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Influences of Spatial Scale and Soil Permeability on Relationships Between Land Cover and Baseflow Stream Nutrient Concentrations

F. Bernard Daniel · Michael B. Griffith · Michael E. Troyer

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Abstract The Little Miami River (LMR) basin, dominated by agriculture, contains two geologically-distinct regions; a glaciated northern till plain with soils three times more permeable than a southern, pre-Wisconsinan drift plain. The influences of two landscape measures, percent row crop cover (%RCC, computed at three spatial scales), and soil permeability (PERM), on baseflow nutrient concentrations were modeled using linear regressions. Quarterly water samples collected for four years were analyzed for nitrate-N (NN), Kjeldahl-N (KN), total-N (TN), and total-P (TP). In till plain streams ($n = 17$), NN concentrations were 8.5-times greater than drift plain streams ($n = 18$), but KN and TP were 20–40% lower at comparable %RCC. These differences resulted in TN/TP molar ratios >80 in till plain streams, but <6 in drift plain streams. For till plain steams regression models based on %RCC accounted for 79% of the variance in NN concentrations but only 27% in drift plain streams. However, regressions on %RCC accounted for 68–75% of the KN and TP concentration variance in the drift plain streams but essentially none in the till plain. Catchment PERM influenced the regional NN/KN ratios which were 10-fold higher in the drift plain streams. For both till and drift streams the catchment scale %RCC gave the best predictions of NN, a water soluble anion, but the smaller spatial scales produced better models for insoluble nutrient species (e.g., KN and TP). Published literature on Ohio streams indicates that these inter-regional differences in nutrient ratios have potential implications for aquatic biota in the receiving streams.

Keywords Land cover · Row crop · Spatial scale · Non-point source · Nutrients · Soil permeability · Water quality · Aquatic biotic integrity

Introduction

In catchments not dominated by urban land use, non-point sources often account for the majority of nitrogen (N) and phosphorous (P) inputs to streams (USEPA 1996; Gburek and Sharpley 1998; Carpenter and others 1998; Howarth and others 2002). Efforts to quantify and apportion the nutrient loads of non-point source inputs in major Midwestern drainages of the U.S. have been stimulated by concerns over the linkages between hypoxic regions in the Gulf of Mexico (Rabalais and others 2001) and exports of N from areas supporting row crop agriculture in the upper Mississippi and Ohio River basins (Burkart and James 1999; Goolsby and others 2001). Similar concerns have been raised for P inputs to Lake Erie and the Chesapeake Bay (Bertram 1993; Jordan and others 1997), as well as smaller streams and water bodies (USEPA 1996).

In addition to impacts at sites distant from their sources, nutrients from the landscape also affect local water quality (Johnson and others 1997; Buck and others 2004) and the biotic integrity of receiving streams (Miltner and Rankin 1998; Hawkins and others 2000; Allan 2004). National stream monitoring programs in the U.S. indicate that

F. B. Daniel (✉)
National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, 26 W. Martin Luther King Drive, Cincinnati, OH 45268, USA
e-mail: daniel.bernie@epa.gov

M. B. Griffith · M. E. Troyer
National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency, 26 W. Martin Luther King Drive, Cincinnati, OH 45268, USA

nutrient enrichment of inland streams and lakes is pervasive and cite eutrophication as the single most important stressor degrading surface water bodies (Parry 1998; Correll 1998; USEPA 2000). Such trends will likely continue, as agricultural lands worldwide receive over 13 million metric tons (Tg) of P and 100 Tg of N, annually (Vitousek and others 1997; Carpenter and others 1998). These nutrient amendments have overwhelmed natural nutrient cycles, and significant proportions are translocated to aquatic ecosystems (Howarth and others 1996).

The quantitative relationship between agricultural land use, such as row crops and livestock production in catchments and stream nutrients has been well documented (Castillo and others 2000; David and Gentry 2000; Schilling and Libra 2000; Jones and others 2001; Jordan and others 2003; Vondracek and others 2005; King and others 2005). However, the land cover–stream nutrients relationship is complex; it is controlled and/or modulated by multiple influences functioning at various spatial scales (Johnson and others 1997; King and others 2005). For instance, the geophysical characteristics of the catchment landscape, such as bed rock geology, topography, soil properties, and hydrologic features, can influence the transport of nutrients and sediments to a water body (Weller and others 2003; Calhoun and others 2002; Franklin and others 2002). The chemical properties of the various nutrient species (e.g., solubility and adsorptivity) also affect their transport to a stream. Water soluble, inorganic N species, such as nitrate-N (NN), may be transported to streams via phreatic flows (Peterjohn and Correll 1984; Lowrance 1992). However, insoluble nutrient species (including many forms of P and organic N) maybe absorbed to particulates, or are particulates per se, and thus are transported with sediments via over surface flow pathways (Gburek and others 2000; McDowell and others 2001; Calhoun and others 2002; Willett and others 2004).

A complete understanding of the relationship between landscape and water quality can be problematic, because the modulating factors are spatially overlain (e.g., slope, soil type, and the distribution of land cover), and it is difficult to separate the multiple, interacting influences on nutrient export (Norton and Fisher 2000; Vondracek and others 2005; King and others 2005; Cundill and others 2007). Yet understanding these interactions is important, because of the implications for nutrient control measures and management plans (Castillo and others 2000; Gburek and others 2000; Heathwaite and others 2000). Some studies have used statistical approaches to decompose the sources of variance and sort out the relative influence of different landscape factors on nutrient export and observed nutrient concentrations in streams (Johnson and others 1997; King and others 2005).

It is suggested here that the Little Miami River (LMR) drainage, bisected by the Wisconsinan glaciation, offers the possibility to directly examine interacting landscape influences on land to stream nutrient transport. Nutrient concentrations are assessed as a function of land cover (percent row crop cover; %RCC) and a geologic measure (catchment soil permeability; PERM) in 35 tributaries (headwater watersheds) during baseflow conditions.

Methods

Study Area and Site Selection

The LMR (Hydrologic Unit Code 05090202; USGS 2003) is a 170-km long tributary of the Ohio River that drains a 4,535-km^2 catchment in southwestern Ohio, USA (Fig. 1). The LMR drainage includes three Omernik Level IV ecoregions (USEPA 2007) from north to south: the Darby Plain; the Loamy, High Lime Till Plain; and the Pre-Wisconsinan Drift Plain. The northern half of the LMR drainage (i.e., Darby and Till Plains, hereafter referred to as the till plains; Fig. 1) was graded by the Wisconsinan glaciers and is characterized by level to gently rolling plains with low-gradient streams. The southern portion of the drainage (hereafter referred to as the drift plains; Fig. 1) lies beyond the terminus of the Wisconsinan glaciation and has more varied surface relief, with low- to medium-gradient streams. The till plain soils, derived from Wisconsinan glacial tills and outwash, are significantly more permeable and less erodible than the older, more weathered soils of the drift plains, which are largely derived from earlier glaciations (USEPA 2007).

The predominant anthropogenic activity across both regions is row crop agriculture, including corn (*Zea mays*), soy bean (*Glycine max*), and winter wheat (*Triticum aestivum*). The geophysical features of the river basin, in addition to the availability of high-resolution, contemporaneous land cover data, makes the LMR watershed a useful platform for comparing the influences of spatial scale and soil characteristics on the relationship between catchment land cover and stream nutrient concentrations.

