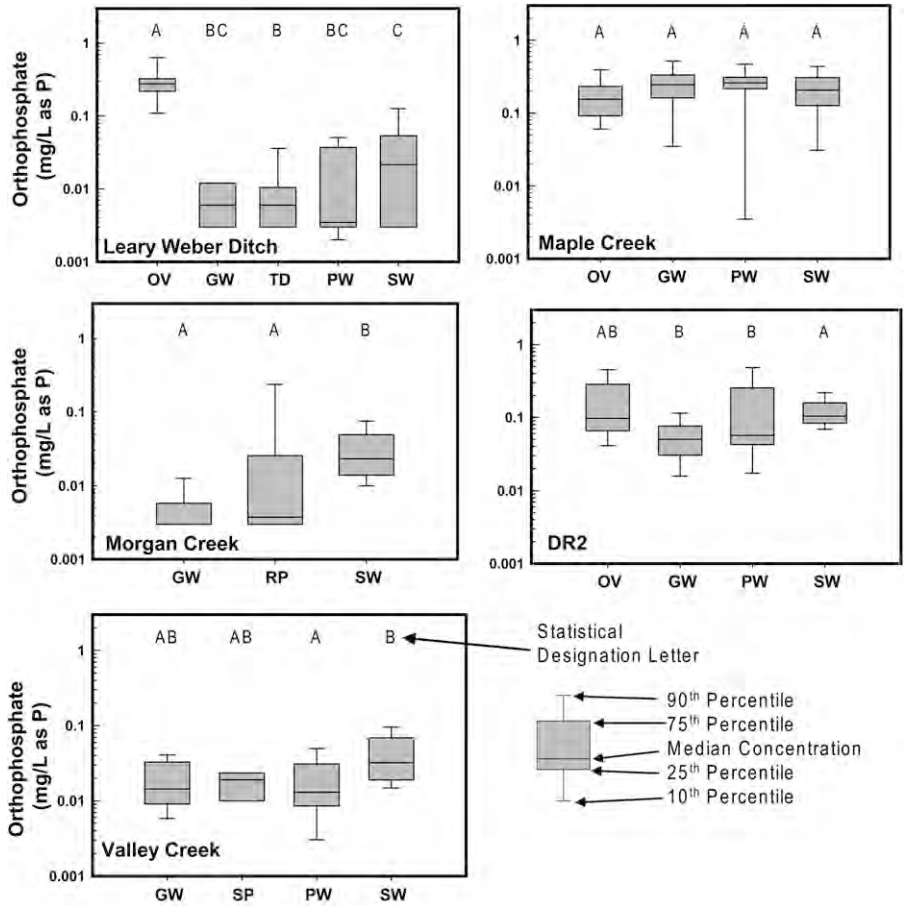

Fig. 3. Orthophosphate concentration (mg/L as P) box plots for streams (SW) and upland groundwater (GW) for each study area. Overland flow (OV), stream-bed pore water (PW), riparian (RP), springs (SP), and tile drain (TD) data are given for selected study areas. Box plots with different statistical designation letters have mean ranks that are significantly different ($P < 0.05$). All concentrations are dissolved.

base flow should increase as BFI increases. This was generally the case for nitrate. The portion of stream flow nitrate that was derived from groundwater increased as the BFI for the watershed increased (Fig. 4). For streams with most of their nitrate load derived from base flow (i.e., Morgan Ck., DR2 and Valley Ck.), a groundwater source of nitrate is further supported by the positive correlation between stream nitrate concentrations and BFI values determined for the day of sampling and by the fact that groundwater concentrations in these watersheds are similar to those found in streams during high base flow periods (Fig. 5). In these streams, stream-water nitrate concentrations increased with increasing base flow, as lower volumes of low-nitrate surface-water runoff diluted groundwater base flow.

If upland ground water at the high BFI sites had moved through the bed conservatively before discharging to the streams, elevated nitrate concentrations should have been observed in stream-bed pore water. However, in watersheds where ground water is expected to be the major source of nitrate (i.e., Morgan Cr., DR2, and Valley Cr., Fig. 4), nitrate concentrations were commonly lower in stream-bed pore water than groundwater or stream surface water during base-flow conditions (i.e., BFI values > 0.8, Fig. 5). Low dissolved oxygen concentrations (Table 2) and elevated concentrations of excess N_2 (Puckett et al., 2008) suggest that nitrate in stream-bed pore water may have been removed by denitrification. These findings suggest that much of the nitrate input occurred via preferential groundwater flow paths not captured in pore-water drivepoints in the stream bed. Other pathways for the

