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Timing of Riverine Export of Nitrate and Phosphorus from Agricultural Watersheds in Illinois: Implications for Reducing Nutrient Loading to the Mississippi River

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Agricultural watersheds in the upper Midwest are the major source of nutrients to the Mississippi River and Gulf of Mexico, but temporal patterns in nutrient export and the role of hydrology in controlling export remain unclear. Here we report on NO_3^-−N, dissolved reactive phosphorus (DRP), and total P export from three watersheds in Illinois during the past 8−12 years. Our program of intensive, long-term monitoring allowed us to assess how nutrient export was distributed across the range of discharge that occurred at each site and to examine mechanistic differences between NO_3^-−N and DRP export from the watersheds. Last, we used simple simulations to evaluate how nutrient load reductions might affect NO_3^-−N and P export to the Mississippi River from the Illinois watersheds. Artificial drainage through under-field tiles was the primary mechanism for NO_3^-−N export from the watersheds. Tile drainage and overland flow contributed to DRP export, whereas export of particulate P was almost exclusively from overland flow. The analyses revealed that nearly all nutrient export occurred when discharge was ≥ median discharge, and extreme discharges (≥ 90th percentile) were responsible for >50% of the NO_3^-−N export and >80% of the P export. Additionally, the export occurred annually during a period beginning in mid-January and continuing through June. These patterns characterized all sites, which spanned a 4-fold range in watershed area. The simulations showed that reducing in-stream nutrient loads by as much as 50% during periods of low discharge would not affect annual nutrient export from the watersheds.

Introduction

Nitrogen and P enrichment from nonpoint sources and resulting eutrophication is a main cause of poor water quality and biotic impairment in many streams and rivers in the United States (*1*). To address nutrient inputs from nonpoint sources, states currently are developing nutrient criteria, numeric standards, and total maximum daily loads (TMDLs) for nutrient-impaired streams and rivers. A TMDL represents the maximum load (kg d^{-1}) of a nutrient that a stream can receive and still maintain water quality sufficient to meet its designated uses. Determination of the TMDL is based on the assimilative capacity of the stream for that nutrient, natural or background sources, point and nonpoint inputs, and a specified margin of safety (*2*). Because the assimilative capacity, discharge, and magnitude of inputs can vary throughout a year, the approach allows for seasonal variation in the TMDL. In streams of the midwestern United States, the effects of eutrophication are most pronounced during periods of low discharge and warm water temperatures in summer and autumn. Nutrient TMDLs tend to focus on critical periods of summer low discharge, while allowing increased nutrient loads during times of high discharge. For example, the Stillwater River drains an agricultural watershed in western Ohio and the approved TMDL for NO_2^- + NO_3^- increases from 3122 kg N d^{-1} in October and November to >6700 kg N d^{-1} for December through June (*3*). The higher load is needed to accommodate the increased discharge and nonpoint source runoff that occur from late winter through spring.

In addition to degrading local water quality, nutrient enrichment of midwestern streams has increased N and P loading to the Mississippi River and Gulf of Mexico (*4*−*6*). Rivers draining agricultural regions of the upper Midwest (i.e., the cornbelt) export large quantities of P and N (predominantly as NO_3^-−N) as a result of extensive fertilization and artificial drainage (*5*, *7*, *8*). Approximately 20 million hectares of cropland in the Mississippi River basin (MRB) are artificially drained by under-field (tile) systems, particularly in intensively farmed and fertilized areas such as Iowa, Illinois, Indiana, and Ohio (*5*, *9*). Tile drainage provides a mechanism by which water and dissolved nutrients can bypass groundwater flow paths and move rapidly from fertilized cropland to streams and rivers (*10*, *11*). Because of channel and hydrological modifications, streams in agricultural watersheds are not efficient at nutrient removal by processes such as denitrification, and a large fraction of the nutrient load in such streams is transported to downstream water bodies (*12*, *13*).