Using the National Hydrography Dataset (NHD; USGS 1999a) stream reach file, 68 small (first- and second-order) streams were identified within the LMR basin. The drainage area (i.e., watershed) for each stream was then delineated (in ArcView 3.3; ESRI, Redlands, CA) using a hydrologic model, and elevation data from the National Elevation Dataset (NED; USGS 1999b). The location of the user-defined pour point for each stream (the most downstream extent of the drainage) was adjusted, as needed, until the delineated watershed was less than 50 km^2 in area; the upper limit for a “headwater drainage,” as defined

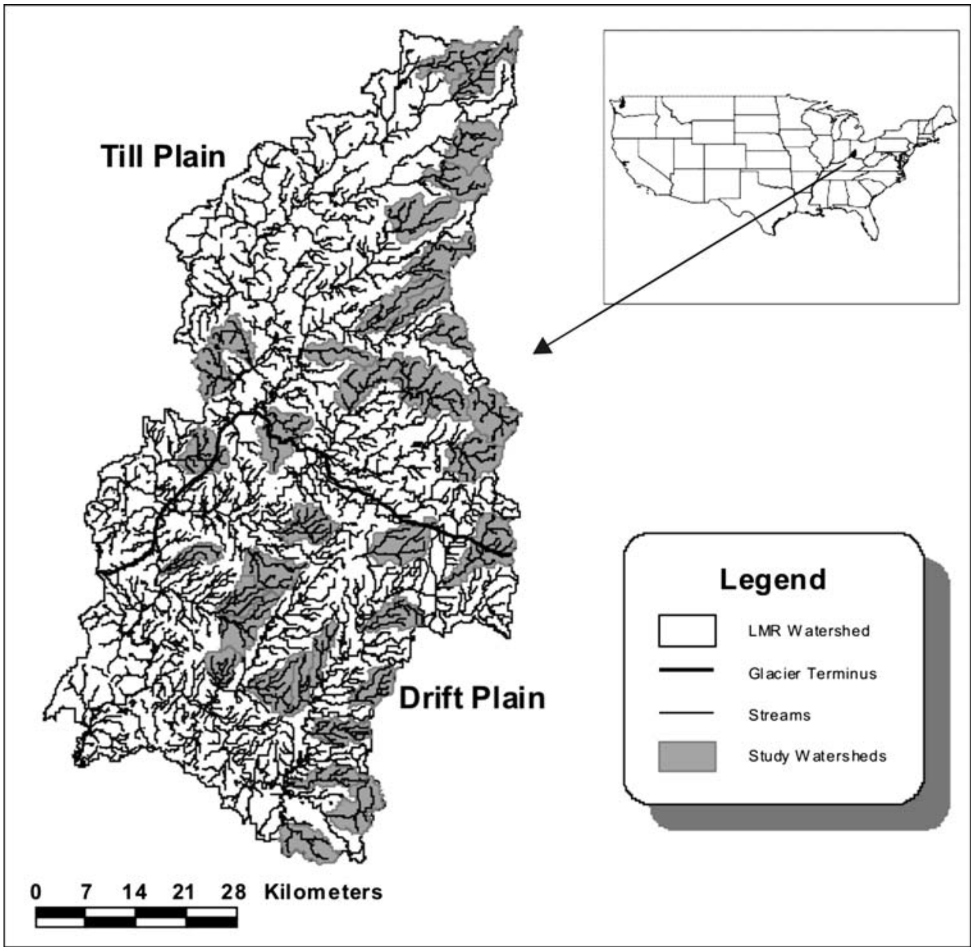

Fig. 1 Map of the Little Miami River (LMR) watershed (Ohio, USA) showing streams, study watersheds, and the division between the geologically-distinct till plain region to the north (Wisconsinan-glaciated) and drift plain region to the south (Illinoisan-glaciated)

by the Ohio Environmental Protection Agency (OEPA 1987).

Three screening criteria were applied to the initial set of 68 watersheds: (1) developed land could not exceed 5% of the catchment area, (2) the streams could have no permitted point discharge sources or public wastewater treatment plant outfalls above the sampling point—the pour point used in the hydrologic model; no effort was made to quantify residential septic drains or agricultural drainage tiles, and (3) all of the sites were hydrologically independent i.e., no site was downstream of any other site. These restrictions resulted in the retention of 35 watersheds (sampling sites) for the study.

Land Cover Dataset and Land Cover Metrics

A high-resolution land cover dataset (HRLD) of the LMR basin was developed from a hyperspectral image acquired via fixed-wing aircraft, at a time midpoint (summer 2002) in the water sampling period. Troyer and others (2006) documents the processing, classification, and quality assurance methods used to develop the HRLD coverage of the LMR basin, as well as the Federal Geographic Data Committee (FGDC)-compliant metadata. The HRLD was rendered in 4-m by 4-m pixels (i.e., 1 pixel = 16 m^2) and divides land cover into 11 categories: water (lentic and lotic), forest, corn, soybean, wheat, dry herbaceous, urban barren, rural barren, grassland, and developed (Troyer and others 2006). A row crop land cover class was created for this study by summing the corn, soybean, and wheat classes.

Within each of the 35 watersheds, the NHD stream reach file was buffered on both sides using 8-m (2 pixels) and 128-m (32 pixels) widths to provide two smaller sets of polygons for land cover analysis. This permitted land cover to be analyzed at three spatial scales: riparian (i.e., the area within the 8-m buffers); intermediate (i.e., the area within the 128-m buffers); and catchment (i.e., the area of the entire watershed).

Using the catchment boundaries created during watershed delineation and the HRLD grid, the status of land cover during the summer of 2002 was assessed at each of the three spatial scales (i.e., catchment, intermediate, and riparian) using ATtILA (USEPA 2004), an ArcView extension used to calculate landscape metrics. Simple land cover metrics (e.g., % area) were calculated for each spatial scale using five cover types: row crop (%RCC), forest, agricultural grassland (i.e., hay fields and pastures), and developed (including roadways), and "other."

Geophysical Properties and Precipitation Estimates

Using the NHD and NED, a set of dimensional, topographical, and hydrologic properties were estimated for each watershed, including area and perimeter, weighted mean slope, total stream length, mean length-weighted stream gradient, and stream density. Three mass-averaged, area-weighted soil parameters: soil permeability (PERM) score; an estimate of soil erodibility potential (i.e., STATSGO K-factor) and the soil percent organic content—were computed for each watershed using the Natural Resources Conservation Service (NRCS) State Soil Geographic (STATSGO) Database for Ohio (USDA 1994). The mass-averaged, area-weighted parameters were computed using methods described by Shirazi and others (2001). The permeability scores and the percent soil organic contents were computed from the upper 76 cm of soil layers (the minimum depth supplied for all soils in STATSGO), while soil erodibility measures were computed using only the surface soil layers within the LMR watershed boundaries. Briefly, the values for each measure were averaged (weighted by mass/depth) using the appropriate layer(s), to create a new set of coverages: "mean soil permeability", "mean soil erodibility", and "mean soil organic content," respectively. These new data layers were then clipped to the extent of each of the 35 sub-watersheds and all soil polygons within each boundary were area-weighted to compute the mass-averaged, area-weighted catchment permeability, erodibility potential and organic content. Precipitation estimates (for each year and for the entire study period) were developed separately for the till and drift plain regions of the LMR drainage. These estimates were based on averaged and weighted monthly surface precipitation data from surrounding National Climate Data Center (NCDC) reporting stations (NOAA 2003).

