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ESTIMATION OF NONPOINT SOURCE NITRATE CONCENTRATIONS IN INDIANA RIVERS BASED ON AGRICULTURAL DRAINAGE IN THE WATERSHED[1]

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ABSTRACT: Subsurface tile-drained agricultural fields are known to be important contributors to nitrate in surface water in the Midwest, but the effect of these fields on nitrate at the watershed scale is difficult to quantify. Data for 25 watersheds monitored by the Indiana Department of Environmental Management and located near a U.S. Geological Survey stream gage were used to investigate the relationship between flow-weighted mean concentration (FWMC) of nitrate-N and the subsurface tile-drained area (DA) of the watershed. The tile DA was estimated from soil drainage class, land use, and slope. Nitrate loads from point sources were estimated based on reported flows of major permitted facilities with mean nitrate-N concentrations from published sources. Linear regression models exhibited a statistically significant relationship between annual/monthly nonpoint source (NPS) nitrate-N and DA percentage. The annual model explained 71% of the variation in FWMC of nitrate-N. The annual and monthly models were tested in 10 additional watersheds, most with absolute errors within 1 mg/l in the predicted FWMC. These models can be used to estimate NPS nitrate for unmonitored watersheds in similar areas, especially for drained agricultural areas where model performance was strongest, and to predict the nitrate reduction when various tile drainage management techniques are employed.

(KEY TERMS: agricultural nitrate; nonpoint source; tile drainage; regression model.)

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INTRODUCTION

Subsurface tile drainage, a common practice on poorly drained agricultural soils in the Midwest, is known to be an important contributor to the high nitrate load coming from the Mississippi River (Mitsch *et al.*, 2001; USEPA, 2007; Randall and Goss, 2008), which is considered the primary cause of large hypoxic zones (Scavia and Donnelly, 2007). Tile drainage changes the balance among different flow paths increasing infiltration, and lowering surface runoff and erosion (Skaggs and van Schilfgaarde, 1999). Subsurface drains can act as conduits and allow rapid movement of the nitrate into surface water (Haag and Kaupenjohann, 2001), increase nitrate loss by reducing denitrification in soils and the chance for interaction with riparian areas (Gilliam *et al.*, 1999; Sprague and Gronberg, 2012).

At the field scale, flow-weighted mean concentration (FWMC) of nitrate-N in tile drainage studies of the Midwest is often above 10 mg/l, the U.S. Environ-

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mental Protection Agency (USEPA) drinking water standard. For instance, Kladivko *et al.* (2004) found the FWMC ranged from 8 to 28 mg/l in southeastern Indiana; Baker *et al.* (2006) reported nitrate-N concentrations varying from 5 to 13 mg/l in central Indiana; Hernandez-Ramirez *et al.* (2011) indicated the long-term flow-weighted mean nitrate-N ranged from 6.2 to 17.3 mg/l. In Illinois, Gentry *et al.* (2000) observed that the nitrate FWMC ranged from 8.3 to 14.9 mg/l in drainage water from a corn/soybean field. In Minnesota, the average nitrate-N was reported to be around 28 mg/l (Randall *et al.*, 1997), and similar drainage studies in Iowa have shown nitrate concentration in drainage water was between 8.6 and 29.3 mg/l (Jaynes *et al.*, 1999).

Although the nitrate loss from tile drains has been fairly well studied at the field scale, less is known about its influence at the watershed scale. A watershed is a complex system with many flow paths including surface runoff, tile flow, subsurface lateral flow, and percolation to groundwater; and it is difficult to measure the water quality impacts of each flow path. Determining the percentage of nitrate in a stream or river that originally flowed through tile drains would be useful in improving understanding of the role that artificial drainage plays in these agricultural watersheds. The percentage of nitrate originating from tile drains could also be used to improve estimates of the potential impact of best management practices for tile drain management, such as drainage water management or woodchip bioreactors, on watershed-scale nitrate loss. A relationship that predicts nitrate loads from tile drain percentage could be used in providing a first estimate of loads as required for USEPA-funded watershed-based plans.

Numerous statistical studies have been conducted to determine the influence of land use and specific agricultural practices such as fertilizer application on nitrogen loads at the watershed scale. Nonlinear models have been developed to predict watershed nitrate-N yield in terms of land use (Tong and Chen, 2002); percent cropland (Crumpton *et al.*, 2006); applied fertilizer, atmospheric deposition, point sources, and basin attributes (Grizzetti *et al.*, 2005); runoff, fertilizer, animal waste, atmospheric N, and population (Booth and Campbell, 2007); area in corn, fertilizer application, soil hydrologic group, and population density (Mueller *et al.*, 1997), all without explicitly examining tile drainage as an influencing factor. Only a few published studies have been identified that included tile drainage in the regression. Spahr *et al.* (2010) included tile drainage as a binary explanatory variable and found it a significant predictor in modeling flow-weighted mean annual total nitrogen concentrations in United States (U.S.) streams. David *et al.* (2010) included tile drainage from estimates at the county scale, along with flow, N consumed by humans (which is an indicator of sewage effluent inputs), and fertilizer use, and they found tile drainage percentages of area explained 17% of the spatial variation in winter/spring Mississippi River Basin nitrate yields. Sprague and Gronberg (2012) found tile drainage percent was positively related to the increasing N export in agricultural watersheds nationwide. SPARROW (SPAtially Referenced Regressions On Watershed attributes), a hybrid statistical and process-based water quality model, also includes a tile-drainage estimate factor (Alexander *et al.*, 2008).