Nutrient export to the Mississippi River and eutrophication of midwestern streams both result from nutrient inputs to surface waters but are associated with different hydrological conditions. Eutrophication of streams is a primarily biological process driven by nutrient uptake when local conditions favor rapid growth of nuisance algae, such as during extended periods of low discharge. Conversely, nutrient export from the Midwest to the Mississippi River is a primarily hydrological process driven by precipitation and drainage of the agricultural landscape (*14*). To address water quality in the Midwest, it is critical to gain a mechanistic understanding of how N and P enter, and are exported from, midwestern streams. There is a particular need for long-term data to address (i) the temporal patterns in nutrient loads and export, (ii) the role of hydrology in controlling export, and (iii) the implications of these patterns for efforts, such as TMDLs, to reduce eutrophication and nutrient export from the agricultural Midwest.

A robust analysis of these issues requires long-term data on NO_3^-−N and P concentrations and river discharge, and a sampling scheme that targets periods of high discharge and rapidly changing nutrient loads. In this paper we use long-term, intensive monitoring data from three agricultural watersheds in Illinois to examine the above issues in relation

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TABLE 1. Location, Watershed Characteristics, Period of Record, and Discharge Statistics for the River Sites Used in the Analysis[a]

river system	site coordinates	watershed area (km^2)	row-crop agriculture (% land cover)	period of record (water years)	maximum discharge ($m^3 s^{-1}$)	median discharge ($m^3 s^{-1}$)	mean discharge ($m^3 s^{-1}$)
Embarras	39°47′29″N, 88°11′08″W	481	91	1994–2005	198	1.6	5.0
Kaskaskia	39°50′09″N, 88°29′18″W	386	91	1998–2005	108	1.0	3.6
Sangamon	40°16′06″N, 88°19′35″W	101	86	1994–2003	71	0.3	0.8

[a] Discharge statistics based on average daily discharge values from the period of record.

to nutrient management scenarios. Using simple simulations of nutrient load reductions, we evaluate how such reductions might affect NO_3^-–N and DRP export to the Mississippi River from areas such as Illinois. Last, we discuss the implications of our results for designing programs to reduce riverine export of nutrients from agricultural regions of the upper Midwest.

Site Descriptions. We used long-term data on discharge and nutrient concentrations from sites in the Embarras, Kaskaskia, and Sangamon river systems in east-central Illinois. The sites range in drainage area and peak discharge but have similar land use dominated by row-crop agriculture, mainly corn and soybean (Table 1). East-central Illinois soils are poorly drained Mollisols and the landscape was mostly wetland and mesic prairie prior to settlement. Much of the landscape is now tile-drained, with tile densities of 3–5 km km^{-2} (*15*), and headwater streams have been extensively channelized and dredged to accommodate high discharges (*16*). Nitrogen losses from the watersheds typically range from 20 to 50 kg N ha^{-1} yr^{-1}, depending on precipitation, and are among the highest in the MRB (*5*, *7*, *17*). In the streams, inorganic N loads are 90% or more NO_3^-–N (*7*). The land use and drainage modifications at the sites are representative of tile-drained and intensively farmed areas of the upper Midwest, and patterns in these streams likely characterize much of the cornbelt region.

Methods

Stream discharge was monitored at the Embarras River and Kaskaskia River sites by the U.S. Geological Survey (stations 03343400 and 05590800, respectively). Discharge at the Sangamon River site was monitored by the Illinois State Water Survey (station 106). For each site, mean daily discharge was determined from hourly or 15-min readings. The Illinois State Water Survey provided precipitation data (Champaign station) and NO_3^-–N concentrations for the Sangamon River site for 1994–1999. All other nutrient concentrations were determined from samples we collected approximately weekly, either manually or with automated samplers. Streams and small rivers in the Midwest have flashy hydrology, and discharge during floods represents a significant fraction of annual discharge (*18*). To account for this, we collected additional samples when discharge was changing rapidly. During most floods samples were collected daily, but in some cases 2–4 samples were collected in a 24-hr period. In total, our analysis is based on >4000 nutrient concentrations determined from >2000 individual water samples collected from October 1993 through September 2005.