Water Chemistry

From December 1999 to December 2003, water samples were collected quarterly during baseflow (flow and turbidity judged to be unaffected by precipitation) conditions in the LMR drainage; the sampling location for each stream was the pour point used for watershed delineation in the hydrologic modeling. Samples were collected at mid-stream in brown, low-density polyethylene containers and placed on ice for transport to the laboratory. Water samples were divided, half the sample filtered through a 0.45 μm nylon membrane, and the two portions stored in the dark at 4°C until analysis. Samples were analyzed for nitrate-N (NN), Kjeldahl-N (KN), total-N (TN), and total-P (TP) using standard USEPA (1983) water chemistry methods. Nitrate-N (NN) was determined by colorimetry on filtered aliquots after cadmium reduction to nitrite, and TP and KN were determined by colorimetry, following the digestion of unfiltered aliquots in the presence of sulfuric acid, potassium sulfate, and a mercury catalyst. Total nitrogen (TN) was defined as the sum of NN and KN. Both KN and TP were observed at higher concentration in the unfiltered samples (implying particulate association). In a few cases, the concentrations of these two analytes were below the detection limit of the analytical method wherein values of one half the detection limit were assigned (Helsel 1990). Two other analytes, nitrite-N and ammonia-N, were also measured but both were generally either zero, or near the method detection limit, and are not reported here. Quality assurance and control processes included collection of field blank samples and the subtraction of field blank values from all stream sample results.

Statistical Analysis

The descriptive statistics and all other statistical analyses were performed using SYSTAT 11 (SPSS Inc., Chicago, IL). The relationship between stream nutrients and %RCC (the land cover metric chosen for analysis) was examined at the riparian, intermediate, and catchment scales using linear, least squares regression; variables were not transformed for this analysis as all met the constraints of the Shapiro-Wilk normality test. Percent row crop cover (%RCC) was the only land cover metric analyzed, as row crops were assumed to be the primary non-point source for the stream nutrients in the LMR drainage and initial analysis confirmed this assumption. In order to examine differences in the relationship between stream nutrient concentration and %RCC in the till plain and drift plain regions, the slopes of the regression lines for the two regions were compared with a dummy variable, [region] X (%RCC), where "region" was assigned a value of "1" or "0". Means for all landscape variables for the two regions were individually tested by ANOVA; $p < 0.05$ was considered significant; and values greater than 2 standard deviations from the mean judged to be "outliers".

Results

Land Cover Metrics

Seventeen (17) of the 35 watersheds analyzed in this study were entirely or predominantly (>50% by area) within the northern till plain region, and the remaining 18 were entirely or predominantly south of the glacial terminus in the drift plain region (Fig. 1). The catchments were comparable in area (circa 20 to 50 km^2) and, the area of the intermediate- and riparian-stream buffer polygons ranged 29–41% and 1.7–2.7% of that, respectively (data not shown).

The distribution of land cover classes varied between the two regions at all three spatial scales. Mean %RCC was greater in the till plain watersheds than those in the drift plain region, although the ranges overlapped (Table 1). The opposite situation existed for mean % forest cover, while the mean % agricultural grassland cover did not differ significantly between the two regions, except at the riparian scale. Developed land cover averaged only about 2% of the total catchment areas in either region. At the catchment scale, row crop was the dominant land cover in both regions and combining row crop with forest, and agricultural grassland cover accounted for approximately 97% of the total area in all 35 watersheds (Table 1). In contrast, forest and agricultural grassland dominated the land cover at the riparian scale.

In both regions, the relative percentages of the various land cover classes varied in a consistent manner with spatial scale. Accordingly, %RCC increased with increasing spatial scale (riparian to catchment), % forest cover decreased, and % agricultural grassland and % developed land were relatively constant (Table 1).

Although the absolute amount of the various land cover classes (e.g. %RCC) varied between the watersheds, a comparison of land cover distribution patterns between the three spatial scales, across all of the 35 watersheds shows a profound uniformity (Table 2). For example, the correlation coefficients for %RCC between the catchment and riparian areas was 0.88 for the drift plain and 0.91 for the till plain, with even stronger correlations (>0.95) for %RCC between catchment and intermediate scale areas (Table 2). Thus, those watersheds with relatively higher proportions of row crop at the catchment scale had, on average, a relatively higher proportion at the smaller spatial scales as well. This same pattern of spatial correlation was also observed for all other land cover classes (data not shown).

Table 2 Correlation of percent row crop land cover (%RCC) across spatial scale in the Little Miami River drainage by region

Scale	Riparian	Intermediate	Catchment
Drift plain region (n = 18)			
Riparian	1		
Intermediate	0.93	1	
Catchment	0.91	0.98	1
Till plain region (n = 17)			
Riparian	1		
Intermediate	0.93	1	
Catchment	0.88	0.93	1

Geophysical Properties and Precipitation Estimates

The precipitation levels observed during the study did not represent significant departures from historical rainfall ranges for the area (USEPA 2007). Over the four year study period, estimated total annual rainfall did not differ significantly between the two regions (ANOVA, Table 3);

Table 1 Comparison of land cover metrics in the Little Miami River basin by region and spatial scale

Scale	Drift plain region (n = 18)		Till plain region (n = 17)		ANOVA	
	Mean (SD)	Range	Mean (SD)	Range	F	p
Row crop						
Riparian	14.7 (7.7)	3.5–29.6	24.9 (12.4)	6.7–49.0	8.59	0.006
Intermediate	28.8 (12.5)	8.4–52.6	45.0 (19.7)	10.4–73.3	12.55	0.001
Catchment	37.6 (12.3)	17.0–58.3	57.1 (16.0)	20.6–77.9	16.33	0.000
Forest						
Riparian	56.0 (13.0)	22.2–84.9	29.5 (22.4)	4.9–75.7	18.47	0.000
Intermediate	38.5 (15.2)	9.5–77.7	18.1 (14.8)	2.1–43.9	19.38	0.000
Catchment	27.7 (10.4)	10.9–55.6	9.6 (8.3)	1.8–27.1	31.89	0.000
Agricultural grassland						
Riparian	29.1 (6.2)	18.9–45.8	41.1 (11.2)	16.6–58.0	15.58	0.000
Intermediate	30.6 (6.6)	19.4–40.4	33.2 (6.9)	22.7–43.7	0.21	0.647
Catchment	31.7 (7.0)	21.6–44.1	29.7 (7.8)	20.2–44.3	0.65	0.425
Developed land						
Riparian	0.9 (0.7)	0.1–2.8	0.7 (0.6)	0.2–2.5	1.04	0.316
Intermediate	1.5 (1.0)	0.3–4.1	1.0 (0.8)	0.3–3.2	2.91	0.197
Catchment	1.7 (1.2)	0.3–5.1	1.2 (0.9)	0.4–3.7	1.55	0.222

Results are the percentage of total area of each cover type at the spatial scale indicated, tested for difference between regions

Table 3 Comparison of mean geophysical measures and estimated precipitation by region

Measures	Drift plain region ($n = 18$) Mean (SD)	Till plain region ($n = 17$) Mean (SD)	ANOVA	
			F	p
Dimension				
Area (km^2)	27.6 (8.3)	34.1 (9.2)	4.85	0.035
Perimeter	36.5 (6.9)	39.5 (6.1)	1.89	0.178
Slope				
Mean slope (degree)	1.3 (0.50)	1.1 (0.1)	2.93	0.096
Hydrology				
Stream reach length (km)	26.1 (7.0)	25.7 (8.3)	0.03	0.866
Stream density (km^{-1})	1.0 (0.2)	0.8 (0.1)	15.97	0.000
Stream reach gradient (degree)	0.6 (0.5)	0.5 (0.4)	0.06	0.455
Soil				
Permeability (PERM; mm/h)	84.4 (32)	285 (100)	64.95	0.000
Erodibility (K-factor)	0.419 (0.013)	0.356 (0.009)	260.18	0.000
Percent organic matter (mg/g)	0.44 (0.05)	0.58 (0.06)	2.61	0.116
Precipitation (1999–2003)				
Total annual rainfall (cm)	116.2 (6.8)	111.9 (5.1)	2.07	0.166
Monthly: low–high (cm)	2.1–26.2	1.2–28.3	–	–

Soil measures are mass-averaged, area-weighted measures

likewise, the variation in precipitation among individual study years and between regions each year were not significant.