Most studies focused on an annual time scale, while the seasonal loading pattern which is vital for forecasting hypoxia (Royer *et al.*, 2006) has seldom been investigated. Monthly nutrient data are often used to estimate the size of the mid-summer hypoxia zone in the Gulf of Mexico. Turner *et al.* (2006, 2008) estimated the size of the hypoxia zone using May dissolved nitrate plus nitrite flux. Scavia *et al.* (2003, 2004) estimated the size based on May total nitrogen flux delivered to the Gulf. Liu *et al.* (2010) also used May-June total nitrogen loads as the primary driver of summer hypoxia. Nitrate-N loss from tile drains varies seasonally, generally high in spring and low in summer and fall. Timing of drain flow varies across the Midwest, but in Indiana drains generally flow from December to June, with load evenly distributed throughout the winter in the southern part of the state, and with higher loads in late spring further north (Brouder *et al.*, 2005). Because of the influence of tile drains, nitrate-N in streamflow is generally higher during the months of high nitrate-N load from drainage tiles (i.e., winter and spring in Indiana) than at other times of the year, especially in watersheds with a high percentage of drained land. In addition to examining seasonal patterns, newer datasets allow finer spatial resolution of inputs, which may provide more insight.

The objective of this study was to estimate the annual and monthly relationships between subsurface tile drainage and nitrate-N concentration at the watershed scale through statistical analysis on multiple watersheds in Indiana. The portion of Indiana that is tile-drained is among the highest of all states, estimated at approximately 32% by Sugg (2007). Quantifying this relationship may further the understanding of the impact of agricultural drainage practice on water quality and provide a tool for estimating the potential effectiveness of management strategies that reduce field-scale nitrate-N loss to reduce nitrate-N loss at the watershed scale.

METHODOLOGY

Training Watersheds

The Indiana Department of Environmental Management (IDEM) monitors water quality at 163 sites throughout Indiana under the Fixed Station program (IDEM, 2006). Water quality data were obtained from the Assessment Information Management System of IDEM staff (Chuck Bell, 2011, personal communication) and developed into an ArcGIS file geodatabase. Sites were selected based on four criteria: (1) a U.S. Geological Survey (USGS) streamflow station was located within 5 km and on the same stream reach; (2) data were available for both the IDEM station and its corresponding USGS station for at least 10 years; (3) the watershed area was between 100 and 2,500 km^2; and (4) the stream was not highly influenced by point sources or karst topography. Twenty-four Fixed Station sites met all criteria. One additional site monitored by the USGS, Sugar Creek, met the criteria and was included (Table 1). Most of the watersheds have monthly nitrate-N records, although one was monitored only every three months from 1991 to 1998 (MC-18). The Sugar Creek station has two or three nitrate-N samples per month. Daily streamflows were obtained from the National Water Information System (http://waterdata.usgs.gov/nwis).

Potential Drained Area Estimation

The potential tile-drained areas (DA) were estimated based on three criteria, following the method of Ale and Bowling (2010): (1) cropland; (2) soil drainage class is very poorly drained, poorly, or somewhat poorly drained; and (3) slope <4%. The cropland information was obtained from the National Agricultural Statistics Service (http://www.nass.usda.gov), drainage class from the State Soil Geographic Database (http://soildatamart.nrcs.usda.gov), and the slope derived from the National Elevation Data (Gesch, 2007).

The watershed boundary for each gaging station was obtained either from the 10-digit hydrologic unit area (Natural Resources Conservation Service [NRCS] Watershed Boundary Dataset, http://datagateway.nrcs.usda.gov/) if the monitoring site coincided with the hydrologic unit outlet, or by delineating the watersheds in ArcHydro based on National

TABLE 1. Watershed and Station Information.

ID	River	IDEM Station	USGS Station No.	Watershed Area (km^2)	Annual Mean Streamflow (m^3/s)	Data Availability[1] (nitrate-N sample number)
1	Burns Ditch	BD-1	04095090	855	15.4	1994-2011 (247)
2	Big Walnut Creek	BWC-4	03357500	844	11.2	1999-2011 (139)
3	Cedar Creek	CC-6	04180000	699	8.0	1999-2011 (134)
4	Deer Creek	DC5	03329700	710	7.9	1998-2011 (148)
5	Eel River	EEL-38	03360000	2,150	30.2	1991-2011 (139)
6	Eel River	ELL-7	03328500	2,035	24.3	1991-2010 (233)
7	Fall Creek	FC-26	03351500	438	6.4	1999-2011 (136)
8	Little River	LR-7	03324000	681	8.0	1998-2011 (148)
9	Mill Creek	MC-18	03358000	635	8.7	1991-2011 (173)
10	Mississinewa River	MS-36	03326500	1,766	20.7	1991-2011 (234)
11	Mississinewa River	MS-99	03325500	344	4.2	1991-2011 (158)
12	Salamonie River	S0	03324500	1,452	15.2	1991-2003 (139)
13	Salamonie River	S-25	03324300	1,101	12.9	1999-2010 (223)
14	Sugar Creek	SC-39	03339500	1,333	15.1	1999-2010 (141)
15	Sugar Creek	SGR-1	03362500	1,228	16.7	1991-2011 (172)
16	St Mary's River	STM-11	04182000	1,974	12.9	1991-2011 (215)
17	Sugar Creek	NA[2]	03361650	243	3.3	1992-2010 (665)
18	Trail Creek	TC-5	04095380	113	3.2	1997-2011 (228)
19	Tippecanoe River	TR-164	03330241	128	1.3	1998-2010 (104)
20	Vernon Fork Muscatatuck River	VF-38	03369500	513	3.2	1998-2011 (155)
21	Wabash River	WB-409	03323500	1,990	7.0	1991-2003 (139)
22	Wildcat Creek	WC-60	03333700	627	7.8	1991-2011 (237)
23	East Fork Whitewater River	WHE-27	03275600	518	7.0	1991-2011 (179)
24	East Fork Whitewater River	WR-309	03347000	624	7.1	1991-2011 (230)
25	Yellow River	YR-12	05517000	1,127	11.5	1999-2011 (138)