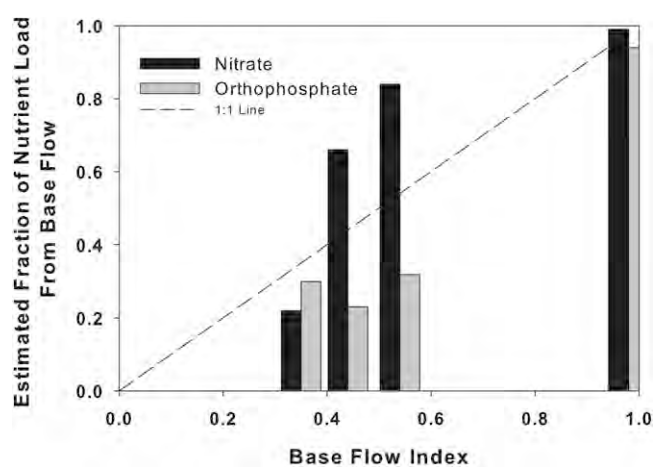

Fig. 4. Estimated fraction of stream nitrate and orthophosphate load that is derived from base flow vs. the base flow index of the stream (based on data from October 2002–September 2004). Dashed line shows 1:1 relation between BFI and the fraction of total load derived from base flow.

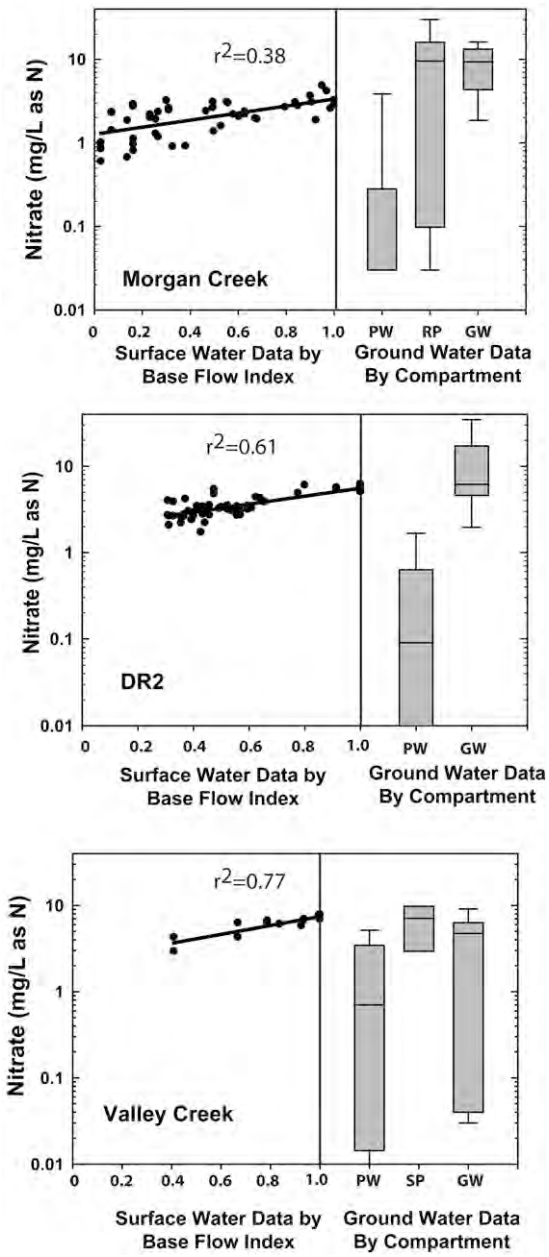

Fig. 5. Nitrate concentrations (mg/L as N) in surface water are plotted against base flow index values determined for the day of sampling for Morgan Creek (top), DR2 (middle) and Valley Creek (bottom). On the right side of each figure box plots show nitrate concentrations in groundwater by compartment: PW, stream-bed pore water; RP, riparian zone; GW, upland groundwater; SP, springs. See Fig. 2 or 3 for box plot explanation.

migration of nitrate in groundwater to move to streams are indicated. Two such flow paths were identified in these systems (riparian zone groundwater in Morgan Creek and springs in Valley Creek) and in both cases, nitrate concentrations in preferential flow paths were significantly higher than stream-bed pore water (Fig. 5). While we did not identify the preferential flow path at DR2, a previous study suggested that discrepancies between stream-bed flux estimates and other flux measurements indicated preferential flow paths via shallow lateral flow paths (Essaid et al., 2008).