On average, the till plain watersheds were slightly, but significantly larger, (24% in area and 8% in perimeter) than those in the drift plains, but the mean stream density in the till plain watersheds was less (~20%) in the drift plain watersheds (Table 3). In contrast, several other, geophysical measures of mean slope, reach length, and gradient were comparable for watersheds in both regions.

However, the mass-averaged, area-weighted soil (PERM) exhibited large and significant inter-regional differences; the mean PERM for soils in the till plain watersheds was over three times greater than those in the drift plain region (Table 3). In contrast, the mean, area-weighted K factor for surface soils in the drift plain watersheds was significantly greater (0.419 ± 0.013 versus 0.356 ± 0.009) than for those in the till plain watersheds. In summary, this indicates that soils in the drift plain watersheds were not only less permeable, but also more erodible. These two mean, area-weighted soil properties were inversely correlated ($r = -0.91$; $p < 0.001$; not shown). The mean, area-weighted percent soil organic matter was not significantly different in the two regions (ANOVA, Table 3).

Water Chemistry

Over the study period, the mean baseflow stream concentrations of most nutrients, and the ratios of these components (e.g., TN/TP or KN/NN), differed significantly between the two regions; the sole exception being KN (Table 4). The mean concentrations of NN, the dominant inorganic nitrogen form, were over eight times greater in the till plain streams, while KN, which includes all organic nitrogen species and ammonia, was slightly (but not significantly) greater in the drift plain streams. Mean TN (where, TN = NN + KN) was almost five times greater in the till plain streams relative to the drift plain streams, and the relative contributions of organic and inorganic nitrogen to total nitrogen concentrations also varied markedly between regions. In the till plain streams, KN (hence referred to as the organic nitrogen fraction as ammonia was negligible) averaged only 9% of TN, whereas it averaged 50% in the drift plain streams (Table 4). TP exhibited an inter-regional pattern similar to KN; mean TP was greater (~50%; $p < 0.01$) in the drift plain streams than in the till plain streams (Table 4). The effect of these patterns for nitrogen and phosphorous resulted in a marked elevation in the TN/TP molar ratio (~14-fold) for the till plain streams compared to the drift plains (Table 4). The relatively higher concentrations of organic nitrogen species in the drift plain streams resulted in molar ratios of organic N to inorganic N (estimated by KN/NN) 11-fold greater; and organic N to TN (estimated by KN/TN) 6-fold greater ($p < 0.001$ for both ratios) in this region compared to those in the till plain. The ratio of organic N to TP (KN/TP) was approximately 2-fold greater in the till plain streams (Table 4).

Table 4 Mean in-stream nutrient concentrations by analyte or analyte ratio by region

Analyte	Drift plain region (n = 18)		Till plain region (n = 17)		ANOVA	
	Mean (SD)	Range	Mean (SD)	Range	F	p
NN	0.67 (0.41)	0.26–1.75	5.67 (1.83)	1.66–8.35	127.24	0.000
KN	0.66 (0.19)	0.35–1.02	0.55 (0.20)	0.29–1.11	2.64	0.114
KN/NN	1.22 (0.54)	0.33–2.35	0.11 (0.05)	0.06–0.21	70.20	0.000
TN	1.32 (0.51)	0.71–2.47	6.22 (1.88)	1.95–8.90	112.74	0.000
KN/TN	0.50 (0.09)	0.37–0.70	0.09 (0.08)	0.05–0.38	199.43	0.000
TP	0.12 (0.06)	0.06–0.26	0.08 (0.04)	0.04–0.2	7.50	0.010
TN/TP	5.9 (3.8)	2.5–16.3	83.4 (32.8)	25.5–131.7	99.03	0.000
KN/TP	5.7 (0.2)	4.0–8.4	7.6 (1.7)	3.9–10.0	14.1	0.001

Units for individual analytes are mg N/l (or mg P/l); KN/TN, TN/TP, and KN/TP are unitless molar ratios

NN nitrate-nitrogen, *KN* Kjeldahl-nitrogen, *TN* total-nitrogen (where TN = NN + KN), *TP* total-phosphorous

Statistical Analysis and Models

Percent row crop cover (%RCC) exhibited a positive, significant relationship with nutrient concentrations at all spatial scales (except for TP and KN in the till plains region). Percent % forest cover presented a significant inverse correlation with %RCC and, therefore, was inversely related to the nutrient concentrations observed. Models based on % agricultural grassland were typically not statistically significant and partial first order correlations suggested that developed land did not explain additional variation in nutrient concentrations after removal of the effects of %RCC for either region (not shown; cf. King and others 2005).

Linear regression showed that up to 79% of the observed variation in NN for the till plain streams could be predicted by catchment-scale %RCC; for the drift plain watersheds, catchment-scale %RCC accounted for only about 27% of the variation in NN (Table 5; Fig. 2a). The estimates of %RCC based on larger spatial scales were better predictors of the variation in NN compared to the two smaller spatial scales, particularly for the till region. For the till plain streams, all three spatial scale estimates of %RCC gave a useful prediction of stream NN concentrations, whereas in the drift plain region, riparian-scale %RCC was not a reliable forecaster of NN (Table 5; Fig. 2a). The slopes for the regressions of NN concentration versus %RCC were 6 times greater ($p < 0.001$) in

Table 5 Relationship between row crop land cover (%RCC) and nutrient concentration by region and spatial scale

Nutrient species	Spatial scale	Drift plain region (n = 18)				Till plain region (n = 17)				Compare slopes	
		Slope (A)	r^2	F	p	Slope (A)	r^2	F	p	t	p
NN	Riparian	0.019	0.12	2.17	0.160	0.113	0.58	20.92	0.000	2.79	0.009
NN	Intermediate	0.017	0.28	6.32	0.023	0.106	0.64	24.39	0.000	2.97	0.006
NN	Catchment	0.017	0.27	5.84	0.028	0.102	0.79	56.14	0.000	5.07	<0.000
KN	Riparian	0.020	0.73	42.27	<0.000	0.003	0.04	0.59	0.456	−2.93	0.006
KN	Intermediate	0.013	0.78	56.47	<0.000	0.003	0.09	1.52	0.237	−2.74	0.010
KN	Catchment	0.013	0.75	46.96	<0.000	0.003	0.04	0.64	0.437	−2.65	0.012
TN	Riparian	0.039	0.35	8.43	0.010	0.116	0.58	20.95	0.004	2.20	0.035
TN	Intermediate	0.030	0.56	20.44	0.000	0.128	0.64	26.33	0.000	2.48	0.019
TN	Catchment	0.031	0.53	18.25	0.000	0.104	0.79	54.78	<0.000	4.31	0.000
TP	Riparian	0.007	0.77	57.00	<0.000	0.001	0.09	1.40	0.255	−4.33	0.000
TP	Intermediate	0.004	0.78	57.87	<0.000	0.001	0.08	1.39	0.257	−4.19	0.000
TP	Catchment	0.004	0.68	39.57	0.000	0.001	0.05	0.79	0.388	−3.76	0.000