Nitrate was determined, after filtration through a 0.45 μm membrane, on an ion chromatograph (Dionex, Inc. model DX-120 or model 2000i). Dissolved reactive phosphorus (DRP) was determined colorimetrically on filtered samples using a spectrophotometer or (after 2001) a Lachat QuikChem8000 flow injection analyzer. Total P was determined as described for DRP except that samples were unfiltered and digested with sulfuric acid and ammonium persulfate prior to analysis. Particulate P is defined as the difference between total P and DRP. Internal and external standards for each nutrient were analyzed routinely throughout the study as part of a quality assurance plan. Daily in-stream nutrient loads were determined by multiplying mean daily discharge (m^3 d^{-1}) by nutrient concentration (kg m^{-3}). Linear interpolation in SAS (*19*) was used to estimate nutrient concentrations between sampling dates. Annual and total nutrient export were determined by summing the daily nutrient loads for each water year or the period of record, respectively. For a 1406 km^2 agricultural watershed in Illinois, weekly NO_3^-–N sampling resulted in a load estimate with a root-mean-square error of <4% (*20*). We examined smaller watersheds (Table 1), but with a greater sampling frequency, and believe our load estimates have similarly small error.

For the period of record at each site, we ranked the daily discharge values and calculated the fraction of the total nutrient export attributable to each day, and the fraction that occurred between various discharge percentiles. This allowed us to assess how NO_3^-–N, DRP, and total P export were distributed across the range of discharge that occurred at each site. The mass of nutrients exported each year from the MRB is controlled to a large extent by precipitation (*14*). To examine patterns across years and account for inter-annual differences in precipitation and export, we constructed graphs of cumulative NO_3^-–N and DRP export based on percentage of the total for each water year.

To examine how reduced NO_3^-–N and DRP loads during different hydrological conditions might affect export of these nutrients to downstream water bodies, we performed three simple simulations for each site. The first simulation reduced in-stream NO_3^-–N and DRP loads by 50% on all days with discharge <50th percentile; this simulation represented the effect of focusing nutrient reductions on periods of low discharge only. The second simulation reduced in-stream loads by 25% on all days with discharge <75th percentile; this represented a smaller reduction in nutrient loads but applied to a larger range of discharge (i.e., more days of the year). The final simulation focused on high flow periods and reduced in-stream loads of NO_3^-–N and DRP by 25% on all days with discharge ≥75th percentile. For all simulations, NO_3^-–N and DRP export during the period of record was recalculated based on the adjusted loads and expressed as a percent of the original export. The reductions used in the simulations were selected to evaluate the interaction between hydrology and nutrient export and do not necessarily reflect management goals, although N load reductions of 20–30% in the Mississippi River will be required to reduce hypoxia in the Gulf of Mexico (*21*).

Results

The volume of water and mass of NO_3^-–N, DRP, and total P exported from the watersheds varied considerably during the study (Table 2), mainly as a consequence of variable precipitation among years. In wet years, such as 1998 and

TABLE 2. Annual Water and Nutrient Export from the Three Watersheds during the Study

water year	discharge (10^6 m^3)	Mg			kg ha^{-1}		
		NO_3^-−N	DRP	total P	NO_3^-−N	DRP	total P
			Embarras				
1994	235	1599	43		33.3	0.9	
1995	125	1081	11		22.5	0.2	
1996	186	1999	24		41.5	0.5	
1997	137	1140	21		23.7	0.4	
1998	228	2219	31		46.1	0.6	
1999	132	1372	21		28.5	0.4	
2000	52	490	4	7	10.2	0.1	0.2
2001	92	962	12	16	20.0	0.2	0.3
2002	290	2728	35	102	56.7	0.7	2.1
2003	53	426	5	9	8.9	0.1	0.2
2004	170	1506	24	51	31.3	0.5	1.1
2005	180	1396	29	51	29.0	0.6	1.1
			Kaskaskia				
1998	179	2223	21		57.6	0.5	
1999	96	1389	8		36.0	0.2	
2000	46	514	3	6	13.3	0.1	0.2
2001	100	1164	10	14	30.2	0.3	0.4
2002	187	2129	13	38	55.2	0.3	1.0
2003	31	292	2	4	7.6	< 0.1	0.1
2004	130	1382	11	45	35.8	0.3	1.2
2005	150	1288	22	40	33.4	0.6	1.1
			Sangamon				
1994	38	262			26.0		
1995	29	328			32.5		
1996	31	318			31.5		
1997	35	337			33.3		
1998	36	369			36.6		
1999	19	216			21.4		
2000	8	91			9.0		
2001	19	193	4	7	19.1	0.4	0.7
2002	34	473	3	8	46.8	0.3	0.8
2003	16	146	1	3	14.5	0.1	0.3