Notes: IDEM, Indiana Department of Environmental Management; USGS, U.S. Geological Survey.
[1]Data availability means both nitrate-N concentration and flow were available.
[2]Station 17 is not monitored by IDEM but rather by the USGS (USGS 03361650).

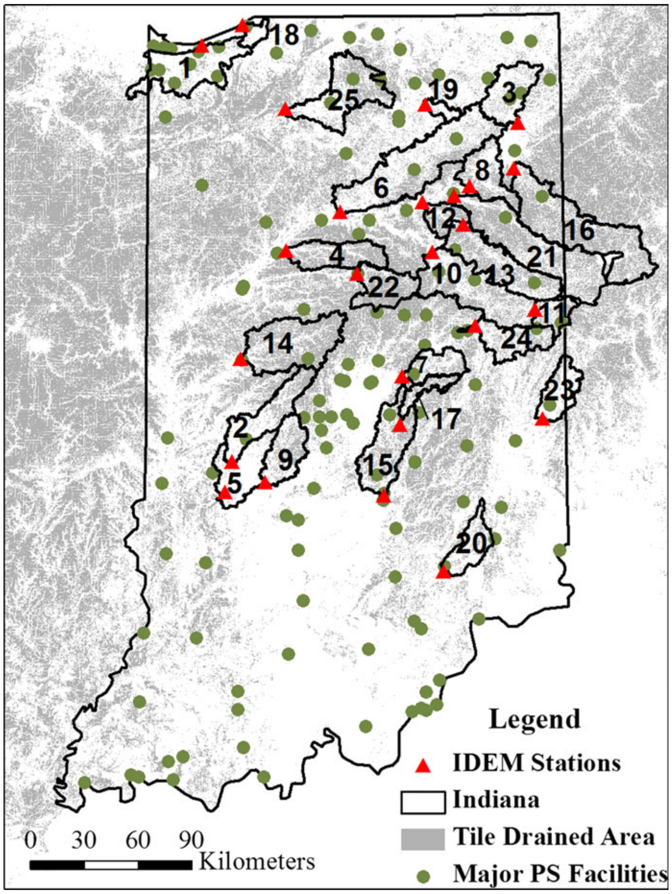

FIGURE 1. Estimated Tile-Drained Area with Delineated Studied Watersheds and Major Point Source Facilities (watershed IDs are explained in Table 1).

Elevation Data (Figure 1). The delineated watersheds and the estimated DA were verified with the USGS published drainage areas.

Monthly and Annual Nitrate-N Load

The analysis was conducted on a monthly as well as an annual basis because the effects of tile drains on nitrate-N concentration in streams or rivers vary widely throughout the year (Brouder *et al.*, 2005; Bakhsh and Kanwar, 2007). The monthly analysis was only appropriate on streams that are unregulated, since reservoirs upstream of the gaging station might reduce the variation in monthly nitrate-N load at the gaging because of the flow detaining effect of the reservoirs. Three monitoring sites, WB-409, S-0, S-25, were considered regulated based on USGS site descriptions. Therefore, 22 watersheds were included in the monthly modeling analysis and 25 watersheds in the annual analysis.

Infrequent sampling limits the accuracy of the load estimation, but the accuracy increases if the best method is used to calculate load. Numerous studies of load estimation uncertainties have found that rating curve estimation methods (e.g., LOADEST) perform poorly for nitrate-N estimation (Guo *et al.*, 2002; Moatar and Meybeck, 2005; Ullrich and Volk, 2007; Birgand *et al.*, 2010, 2011b; Stenback *et al.*, 2011). Two other methods are generally found to give better load estimates for nitrate-N. Birgand *et al.* (2011a, b) found that a method that used only the flow on days when concentration was measured performed better. Moatar and Meybeck (2005), Tiemeyer *et al.* (2010), and Zamyadi *et al.* (2007) indicated estimation of concentration through linear interpolation between measured values gave the best results based on monthly sampling when nutrient concentrations display seasonal variability over the year, and their method was used here. Daily loads calculated from measured flow and interpolated concentration were summed to obtain monthly or annual loads (Equation 1):

$$\mathrm{Load_{Total}} = K \sum\nolimits_{j=1}^{n} C_j Q_j \tag{1}$$

where $\mathrm{Load_{Total}}$ is in kg/month or kg/yr, K is a unit conversion factor, C_j is the daily nitrate-N concentration (mg/l) obtained by linear interpolation between concentration measurements, Q_j is the daily observed streamflow (m^3/s), and n is the number of days in the estimation period. The annual and monthly nitrate-N loads calculated using this method will be referred to as the "observed" load.