The model tested is [nutrient concentration] = A*[%RCC] + C. The F and p values for each region indicate whether the model slope differs from zero and the r^2 value is the correlation coefficient for the respective model. The t and p values refer to test of the slopes difference between regions for each set of models

NN nitrate-nitrogen, *KN* Kjeldahl-nitrogen, *TN* total-nitrogen (where TN = NN + KN), *TP* total-phosphorous

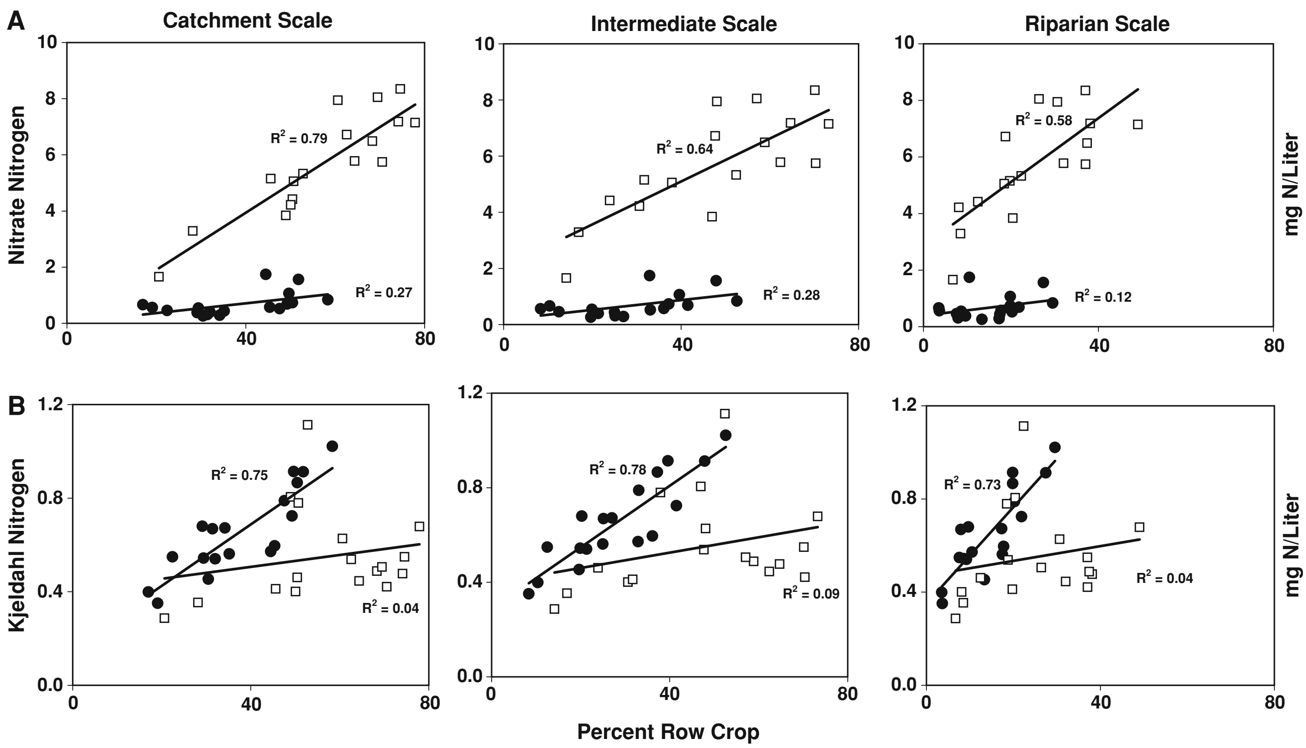

Fig. 2 Least squares scatter plots of the nutrient concentrations for **a** nitrate-N (NN) and **b** Kjeldahl-N (KN) versus percent row crop land cover at three spatial scales. Open squares denote till plain sites and closed circles denote drift plain sites. Each symbol represents the mean concentration based on four years (1999–2003) of quarterly sampling during baseflow conditions. For the till plain KN concentrations, removal of the one obvious, outlier point has an insignificant influence on the slopes/regressions and does not alter the conclusions. The excess KN appears to be from livestock access at a point above the sampling station (personal observations)

the till plain streams than in the drift plains (Table 5; Fig. 2a).

An opposite pattern was found for the relationship of %RCC and KN (Table 5; Fig. 2b). The regressions for %RCC versus stream KN concentration were significant at all three spatial scales in the drift plain region ($r^2 = 0.73$–0.78). In contrast, for the till plain watersheds, regardless of the spatial scale employed, the slopes of the corresponding regressions for KN versus %RCC were not different from zero (i.e., $p > 0.05$; Table 5; Fig. 2b).

The relationship between %RCC and TN was similar to the pattern for NN, with significant relationships observed for both regions and at all three spatial scales. As with NN, the regression for %RCC accounted for more of the variation in TN in the till plain streams compared to the drift plain streams (Table 5; Fig. 3a). In both regions, the r^2 value was greater for models of %RCC versus TN when they were based on the land cover at larger spatial scales, and the smallest r^2 value occurred with the riparian scale data (Table 5). The slopes for the regression of %RCC versus TN were three to four times greater ($p < 0.001$) based on the larger spatial scales for the till plain watersheds (Table 5; Fig. 3a).

The regressions for %RCC versus TP followed patterns similar to those for KN (Table 5; Fig. 3b). In the drift plain streams, %RCC accounted for 68–78% of the variation in TP, with greater r^2 values obtained for the regression of TP when %RCC was measured at the two smaller spatial scales (Table 5). In the till plain streams, relationships between stream TP concentration and %RCC were not significant at any spatial scale, and the slopes of the corresponding regressions were statistically indistinguishable from zero (Table 5; Fig. 3b).

Regressions using the soil measure PERM as the independent variable, instead of %RCC, did not produce statistically-significant relationships for any of the four nutrient species in the till plain streams (Table 6). For the drift plain streams, the regressions based on PERM accounted for 28% and 31% of the variation in TP and KN, respectively, and the regressions for both nutrient species exhibited a negative slope, indicating that stream concentrations of TP and KN in the drift plain region were inversely related to soil permeability (therefore directly related to soil erodibility; Table 6).