2002 (117 and 108 cm of precipitation, respectively), NO_3^-−N yields ranged from 45 to 55 kg ha^{-1}. In dry years, such as 2003 (82 cm of precipitation) yields were <15 kg ha^{-1}. Across the sites there was a clear pattern of nutrient export occurring predominantly at the high end of the discharge range (Figure 1). During the period of record, days with discharge ≥ median discharge accounted for 97−98% of the NO_3^-−N export and 98−99% of the DRP export (Table 3). Extremes in discharge (>90th percentile) accounted for an average of 56% of the total NO_3^-−N export and 84% of the DRP export.

The temporal distribution of NO_3^-−N export indicated that the majority of the annual export occurred during a 5.5 month period from mid-January through June across all sites and years (Figure 2). Within a water year, the first 3.5 months (October−mid-January) and the last 3 months (July−September) together typically accounted for <30% of the annual NO_3^-−N export. Within the January−June period, NO_3^-−N export often occurred in discrete events, as evidenced by the abrupt increases in the slopes of the lines in Figure 2. The watersheds spanned a 4-fold range in size, but the pattern in temporal distribution of NO_3^-−N export was consistent across sites. For P, we focus on DRP rather than total P because we have longer records for DRP and it represents the immediately available P. As with NO_3^-−N, DRP export occurred mainly from January to June in most years, although substantial export occasionally occurred later in the summer (Figure 3). Export of DRP was often associated with individual floods and in several years 40−80% of the annual DRP export occurred during a period of <1 month.

Mechanistically, NO_3^-−N, DRP, and total P responded differently to the occurrence of overland flow and we illustrate these differences with the 2002 and 2003 water years (wet

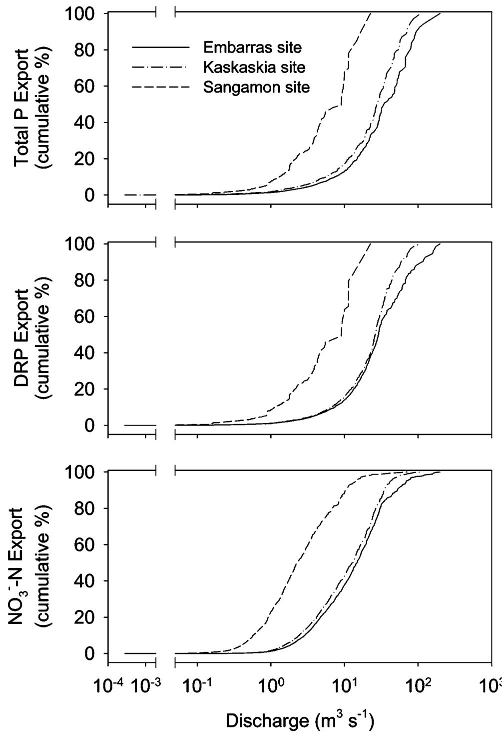

FIGURE 1. Cumulative nutrient export as a function of discharge during the period of record for each site.

TABLE 3. Percentage of the Total Nutrient Export that Occurred at or above Various Discharge (*Q*) Percentiles during the Periods of Record

river system	% of export		
	Q ≥ 90th percentile	*Q* ≥ 75th percentile	*Q* ≥ 50th percentile
	NO_3^-−N		
Embarras	54	81	97
Kaskaskia	58	84	98
Sangamon	57	82	97
mean	56	82	97
	DRP		
Embarras	80	94	98
Kaskaskia	85	96	99
Sangamon	86	94	98
mean	84	95	98

and dry years, respectively) at the Embarras River site (Figure 4). In 2002 a series of precipitation events from February through mid-April initiated flow through agricultural tile drains, increased discharge, and resulted in a steady export of NO_3^-−N, with that period accounting for approximately 55% of the total 2002 NO_3^-−N export. During that same period, DRP and total P exports were 33 and 17%, respectively, of 2002 annual export. From April 8 through May 17, 2002, total precipitation was 21 cm and much of that water entered the Embarras River as overland flow and caused sustained flooding. There also were several periods of high discharge through tile drains throughout the Embarras River watershed. During these floods and high tile discharge periods, DRP and total P export increased substantially from the previous months, whereas NO_3^-−N export continued at approximately the same rate (Figure 4). Overland flow was not important for NO_3^-−N export from the watershed, but during 2002 overland flow was important for export of DRP and total P (with particulate P accounting for a large fraction of total P).