Point Source Nitrate-N Load Estimation

To determine the nonpoint source (NPS) nitrate loads, the nitrate-N loads from point sources were estimated and subtracted. This involves considerable uncertainty, because although these facilities are permitted, most are not required to report nitrate-N concentration in their effluent. Effluent flow data for major facilities located within each watershed were obtained from the Integrated Compliance Information System-National Pollutant Discharge Elimination System (ICIS-NPDES) database, accessed through the USEPA, Enforcement and Compliance History Online (ECHO) web site (http://www.epa-echo.gov/echo/compliance_report_water.html). An average nitrate-N concentration of 10.35 mg/l was used based on the typical concentration for municipal wastewater treatment plants that do not have advanced nutrient treatment found by Maupin and Ivahnenko (2011) and nitrate-N concentrations estimated by Carey and Migliaccio (2009). Therefore, in each watershed, the total nitrate-N loads from point sources were calculated by multiplying the annual average effluent and estimated nitrate-N concentration using Equation (2):

$$\mathrm{Load_{PS}} = \sum\nolimits_{k=1}^{K} \sum\nolimits_{i=1}^{n} C \times Q_{k_i} \quad (2)$$

where $\mathrm{Load_{PS}}$ is the total nitrate loads from point sources (kg/month or kg/yr), K is the total number of the major dischargers, n is the days of a month or a year, the C is the average nitrate-N concentration, which is taken as 10.35 mg/l for all point source discharges, and Q_{k_i} is the daily major facility discharge volume.

Among the uncertainties in this estimate is the fact that minor facilities, defined as those that discharge <1 million gallons per day (3,785 m^3/day), were not included. However, Maupin and Ivahnenko (2011) found that minor facilities are responsible for only 13% of nitrogen loads from point sources in the Mississippi River Basin, although they comprise >90% of permitted facilities. To check whether they might be a more important source in small watersheds, the contribution of minor facilities (provided in the ICIS-NPDES database for Indiana, although not for all states) was evaluated for the five smallest watersheds in the study and found to be <1.2% of the nitrate-N load. Although uncertain, point source loads were estimated to be <5% of the nitrate-N load for most watersheds, with an estimated range of 0-34%. The contribution may be underestimated since facility discharge reporting may be incomplete and minor facilities have not been included, but point sources are still likely to be small contributors to nitrate load.

Nonpoint Source Nitrate-N Flow-Weighted Mean Concentration Determination

The estimated point source nitrate-N load was subtracted from the total load in each watershed (from Equation 1) to obtain the NPS nitrate-N load. To better examine the relationship between the nitrate-N loss and tile drainage, the nitrate-N was expressed by the FWMC instead of the load, to reduce the influence of the variation in flow among years, since the years of record were not the same among watersheds. The resulting variable, referred to as the NPS nitrate-N concentration ($\mathrm{FWMC_{NPS}}$) was calculated as shown in Equation (3):

$$\mathrm{FWMC_{NPS}} = \frac{\mathrm{Load_{Total}} - \mathrm{Load_{PS}}}{\sum_{i=1}^{n} Q_i} \quad (3)$$

where n represents the number of days in a month or a year.

Uncertainty of Load and Flow-Weighted Mean Concentration

The uncertainty of nitrate-N loads calculated using the linear interpolation method has been studied, but only on an annual basis. Moatar and Meybeck (2005) indicated the uncertainty in terms of root mean square error (RMSE) ranged from 4 to 6% for a very large (31,000 km^2) watershed in France, and Birgand *et al.* (2011a) reported a 30% RMSE for small (40 km^2) forested or mixed-use watershed (15.3 km^2) in North Carolina.

To assess the uncertainty in both monthly and annual load estimates, an additional analysis was conducted using sub-daily water quality and streamflow data from the National Center for Water Quality Research at Heidelberg College (Richards *et al.*, 2010), the closest available high-resolution data for three watersheds of similar size to the watersheds used in this study for which at least five years of data were available. A bootstrap approach was used to quantify the uncertainty of the monthly FWMC and load estimates calculated using the linear interpolation method and based on monthly samples. Both load and FWMC were calculated for annual and monthly periods. Results of 500 simulations were averaged to represent the long-term uncertainty as a root mean squared error. Since this study used FWMC, the average magnitude of error was also calculated, on both an absolute and relative percentage basis. Details related to uncertainty analysis can be found in Data S1.

Test for Trends in Nitrate-N Concentration over the Period

Because this study uses long-term data, a trend analysis was conducted to determine whether nitrate-N concentrations changed over time, potentially affecting model validity. The Seasonal Mann-Kendall test was used on the monthly mean nitrate-N concentrations of the studied watersheds over the study period using the USGS program described by Helsel *et al.* (2006). Out of the 25 watersheds, no trends were significant at the 95% confidence level for the 15 watersheds. For the ten watersheds that indicated a significant trend, seven slightly decreased and three slightly increased, with only one greater than 0.1 mg/l/yr (Table 2). This test indicates that the trends were small, suggesting that any changes of nitrate-N concentration occurred during the studied period were minor and, therefore, the analysis using long-term data would be valid.

TABLE 2. Seasonal Mann-Kendall Test for the 10 Watersheds with Significant Changes.