While the proportion of stream nitrate derived from groundwater exhibited an overall pattern related to BFI values determined for the 2-yr sampling period, OP did not. A major difference between nitrate and OP is that nitrate is often transported conservatively, whereas OP can have strong sediment interactions (e.g., retention in the soil zone by sorption to Fe and Al oxides). As a result, concentrations of OP in groundwater are typically low, even in agricultural settings (median OP concentrations = 0.01 mg/L; Nolan and Stoner, 2000). At all of the study sites examined here except Maple Creek, concentrations of OP in groundwater and in stream-bed pore water were typically lower than stream concentrations (Fig. 3), and groundwater contributions to stream flow OP are often minor (Fig. 4). Furthermore, negative correlations between OP concentrations and BFI values determined for the day of sampling were observed at all sites except Maple Creek. This is additional evidence that groundwater discharging to these streams has lower concentrations of OP than found in rapid pathways in all watersheds except Maple Creek.

However, groundwater discharge can be an important source of OP. When stream flow is dominated by base flow (e.g., Valley Creek, BFI = 0.98), loads from this source may also be dominant. Base-flow loads of OP can also be a large fraction of the total load if the geochemical conditions are favorable (e.g., Maple Creek). Soils with little or no iron and aluminum oxides will favor the mobility of OP. High concentrations of sulfate and silica, which compete for sorption sites with OP (Caraco et al., 1989; Geelhoed et al., 1997) and reduce the surface charge of iron oxides (Schwertmann and Fechter, 1982), will also increase the mobility of OP. Low concentrations of dissolved oxygen may also enhance the mobility of OP through the reductive dissolution of iron oxides, which may have sorbed OP (Miller et al., 2001). Geochemical conditions in groundwater in the Maple Creek watershed (e.g., low dissolved oxygen, high sulfate, and silica) may, in part, explain the high groundwater concentrations of OP in this watershed (Fig. 3, Table 2). Groundwater discharge containing high OP concentrations likely sustains the high rates of primary productivity that have been observed in this stream during the growing season (Duff et al., 2008) and the high surface water OP concentrations observed during nongrowing season base-flow conditions. Groundwater OP also may be an important source of OP in streams elsewhere in this region; high concentrations of OP in streams (Omernik, 1977) and groundwater (Helgeson et al., 1994; Burkart et al., 2004) have been observed in eastern Nebraska and Iowa.

Implications for Nutrient Management

A groundwater source of nitrate or OP has important implications for nutrient management strategies. Groundwater pathways can have much longer lag times between nutrient applications to the land surface and discharge to streams than "quick" pathways such as overland flow. As a result, changes in water quality due to changes in land use practices will be delayed to the extent that nutrients travel along these longer flow paths. For example, at the Maple Creek, Nebraska site, elevated OP concentrations in groundwater are ubiquitous and do not decrease with depth, as might be expected for an anthropogenic

source. As a result, groundwater discharge of OP in this watershed (and others like it in the region) will likely temper any management changes that limit OP transport along quick pathways. In fact, elevated OP concentrations (>0.10 mg/L) discharging from groundwater to Maple Creek and other streams in the area (Burkart et al., 2004) may affect the capacity of streams to meet the recommended total P criteria (0.076 mg/L; Ecoregion VI, Corn Belt and Northern Great Plains, USEPA, 2000). Similarly, in moderate to high base flow agricultural watersheds much of the nitrate in these streams is likely derived from groundwater, resulting in lag times that will depend on the age of discharging groundwater. Determining the age range of discharging groundwater in watersheds having a significant portion of surface water nutrients that have moved along this "slow" pathway will be critical if time lags between changes in land surface practices and stream water quality are to be more fully understood.

Summary

The portion of stream flow nitrate derived from groundwater increased as BFI values determined for the 2-yr sampling period increased, while no such pattern was observed for OP. The major source of nitrate in base-flow dominated streams was groundwater, while rapid flow pathways were the major source of nitrate in streams with low BFI values. In all streams, stream-bed pore-water nitrate concentrations were generally much lower than in stream water during base-flow conditions and in groundwater. We conclude that in base-flow dominated streams, nitrate does not move uniformly through the bed but rather through preferential flow paths, either through high conductivity steam-bed sediments or as bankside seeps or springs. This illustrates the importance of measuring riparian groundwater and stream-bed pore-water environments when assessing nutrient transport to streams.

In contrast to nitrate, the proportion of stream OP that is derived from groundwater did not systematically increase as BFI values determined for the 2-yr sampling period increased. The OP concentrations were generally lower in stream-bed pore water and in groundwater than in stream water, suggesting that rapid flow processes such as overland flow and tile-drain discharge were responsible for most of the OP transport to these agricultural streams. However, in one low BFI watershed, elevated OP concentrations in groundwater contributed approximately 30% of the stream OP load and may be a major contributor to nutrient enrichment effects during summer base flow periods. A groundwater source of nitrate and in some cases OP has important implications for nutrient management strategies. Groundwater derived nitrate and OP in these agricultural watersheds can result in increased time lags between when changes in land use practices occur and when the effects these changes have on stream water quality are observed.

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