We cannot assign precise values to the fraction of the DRP and total P export originating from tile drainage versus

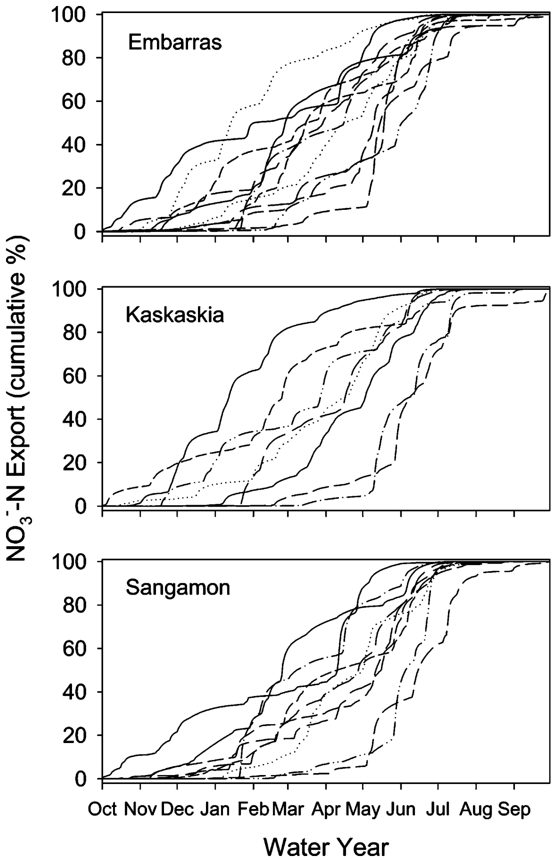

FIGURE 2. Cumulative NO_3^-−N export during each water year during the period of record for each site.

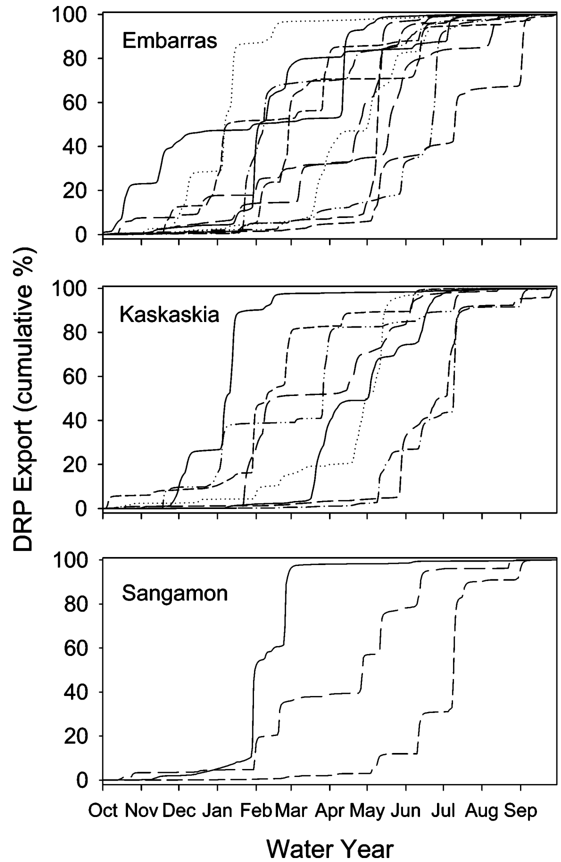

FIGURE 3. Cumulative DRP export during each water year during the period of record for each site.

overland flow, because DRP export through tiles is greatest during peak tile flows but then decreases rapidly and disproportionately as tile discharge declines (*11*). This contrasts with NO_3^-−N export which continues via tile drainage approximately in proportion to tile discharge (*10*). This pattern is evident in the dry 2003 water year, when DRP and total P both increased along with NO_3^-−N in the first flow event in May, but then diverged from NO_3^-−N as discharge and tile flow declined (Figure 4). Dissolved reactive P and total P export increased discretely during the other two flow events, but these were much smaller than the 2002 floods and not associated with surface runoff. Therefore, in a dry year with small N and P export (Table 2), nearly all DRP and total P inputs to the river appeared to be from tile drainage.