ID	IDEM Station	Tau Correlation Index[1]	p-Value[2]	Slope of Trend (mg/l/yr)
2	BWC4	−0.27	0.035	−0.10
3	CC6	−0.15	0.023	−0.03
5	EEL38	−0.25	0.000	−0.06
12	S-0	0.13	0.038	0.08
14	SC-39	−0.18	0.005	−0.13
18	TC-5	−0.15	0.015	−0.02
19	TR-164	0.17	0.005	0.01
23	WHE-27	−0.30	0.000	−0.06
24	WR-309	0.14	0.004	0.04
25	YR-12	−0.15	0.017	−0.07

Notes: IDEM, Indiana Department of Environmental Management.
[1]The Kendall correlation coefficient (Tau) provides a general nonparametric measure of monotonic association. The sign of Tau indicates a decreasing or increasing trend.
[2]p-value corresponds to the confidence level of Tau correlation index.

Statistical Model for Predicting Nonpoint Source Nitrate-N

Subsurface tile drainage from agricultural production systems has been identified as a major source of NPS nitrate entering into surface waters in the Midwest (Mitsch *et al.*, 2001; Randall and Goss, 2008), therefore, tile drainage and cropland area were considered the two most important predictors. The statistical relationship between the NPS nitrate-N FWMC and the percentages of tile-drained land and cropland was explored using general linear model fitting. A range of model combinations and formats, including polynomial regression and multiple linear regression were evaluated based on the goodness of fit (adjusted R^2 and Mallow's Cp) and parameter significance (t-test). Regression diagnostics were performed to examine the residuals and outliers.

Model Testing in Additional Watersheds

The models developed were tested in 10 additional watersheds in Indiana, which were excluded from the original selection either because their watershed scale exceed 2,500 km^2 or the distance between the IDEM station and USGS station is larger than 5 km. However, all the linked IDEM and USGS stations in this study were within 10 km and no major tributaries entered the river between stations. All testing watersheds have no or <50% of area overlapping with the modeled watersheds and their scale ranges from 360 to 6,957 km^2 (Table 3). The testing watershed map can be found in Data S1.

The predicted NPS and total nitrate-N load and FWMC were estimated using the methods described above. Both annual and monthly models developed were compared with observed values. Three statistical criteria, the absolute error (E_{abs}), weighted coefficient of determination (wr^2), and the Nash-Sutcliffe efficiency (E) were used in assessing the prediction of NPS nitrate-N concentrations and total nitrate-N loads. The absolute error (E_{abs}) was calculated as shown in Equation (4):

$$E_{\text{abs}_i} = \text{P}_i - \text{O}_i \tag{4}$$

where P_i and O_i represent the ith predicted and observed values of nitrate-N concentrations or loads averaged over the study period.

Krause *et al.* (2005) developed the weighted coefficient of determination wr^2 (Equation 5), which combined the information of r^2 and slope. This index can avoid the drawback of the coefficient of determination (r^2) that allows a good r^2 (close to 1.0) to be obtained even if a model systematically overpredicts or underpredicts. The value of wr^2 ranges from 0 to positive infinity.

TABLE 3. Watersheds Used for Testing (arranged from lowest to highest drained area percentage).

Site ID	IDEM Station	USGS Station No.	Area (km^2)	Tile-Drained Percentage	Water Body Name	Data Period (number of nitrate-N samples)
T1	LMJ120-0009	04099750	795	8	Pigeon River	1999-2010 (137)
T2	LEJ100-0002	04180500	2,745	21	Saint Joseph River	2001-2010 (100)
T3	WLV190-0012	03341300	1,160	29	Big Raccoon Creek	1999-2010 (138)
T4	LEM010-0014	04183000	5,094	34	Maumee River	1991-2010 (232)
T5	UMK080-0001	05517530	3,564	36	Kankakee River	1999-2010 (135)
T6	WTI150-0011	03333050	4,841	41	Tippecanoe River	1991-2010 (232)
T7	WLV160-0001	03340800	360	44	Big Raccoon Creek	1999-2010 (139)
T8	WUW160-0006	03327500	6,957	47	Wabash River	1991-2010 (230)
T9	WAW050-0005	03335000	2,056	55	Wildcat Creek	1998-2010 (173)
T10	WWU080-0002	03349510	339	75	Cicero Creek	2004-2010 (73)

Note: IDEM, Indiana Department of Environmental Management; USGS, U.S. Geological Survey.

$$\mathrm{w}r^2 = \begin{cases} |\, b \,| \cdot r^2 & \text{for } b \leq 1 \\ |\, b \,|^{-1} \cdot r^2 & \text{for } b > 1 \end{cases} \tag{5}$$

where b represents the slope of a linear regression between modeled and measured values when the intercept is forced to equal 0, and r^2 is the coefficient of determination.

The Nash-Sutcliffe efficiency (E) is a commonly used criterion in assessing hydrologic models. A value close to one indicates a good correspondence between modeled and observed values, while a value lower than zero indicates the model results are worse than those simply using the mean value of the observed time series (see Equation 6).

$$E = 1 - \frac{\sum_{i=1}^{n}(\mathrm{O}_i - \mathrm{P}_i)^2}{\sum_{i=1}^{n}(\mathrm{O}_i - \overline{\mathrm{O}}_i)^2} \tag{6}$$

where O and P represent observed and predicted values, and n represents the total number of examined days.

Modeled Nitrate-N Load

After the coefficients of the regression models were determined, the nitrate-N loads were estimated for the training watersheds, to provide a basis for use in load estimation studies. The normal average monthly/annual flow was available in the USGS Annual Water Data Report (USGS, 2012). Modeled nitrate-N loads from NPS were obtained by multiplying the monthly/annual average flow and estimated NPS nitrate-N FWMC. The same approach was used in the calculations for testing watersheds.