Analyses using both landscape metrics, catchment-scale %RCC and PERM, for prediction of stream nutrients (i.e.,

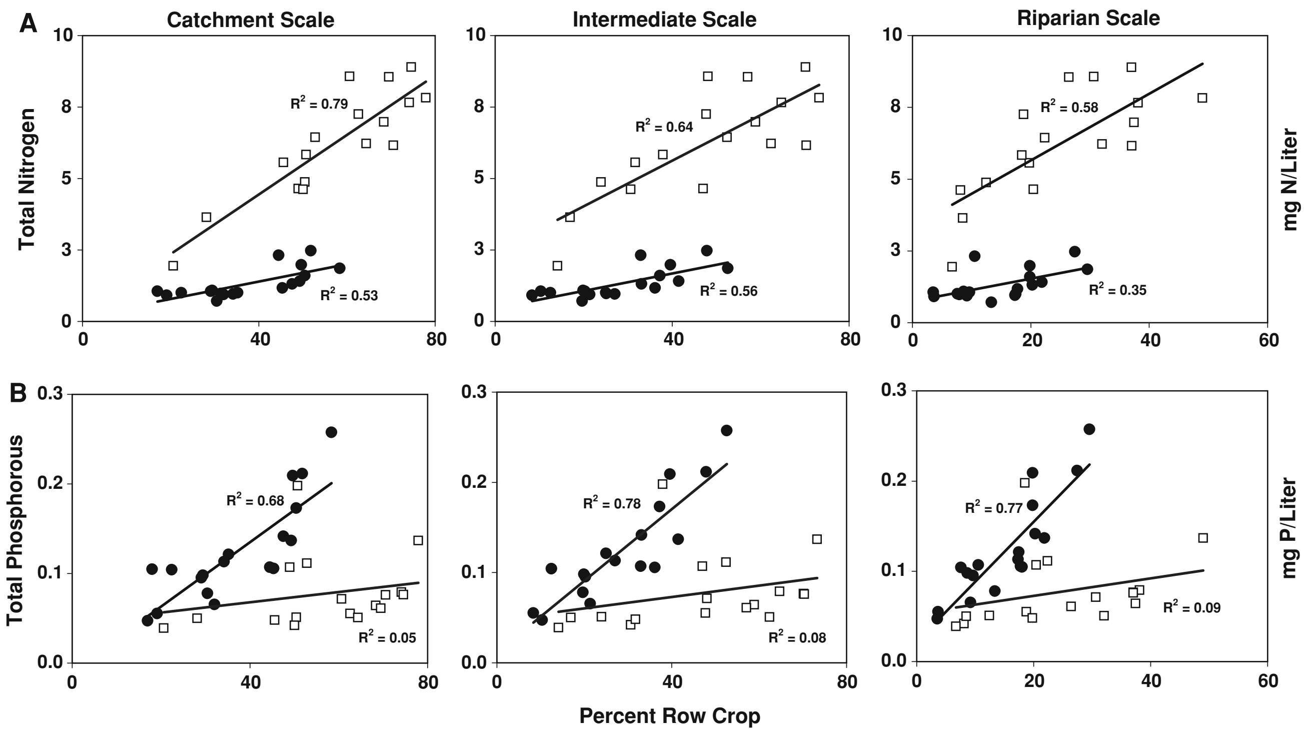

Fig. 3 Least squares scatter plots of the nutrient concentrations for **a** total-N (TN) and **b** total-P (TP) versus percent row crop land cover at three spatial scales. Open squares denote till plain sites and closed circles denote drift plain sites. Each symbol represents the mean concentration based on four years (1999–2003) of quarterly sampling during baseflow conditions. For the till plain TP concentrations, removal of the one obvious, outlier point has an insignificant influence on the slopes/regressions and does not alter the conclusions. The excess TP appears to be from livestock access at a point above the sampling station (personal observations)

Table 6 Relationship between catchment-scale mean soil permeability (PERM) and nutrient concentration by region

Nutrient species	Drift plain region (n = 18)				Till plain region (n = 17)				Compare slopes	
	Slope (B)	r^2	F	p	Slope (B)	r^2	F	p	t	p
NN	0.0025	0.04	0.62	0.444	0.0076	0.17	3.09	0.099	0.51	0.604
KN	−0.0032	0.31	7.17	0.017	0.0009	0.22	4.16	0.060	3.04	0.005
TN	−0.0008	0.00	0.04	0.853	0.0085	0.20	3.86	0.068	0.92	0.367
TP	−0.0009	0.28	6.08	0.025	0.0001	0.05	0.76	0.397	2.79	0.009

The model tested is [nutrient concentration] = B*[PERM] + C. The F and p values for each region indicate whether the model slope differs from zero and the r^2 value is the correlation coefficient for the respective model. The t and p values indicate whether the slopes differ between regions for each set of models

NN nitrate-nitrogen, *KN* Kjeldahl-nitrogen, *TN* total-nitrogen (where TN = NN + KN), *TP* total-phosphorous

[mg/l] = a*(%RCC) + b*(PERM) + c; Table 7) also produced region-specific results. In the drift plain streams, these regressions accounted for more of the variation in NN and TN compared to %RCC alone (i.e., r^2 for NN increased from 0.27 to 0.57; r^2 for TN increased from 0.53 to 0.69; compare Tables 5 and 7). Using both catchment-scale %RCC and PERM did not significantly improve the models for NN or TN in the till plain streams, nor did it improve those for KN or TP in either region (Tables 5, 7).

Discussion

Overview

In this study, a direct examination of the relationship between landscape measures and stream nutrient concentrations was made by exploring water chemistry data from 35 agriculturally-dominated watersheds nested in a single, larger drainage, exhibiting geologically-distinct

Table 7 Relationship between row crop land cover (%RCC) and soil permeability (PERM) and nutrient concentration by region

Nutrient species	Drift plain region (n = 18)					Till plain region (n = 17)				
	Slope (A)	Slope (B)	r^2	F	p	Slope (A)	Slope (B)	r^2	F	p
NN	0.029	0.008	0.57	10.02	0.002	0.097	*0.0019*	0.80	27.70	<0.001
KN	0.012	*−0.0008*	0.76	23.62	<0.001	*0.0005*	*0.0009*	0.22	1.95	0.179
TN	0.041	0.008	0.69	17.09	<0.001	0.098	*0.0028*	0.80	28.73	<0.001
TP	0.037	*−0.0002*	0.74	21.65	<0.001	*0.0004*	*0.0006*	0.07	0.54	0.592

The model tested is [nutrient concentration] = A*[%RCC] + B*[PERM] + C. The F and p values for each region indicate whether the model slope differs from zero and the r^2 value is the correlation coefficient for the respective model. The Pearson correlation coefficient between %RCC and PERM was 0.53 and −0.35 for drift and till plain sites, respectively

Italicized slope terms indicate term does not contribute significantly to the overall model

NN nitrate-nitrogen, *KN* Kjeldahl-nitrogen, *TN* total-nitrogen (where TN = NN + KN), *TP* total-phosphorous

regions. Two landscape parameters were selected for the assessments:

(1) The land cover measure chosen for analysis, %RCC, is an indicator of the level of agricultural activity within the watersheds. Lands supporting row crops are often amended with fertilizers that may reach 100 kg N/ha-year and 50 kg P/ha-year (David and Gentry 2000; Weller and others 2003) and thus export nutrient loads 30–100 times those from lands covered in perennial vegetation such as hay, pasture, or forest (Campbell and others 2000; Randall and Mulla 2001). Analysis of nutrient budgets in agriculture-dominated basins reveled that 84–86% of N and 53–75% of P in riverine exports could be traced to row crop operations (David and Gentry 2000; Jordan and others 2003).

(2) The mass- and area-normalized catchment soil permeability score (PERM) was selected as the geophysical measure in this analysis. Catchment soil permeability provides an indication of the preferential flow pathways between a catchment and stream and thus, can be used to predict the movement of nutrients to streams (Lowrance 1992; Norton and Fisher 2000; Calhoun and others 2002).