The simulations showed that a 50% reduction in NO_3^-−N and DRP loads during periods of low discharge (i.e., <median discharge) would reduce total export of these nutrients by <2% in the case of NO_3^-−N and <1% in case of DRP (Table 4). Reducing loads 25% across a wider range in discharge (<75th percentile) resulted in a larger, but nonetheless disproportional, reduction in total export, with an average decline of 13.0% for NO_3^-−N and 4.2% for DRP. Conversely, reducing loads 25% during periods of high discharge (≥75th percentile) gave a nearly proportional reduction in total export of NO_3^-−N (20.7%) and DRP (23.6%) (Table 4).

Discussion

In midwestern agricultural watersheds, in-stream nutrient concentrations are greatest during winter through spring because of the increase in runoff that occurs during that time (*22*, *23*). This pattern has been previously documented in the streams we examined (*7*, *12*, *24*) and we believe that

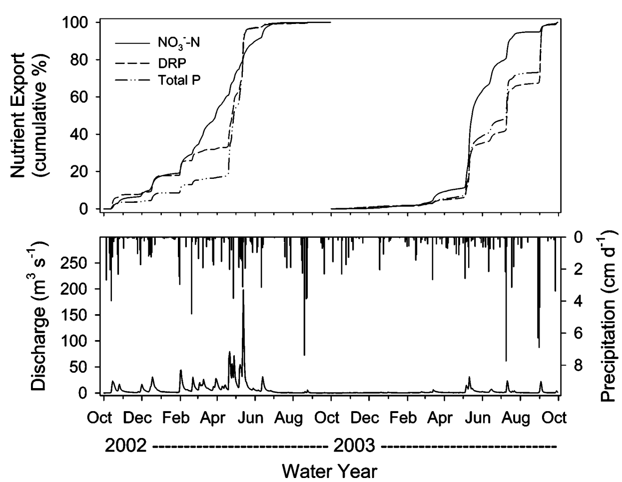

FIGURE 4. Cumulative nutrient export (upper) and precipitation and discharge (lower) from the Embarras River site during the 2002 and 2003 water years.

our study sites, although limited geographically to east-central Illinois, are representative of intensively drained and farmed watersheds of the upper Midwest. Our analyses revealed two important characteristics regarding the export of nutrients from the agricultural Midwest during the past 8−12 years. First, nearly all nutrient export occurred when discharge was ≥ median discharge, and extreme discharges (Q ≥ 90th percentile) were responsible for >50% of the NO_3^-−N export and >80% of the P export. Second, the annual export of NO_3^-−N and P from the watersheds occurred consistently from mid-January through June.

As discharge increases, there is less opportunity for the exchange of nutrients between the water column and the

TABLE 4. Decrease in Total Nutrient Export (%) as a Result of Simulated Load Reductions during Various Hydrological Conditions

river system	simulated reduction in nutrient loads: loads reduced 50% on days with Q < 50th percentile	loads reduced 25% on days with Q < 75th percentile	loads reduced 25% on days with $Q \geq$ 75th percentile
	NO_3^--N		
Embarras	1.7	14.2	20.3
Kaskaskia	0.9	11.8	21.1
Sangamon	1.4	13.2	20.6
mean (1 SD)	1.3 (0.4)	13.0 (1.2)	20.7 (0.4)
	DRP		
Embarras	1.0	4.6	23.5
Kaskaskia	0.5	3.3	23.9
Sangamon	0.9	4.6	23.5
mean (1 SD)	0.8 (0.2)	4.2 (0.8)	23.6 (0.3)

benthic sediments where biological uptake and denitrification occur (*12*). Streams can switch from a nutrient retention and processing mode at low discharge, to a through-put mode at high discharge in which nutrient inputs from the landscape are transported downstream without biological processing (*25*). For the streams we examined, median discharge appeared to be the approximate transition point at which the streams switched from a state of nutrient retention to a state of nutrient export. For example, 97% of the NO_3^-−N export occurred above median discharge when denitrification in these streams has little effect on NO_3^-−N retention (*12*, *26*). The hydrology of the agricultural landscape in the upper Midwest has been greatly altered during the last 125 years by wetland drainage, stream channelization, and installation of under-field (tile) drainage systems (*16*). Thus the patterns we observed, although characteristic of the upper Midwest, may not represent landscapes with less altered hydrological regimes.