RESULTS

Observed Annual Nitrate-N Loads and Flow-Weighted Mean Concentration

The average annual nitrate-N load in the 25 training watersheds varied from 2.3 to 21.7 kg/ha/yr, with the highest load in watershed 14 and lowest in watershed 19. These values are consistent with the annual nitrate-N yields from the SAB hypoxia report (USEPA, 2007) as 10.7 and 6.4 kg/ha/yr; and 5.9 and 7.2 kg/ha/yr from David *et al.* (2010). The FWMC values are within the range of riverine FWMC of total nitrogen (1-10 mg/l) in Indiana estimated by Spahr

TABLE 4. Drainage Characteristics and Annual Nitrate-N Estimation.

ID	Tile-Drained Area (%)	Crop Land (%)	Point Source Nitrate-N Load (number of major facilities) (Mg/yr)	Nonpoint Source Nitrate-N Load (Mg/yr)	FWMC of Total Nitrate-N (point and nonpoint sources) (mg/l)	FWMC Attributable to Nonpoint Sources (mg/l)	NPS Nitrate-N Load/Total Nitrate-N Load (%)
1	7.1	16.7	316 (7)	510	1.51	0.86	70
2	28.3	50.8	26 (1)	1,194	3.45	3.38	98
3	20.8	46.1	25 (2)	797	3.27	3.07	97
4	65.1	79.6	NM[1]	1,489	5.98	5.98	100
5	24.9	44.9	26 (1)	2,467	2.62	2.59	99
6	26.8	61.3	34 (1)	2,703	3.58	3.53	99
7	36.3	55.5	18 (1)	547	2.81	2.72	97
8	46.0	57.7	NM[1]	1,098	4.33	4.33	100
9	33.6	61.9	NM[1]	1,191	3.54	3.54	100
10	41.4	67.1	50 (3)	2,255	3.75	3.67	98
11	35.8	76.2	14 (1)	485	4.93	4.83	97
12	50.9	68.9	132 (2)	1,505	3.41	3.13	92
13	49.7	70.4	18 (3)	1,405	3.50	3.46	99
14	63.7	77.7	65 (2)	2,891	6.19	6.05	98
15	45.7	60.9	65 (3)	1,523	3.02	2.89	96
16	59.0	68.4	26 (1)	1,987	4.96	4.89	99
17	45.2	70.2	NM[1]	354	3.39	3.39	100
18	8.7	12.6	138 (1)	61	1.97	0.60	31
19	10.1	42.7	NM[1]	30	0.72	0.72	100
20	22.6	33.7	24 (1)	144	1.66	1.42	86
21	52.2	67.4	26	1,224	5.67	5.55	98
22	70.0	76.7	165 (1)	1,317	6.06	5.38	89
23	16.0	43.2	170 (1)	629	3.61	2.83	79
24	33.1	61.8	241 (1)	460	3.15	2.06	66
25	35.7	58.1	44 (2)	1,644	4.66	4.53	97

Notes: FWMC, flow-weighted mean concentration; NPS, nonpoint source.
[1]NM means no major facility in watershed.

et al. (2010), but generally lower than values calculated by the SPARROW Online Decision Support System (http://cida.usgs.gov/sparrow/), which was 2.8-15 m/l for annual total nitrogen FWMC. NPS nitrate-N comprised >80% of total annual nitrate-N loads in 21 of the watersheds, as shown in Table 4. Only one, watershed 18, was dominated by point sources (69% of the total nitrate-N load), and the highest point source load was approximately 316 Mg/yr. Cropland percentages and the corresponding estimated DA percentages are also shown in Table 4. The watersheds with higher percentage of DA generally had higher nitrate-N concentrations. The estimated DA ranged from 7.1 to 70.0%, with the NPS nitrate-N FWMC varying from 0.72 to 6.19 mg/l. These values are less than the FWMC found at the outflow of tile-drained fields (Kladivko *et al.*, 2004; Baker *et al.*, 2006; Hernandez-Ramirez *et al.*, 2011) since the contributions of tile drains are diluted by water from other flow paths.

The nitrate-N variations demonstrated a highly seasonal pattern, as shown in Figure 2 which shows the long-term average FWMC grouped into four categories by the DA percentage (<10, 10-30, 30-50, and >50%). From December to June, when tiles usually flow (Kladivko *et al.*, 2004), concentrations were high and showed a strong dependence on drained percentage. Tile drainage nearly stops in late summer (July to September) and attain maximum values from winter to spring (December to June) when rains move nitrate-N through the soil to rising water tables, and field tile drains transport nitrate-N in soil water and high water tables to streams. This pattern is consistent with other observed patterns of tile drainage flow in the midwestern U.S. (Helmers *et al.*, 2005; Royer *et al.*, 2006; Hernandez-Ramirez *et al.*, 2011). Because of the high seasonal variation, monthly models were developed in addition to the annual model.