Water sampling in this study was conducted during baseflow conditions. The bulk of nutrient loads are exported during storm events, limiting the usefulness of baseflow data for addressing questions related to total nutrient export (David and others 1997); however, baseflow conditions, including nutrient concentrations, do have important implications for aquatic biota in the immediate receiving streams (Johnson and others 1997). Storm event flows typically disturb and/or scour streambeds and aquatic assemblages are re-established during baseflow conditions (Lane and Borland 1954). This is particularly true for periphyton, one of the aquatic assemblages most sensitive to nutrient flux. (Griffith and others 2002; Stevenson 2006). Models based on over two decades of stream monitoring in Ohio show inverse correlations between increasing nutrient concentrations and metrics of biological integrity (Miltner and Rankin 1998).

Nitrate Nitrogen

The concentration of NN was dependent on %RCC, in both regions although the strength of this relationship varied both by region (i.e., PERM), spatial scale, and by nutrient chemistry; findings in concordance with other studies (Johnson and others 1997; Jordan and others 1997; Castillo and others 2000; Schilling and Libra 2000; Jones and others 2001; King and others 2005). Stream concentrations of NN in the till plain streams were better accounted for in terms of %RCC, were higher for a given %RCC, and increased at a greater rate with increasing %RCC compared to those concentrations in the drift plain streams. In both regions, the best correlations of NN (i.e., the largest r^2 value) were observed with %RCC measured at the larger (e.g., catchment) spatial scales. Other studies have also observed that for NN (and perhaps other soluble nutrients) the use of larger spatial scales to compute %RCC increases the predictive power of the models (Williams and others 2005). It is worth noting that the obvious correlation in land cover percentages across the three spatial scales, as seen in this study and others (King and others 2005; Dodds and Oakes 2008) limits our ability to establish the magnitude of this phenomenon using the simple linear regressions employed herein.

These results are also consistent with the observation that most NN is exported to streams via sub-surface flows (Lowrance 1992). This study shows that in the till plain, with more permeable soils (mean PERM = 285 mm/h), a stronger relationship (correlation and slope) between %RCC and NN concentrations was obtained compared to the drift plain streams (mean PERM = 84.4 mm/h). Likewise, Howarth and others (1996) found that stream TN (predominately NN) per mass unit of fertilizer applied to arable lands was as much as eight-fold greater in watersheds with sandy soils compared to those with loamy or clayey soils. Calhoun and others (2002) reported similar observations in the Maumee River basin (Ohio), where NN concentrations in drainage water from watersheds with sand- (<30% clay) and glacial till-dominated soils (35–55% clay) were 1.7 to 2.3 times greater than those with lacustrine soils (>60% clay).

The use of catchment PERM alone in these models was not successful in accounting for the variance in NN for either region (Table 6). However, combining PERM and %RCC improved the prediction of NN (i.e., increased r^2 compared to %RCC alone) for both regions, but this enhancement was statistically significant only for drift plain streams (Table 7). This apparently counterintuitive observation seems likely related to the regional differences in PERM. The till plain watersheds are set in relatively permeable soils (i.e., PERM >200 mm/h), whereas the soils of the drift plain watersheds are comparatively impermeable (i.e., PERM <100 mm/h). As a result, small increases in catchment soil permeability within the drift plain region might have a relatively more profound influence on water percolation and subsurface flows (and thus, on stream NN concentrations) than similar increases in soil permeability in till plain catchments.

It could be suggested that these inter-regional differences in the relationship between %RCC and NN observed are actually related to sub-surface tile drainage systems which can increase exports of the nutrient as much as five-fold compared to streams that were not tiled (Fenelon and Moore 1998; McIsaac and Hu 2004). Tile drains are more commonly employed in areas with permeable soils (till plain) and less so in areas with clayey, less permeable soils and with more surface relief (drift plain) which both reduce their transport efficiency and also enhance overland flows (David and Gentry 2000). However, tile drains do not seem a reasonable explanation for the roughly one-to-one relationship between mean catchment PERM and the slope of %RCC versus stream NN observed in this study. First, the water samples for this study were collected at baseflow conditions (i.e., visually undisturbed by precipitation), and second those drainage tile outpipes observed during water sampling events at all of the sites were typically dry. Thus, the differences in the relationships between %RCC and stream NN observed herein seem attributable primarily to differences in natural soil percolation rates and transfer to subsurface flows, rather than artificial drainage.

Total Phosphorous

The relationships between TP and %RCC also showed inter-regional differences, but the pattern contrasted from that seen for NN. In the drift plain streams, the models with %RCC accounted for much of the variance in stream TP ($r^2 = 0.68$–0.78), and models where land cover was assessed at smaller spatial scales gave better predictions. These findings parallel observations of Johnson and others (1997) which showed that row crop cover in a 100-m stream-side buffer gave better prediction of TP concentrations in Michigan streams than at the catchment scale. For the till plain streams, however, the concentration of TP was not significantly related to %RCC, regardless of spatial scale ($r^2 < 0.1$).

The concentration of TP was inversely related to PERM for the drift plain watersheds and thus was directly correlated with watershed soil erodibility (not shown; see Methods). Regression models based on both %RCC and PERM provided some additional accounting for the TP concentration variance (compared to using %RCC alone) in the drift plain streams but not the till plain (Table 5 vs. Table 7).

Overall, these results suggest that both land cover (including spatial scale) and geology affect stream TP concentrations; specifically, catchment soils can modulate the relationship between %RCC and in-stream TP concentrations. Many phosphorous compounds are relatively insoluble and hydrophobic with a propensity to adhere to sediment components such as clays and other particulates (Sharpley and Tunney 2000). As a result, they are typically transported to streams via overland run-off, rather than by subsurface flows (Gburek and others 2000; Calhoun and others 2002; Buck and others 2004) and correlations between erodible soils, fine sediments, and in-stream TP have been established (Baker and Richards 2002; Calhoun and others 2002; Buck and others 2004). Consequently, the management of phosphorous exports from agricultural lands typically considers hydrological pathways, erosion control (McDowell and Sharpley 2002), and phosphorous levels in soils proximate to the stream (Gburek and others 2000; McDowell and Sharpley 2002). The results of this study support the inclusion of these considerations for management of phosphorous exports.

The marked difference in the relationship between %RCC and stream TP observed in this study, between the two geologically-distinct regions of the LMR drainage, may help reconcile conflicting reports published previously on this association. Some studies have reported a correlation between the extent of agricultural activity and stream TP (Jordan and others 2003; Weller and others 2003), as seen here for the drift plain streams, while others have reported that TP concentrations are not correlated with %RCC (Osborne and Wiley 1988; Dodds and Oakes 2006), as observed in the till plain streams. If the observations in this study are typical, a mechanistic explanation may exist for these differences; namely, that watershed geology (in this case soil permeability) influences the relationship between TP and land cover (Richards and others 1996; Castillo and others 2000).