In addition to the association with high discharge, nutrient export from our sites occurred mainly during late winter through spring of each year. Elevated nutrient concentrations during spring are common in agricultural streams, and the present analysis clearly documents the extent to which nutrient export is generally confined to this time period. These patterns in the timing of nutrient export likely result from the seasonality of fertilizer application and the prevalence of tile drainage within the watersheds, both of which influence the timing and magnitude of nutrient loads (*23*). From 1994 to 2003, an average of 55% of the annual N fertilizer used in east-central Illinois was applied during autumn (*27*). This fertilizer is susceptible to nitrification and loss during late winter and spring as NO_3^-−N in drainage water. In intensively farmed areas, fertilizer use and disturbance from tillage appear to interact to produce large losses of NO_3^-−N through tiles (*7*), and evidence suggests that spring peaks in NO_3^-−N concentrations in the lower Mississippi River are a result of increased fertilizer use in the MRB during the past 50 years (*6*). Our analysis of watersheds in Illinois supports these conclusions.

Water entering the Embarras River through tile drains can at times have NO_3^-−N concentrations >30 mg L^{-1} and N input to the river from tiles can exceed 45 kg ha^{-1} yr^{-1} (*7*). Artificial drainage through under-field tiles is clearly a mechanism by which NO_3^-−N entered the streams we examined. Phosphorus also can enter streams through tile drainage in the Midwest (*11*), although this mechanism appears relatively more important in dry years with limited or no overland flow (Figure 4). Phosphorus transport processes are more difficult to separate in tile drained watersheds, because DRP inputs occur by either mechanism. The ratio of total P to DRP can be used to examine these flow paths, with larger ratios indicating more surface transport of particulate P (Table 2). This ratio was 2.9 in 2002, a wet year with significant overland flow and particulate P export, but only 1.8 in 2003, a dry year with no overland flow and much less particulate P export. However, regardless of the mechanism or the form of the P, extreme discharges were the driving factor for P export from the watersheds. For example, extreme discharges (≥ 90th percentile) accounted for >80% of the DRP and total P export, compared to 56% of the NO_3^-−N export.

Implications for Nutrient Loading to the Mississippi River. Reducing riverine export of NO_3^-−N from the Midwest is a key component to addressing hypoxia in the Gulf of Mexico (*6*). Likewise, reducing in-stream nutrient concentrations is an important step toward protecting water quality and aquatic life in the streams and rivers of the Midwest. In east-central Illinois, peak algal productivity and associated dissolved O_2 depletion occur most commonly during summer and early autumn when discharge is low (*26*, *28*). These same time periods, however, account for little of the annual NO_3^-−N or DRP export (Figures 2 and 3) due to low discharge and high nutrient uptake in the streams. There is therefore a temporal separation between periods of poor water quality and periods of high nutrient loads and export. Nutrient export from other areas of the Midwest also occurs mainly during high discharge (*22*, *29*) and we conclude that concerns about nutrient loading to the Mississippi River and Gulf of Mexico (*6*) must be addressed by reducing nutrient export from the Midwest during times of high discharge. The simulations support this conclusion, showing that nutrient export from the watersheds could be reduced only by reducing in-stream loads during high discharge (Table 4).

Efforts are underway to restore and protect local water quality using the TMDL approach and the development of nutrient criteria (*30*). Local water quality in the Midwest and nutrient loading to the Gulf of Mexico are both nutrient-related problems, but the TMDL approach, with its current focus on periods of low discharge, is not conducive to reducing nutrient loads at times relevant to affecting water quality in the Mississippi River and hypoxia in the Gulf of Mexico. However, our analysis indicates that if TMDLs in the Midwest are directed at reducing nutrient loads during periods of high discharge in late winter and spring, such efforts could reduce nutrient export from agricultural watersheds to the Mississippi River.

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