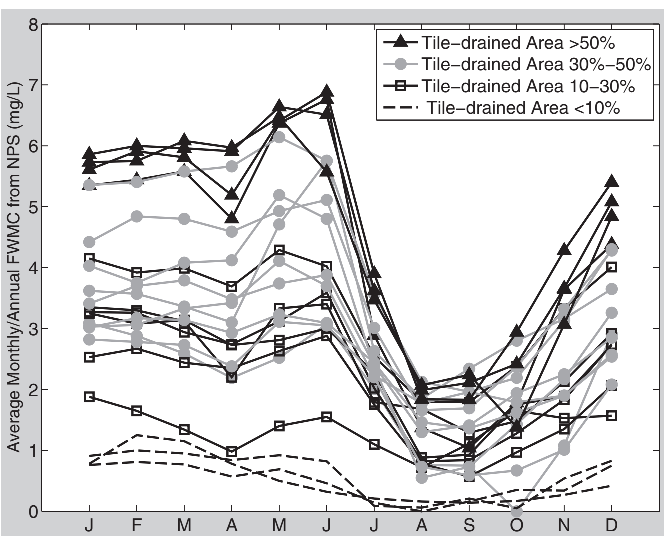

FIGURE 2. Monthly and Annual Flow-Weighted Mean Concentrations (FWMC) of Nitrate-N from Nonpoint Sources (NPS), Symbolized by Tile-Drained Percentage of the Watershed.

Estimated Uncertainty in Calculated FWMC and Load

On the basis of the analysis of Ohio data, the RMSE of annual load estimates was from 11.4 to 15.7%, similar to that found in previous studies. The monthly values were higher, generally ranging from 20 to 40% except for June to August when concentrations had more variability. The estimated average magnitude of relative error in annual FWMC ranged from 9.4 to 21.0%, and the monthly values were somewhat higher than the annual (Table 5). This uncertainty in the dependent variable, FWMC, increases the value of the noise term in the regression models, making it less likely to detect a statistically significant relationship when one exists.

Model Selection and Fitting

Three model candidates examining combinations of DA percentage and percent cropland (Crop) were found to have similar predictive power: the linear regression model (Equation 7), the second-order polynomial model ($FWMC_{NPS} = \beta_0 + \beta_1 \times DA + \beta_2 \times DA^2 + \varepsilon$), and the multiple regression model ($FWMC_{NPS} = \beta_0 + \beta_1 \times DA \times Crop + \varepsilon$). On the basis of the Minimum Message Length theory (Wallace, 2005), if given candidate models are of similar predic-

TABLE 5. Annual and Monthly Uncertainty in Flow-Weighted Mean Concentration (FWMC) Based on Monthly Sampling, for Three Watersheds with Sub-Daily Data.

	Great Miami River		**Cuyahoga River**		**Honey Creek**	
Watershed	**Annual**	**Monthly**	**Annual**	**Monthly**	**Annual**	**Monthly**
Average magnitude of absolute error of $FWMC_{est}$ (mg/l)	0.4	0.3-1.1	0.4	0.3-0.9	0.7	0.7-3.6
Average magnitude of percent error of $FWMC_{est}$ (%)	9.4	10.6-27.3	21.0	19.2-28.6	12.4	12.3-34.9

tive or explanatory power, the simplest model is most likely to be correct. The linear regression model was finally selected, since it balances the need for both goodness of fit and structural simplicity. The model residuals were independent and identically distributed, and the Shapiro-Wilk Normality test (using the Shapiro test function in R) indicated the distribution could be assumed to be normal. The Cook's distance values (using the regression diagnostics function in R) showed that no significant outliers were found. Regression diagnostics can be found in Data S1.

$$\mathrm{FWMC_{NPS}} = \beta_0 + \beta_1 \times \mathrm{DA} + \varepsilon \quad (7)$$

where $\mathrm{FWMC_{NPS}}$ is the flow-weighted mean NPS nitrate-N concentration (monthly or annual); DA represents the drained area percentage; β_0 and β_1 are model regression coefficients; and ε represents the error term. The annual model and all monthly models were statistically significant at 95% confidence level (Table 6). The annual model explained 71% of the variation, and a strong linear relationship between DA and $\mathrm{FWMC_{NPS}}$ was observed in monthly models especially for the winter-spring period (December to June) (see Figure 3).

Model Evaluation

The model was then applied to the 10 test watersheds that were not used in the regression model development. The observed annual average NPS nitrate-N concentrations ranged from 1.74 to 5.56 mg/l (Figure 4) in the test watersheds, and their residuals had no trend with nitrate yields (the term "Observed" NPS nitrate-N FWMC means the value

TABLE 6. Model Regression Coefficients and Goodness of Fit.

	Coefficients			Goodness of Fit	
	Intercept (β_0)	DA (β_1)	p-Value from the t-Test	R^2	Adjusted R^2
Annual	0.67	7.4	1.1×10^{-7}	0.71	0.70
January	0.94	7.2	7.9×10^{-7}	0.71	0.70
February	0.95	7.3	6.2×10^{-7}	0.72	0.71
March	0.78	7.7	6.2×10^{-7}	0.72	0.71
April	0.49	7.7	8.1×10^{-7}	0.71	0.70
May	0.49	9.3	8.3×10^{-7}	0.77	0.76
June	0.56	9.2	2.7×10^{-7}	0.74	0.73
July	0.45	5.0	8.0×10^{-7}	0.71	0.70
August	0.30	2.5	4.5×10^{-4}	0.47	0.44
September	0.34	2.5	7.1×10^{-4}	0.44	0.42
October	0.61	2.6	8.7×10^{-3}	0.30	0.26
November	0.51	4.7	6.9×10^{-5}	0.56	0.53
December	0.79	6.3	3.4×10^{-6}	0.67	0.65

Note: DA, drained area.