Kjeldahl Nitrogen

Stream KN concentrations exhibited a similar pattern to that observed for TP in both regions. A positive relationship between %RCC and stream KN was observed in the low-permeability drift plain streams, where KN accounts for half of the total nitrogen (TN) concentrations. In this region, %RCC accounted for 73–78% of the variation in KN, regardless of the spatial scale. In contrast, for the till plain region, where KN represents only about 9% of TN concentrations, there is no significant relationship with %RCC at any spatial scale. As with TP, stream KN concentrations in the drift plain streams were inversely correlated with PERM and therefore directly associated with soil erodibility (i.e., surface layer K-factor; data not shown); no relationship between KN concentration and the measured soil attributes was observed in the till plain streams. As could be deduced from the proceeding discussions on these two nutrient species, the concentrations of KN and TP are strongly correlated ($r = 0.84$; $p < 0.01$) across these LMR streams.

The correlation of stream KN with %RCC in the drift plain region suggests that activities associated with row crop agriculture are a source of these nutrients. Known and implicated sources of organic nitrogen species in soil and water includes plant root extrudates (Jones and others 2005); decomposition of plant litter and detritus (Willett and others 2004); leeching from organic rich soils (Cundill and others 2007); metabolic transformations by microbes (Caraco and Cole 2002; Findlay and Sinsabaugh 2003); fertilizers and manures (Richards and Baker 2002); and atmospheric deposition (Neff and others 2002).

In agriculturally-dominated watersheds, the transport pathways whereby KN fractions reach streams are not definitively established. However, in studies from forested watersheds, stream organic-nitrogen loads exhibit strong correlations ($r^2 \sim 0.9$) with both overland runoff (Lewis and others 1999) and stream discharge (Vanderbilt and others 2003). Other studies have also shown that the ratio of organic carbon to organic nitrogen found in streams reflects that found in the catchment soils (Campbell and others 2000; Willett and others 2004). In this study the mean percent soil organic matter was not different between the two regions and did not account for variation in KN for either group of watersheds (data not shown; cf. Chin 2002). Finally, analysis of water quality trends over a two decade period indicates correspondence between KN and suspended solids concentration in northwestern Ohio rivers (Richards and Baker 2002).

The observations reported herein, namely that the relationships between KN and the two landscape measures, %RCC and PERM, are similar to those observed for TP in both the drift and till regions seems to suggest a similar transport pathway, and perhaps a similar source for these two nutrient species. Thus, the tentative conclusions from this study is that KN concentrations observed in the LMR streams were associated with the intensity of row crop operations, and that the bulk of these compounds reach the streams associated with particulates transported to streams via overland flow.

There is limited consensus as to the biological significance of organic nitrogen in the environment, because the presence of these fractions was under-appreciated until relatively recently due to shortcomings in analytical procedures (Willett and others 2004; Brookshire and others 2005). However, the examination of nitrogen budgets for streams draining undisturbed catchments revealed that up to 85% of TN is exported as organic N (Lewis and others 1999; Vanderbilt and others 2003; Brookshire and others 2005). The relative abundance of organic nitrogen is more variable in disturbed watersheds, but can still constitute significant proportions (e.g., 30–70%) of nitrogen exports (David and Gentry 2000; Willett and others 2004; Cundill and others 2007). Further, at least a portion of exported organic nitrogen is bioavailable (Willett and others 2004), and some simple organic nitrogen compounds, such as amino acids and urea, are utilized by aquatic biota (Findlay and Sinsabaugh 2003; Brookshire and others 2005) and can stimulate the growth of bacteria and phytoplankton (Seitzinger and Sanders 1999). The overall importance of organic nitrogen as a nutrient source for biota in streams draining agricultural watersheds is unresolved (Jones and others 2005), but Neff and others (2003) suggest that organic nitrogen may represent a short-circuit in global N-cycles and that it contributes (along with inorganic nitrogen) toward eutrophication in aquatic ecosystems (Seitzinger and Sanders 1999).

Total Nitrogen

The concentrations of TN in the till plain streams were approximately five times those in the drift plain streams (overall) and over three times greater when comparing watersheds with equal %RCC (data not shown). The relationship of TN concentration to %RCC also varied between the two regions and can be traced to differences in inorganic to organic nitrogen ratios (i.e., NN/KN) in the two groups of streams. For the till plain streams, which were dominated by NN, the relationship of %RCC to TN was similar to that observed for NN. In the drift plain streams, where concentrations of inorganic and organic nitrogen were comparable, the TN dependence on %RCC presents as a combination of NN and KN dependencies.

Stream Biota

The regional differences in baseflow nutrient concentrations observed in this study have potential consequences for stream biotic assemblages. As noted previously, aquatic assemblages rebuild under baseflow conditions following storm events (Miltner and Rankin 1998; Hawkins and others 2000; Griffith and others 2002; Allan 2004; Stevenson 2006). The Redfield ratio (atomic TN/TP = 16; Redfield 1958) has historically been accepted as an ideal nutrient balance for algal growth and has been supported by both laboratory (Dodds and Priscu 1990) and stream studies (Smith 1982). Nitrogen limitation can occur at TN/TP ratios less than 20, while phosphorous limitation is possible when the ratio of TN/TP is greater than 40. Using these guidelines, the TN/TP ratios observed in this study could imply that algal growth in the drift plain streams may be nitrogen-limited, but phosphorous-limited in the till plain. Both nitrogen and phosphorous can be limiting nutrients in freshwater systems and lead to eutrophication. Excessive algal blooms can have consequences ranging from mere aesthetics to the production of toxic metabolites (Dodds and Welch 2000) and impairments to other biota (Miltner and Rankin 1998).

The Ohio Environmental Protection Agency (OEPA) established empirical models for examining relationships between biotic assemblages, including benthic invertebrates and fish, and in-stream nutrients, based on monitoring data from 1,650 streams (Miltner and Rankin 1998). Using the OEPA models, 82% of the drift plain streams were below the 50th percentile of Ohio headwater drainage for both NN and TP concentrations (1.37 and 0.17 mg/l, respectively; data not shown). In the till plain region, all the streams were below the 50th percentile for TP, and 40% were below the 25th percentile (0.06 mg/l; data not shown). For NN, only 12% of till plain streams were below the 75th percentile (3.61 mg/l) and 88% of these streams approached or exceeded the 90th percentile concentration (7.71 mg/l).

While there is uncertainty in these patterns, as stream nutrients are typically covariant with other influences on aquatic organisms, such as canopy cover (i.e., temperature and light), fine sediments, other habitat measures, and flow regimes (Miltner and Rankin 1998; Griffith and others 2009), the OEPA models provide perspective on the potential biological significance attributable to the nutrient levels seen in this study. The OEPA models suggest that based only on the effects of nutrients, better fish and macroinvertebrate assemblage scores could generally be predicted for the drift plain streams (Miltner and Rankin 1998). Further, the observed inter-regional differences in nutrient concentrations (and corresponding consequences to stream biota) would likely increase, if row crop operations in the basin were intensified for the production of biofuels (Hill and others 2006).

Analysis of the biotic assemblages (i.e., periphyton, benthic macroinvertebrates, and vertebrates) present in the LMR streams is on-going in our laboratory. Using path analysis to distinguish the direct versus indirect effects of nutrients on these streams, several periphyton metrics, including total algal biomass and relative abundance of cyanobacteria, have recently been found to be correlated with TN, while others, such as the relative abundance of Chlorophyta, were found to be correlated with TP (Griffith and others 2009).

Lastly, it is noted that the entire LMR basin, both the till and drift regions, lie within USEPA's Nutrient Region VI (USEPA 2000). One interpretation of the data presented herein could be that stream baseflow nutrient status may vary in a biologically significant manner over spatial scales considerably smaller than those proposed for the development of water quality criteria.

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