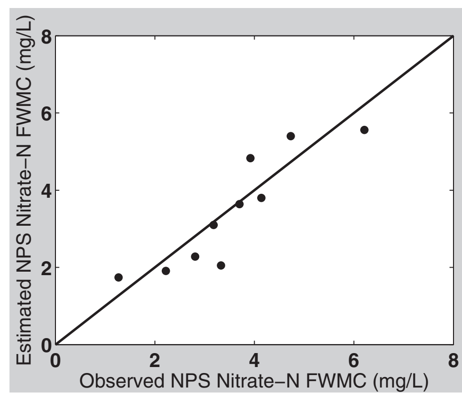

FIGURE 4. Estimated Nonpoint Source (NPS) Annual Average Nitrate-N Flow-Weighted Mean Concentration (FWMC) Compared with Observed Values in Additional Watersheds Used for Testing the Model.

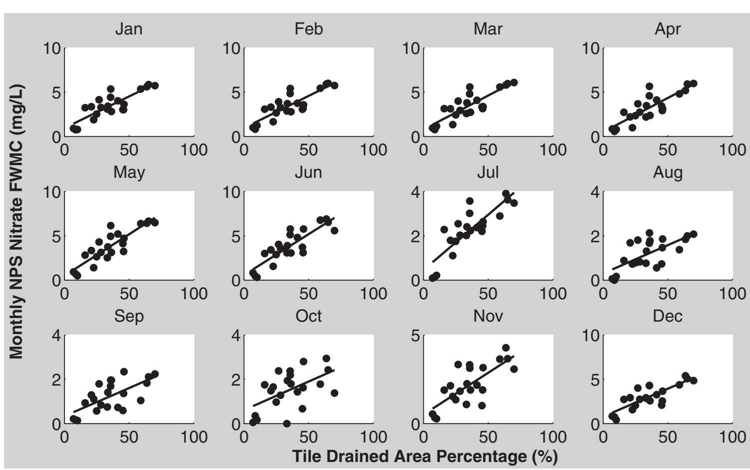

FIGURE 3. Monthly Regression Models.

TABLE 7. Nitrate-N FWMC and Model Evaluation.

ID	Observed Annual Total Nitrate-N FWMC (mg/l)	Modeled Annual NPS Nitrate-N FWMC (mg/l)	E_{abs} of Modeled Annual Total Nitrate-N FWMC (mg/l)	E_{abs} of Annual Estimated Total Nitrate-N Load (Mg/yr)	wr^2 of Modeled Monthly NPS Load/FWMC	E Index of Modeled Monthly Load
T1	1.83	1.27	−0.48	−157	0.47	0.61
T2	1.97	2.22	0.32	304	0.56	0.66
T3	2.34	2.81	0.54	246	0.67	0.60
T4	3.52	3.18	0.09	150	0.62	0.69
T5	2.44	3.33	1.29	1,726	0.31	0.61
T6	3.68	3.70	0.06	108	0.50	0.71
T7	4.83	3.92	−0.91	−121	0.67	0.82
T8	3.90	4.14	0.34	787	0.59	0.68
T9	5.43	4.73	−0.67	−4,802	0.70	0.87
T10	5.67	6.21	0.65	100	0.71	0.67

Note: FWMC, flow-weighted mean concentration; NPS, nonpoint source.

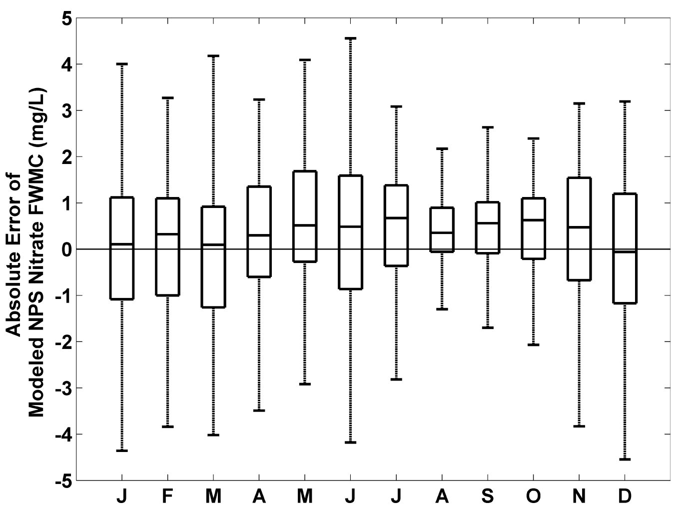

FIGURE 5. Absolute Error of Monthly Modeled Nonpoint Source (NPS) Nitrate-N Flow-Weighted Mean Concentration (FWMC) (80-128 samples were included for each month, box plots illustrate the 25th, 50th, and 75th percentiles; whiskers indicate the 5th and 95th percentiles).

calculated by subtracting calculated point source load from the total load). The absolute error (E_{abs}) of modeled annual NPS nitrate-N FWMC ranged from −0.91 to 1.29 mg/l (Table 7). For the monthly models, the weighted coefficient of determination (wr^2) ranged from 0.50 to 0.93, showing a reasonably good fit of modeled monthly concentrations and observations. The Nash-Sutcliffe efficiency (E) of monthly modeled concentration was relatively low. However, when multiplying by streamflow and calculating the monthly loads, E was significantly enhanced (ranging from 0.61 to 0.87).

The absolute errors (E_{abs}) of modeled nitrate-N concentration summarized based on months show the variability over time (Figure 5). Generally, the 25th and 75th percentile E_{abs} were within ±1 mg/l, except for June, November, and December. Overpredictions were more common than underpredictions.

To further evaluate the model for different drainage percentages over time, the model output and observations were plotted and compared for three selected sites (Figure 6). The model tended to better capture the loading patterns in medium and highly drained watersheds, as the weighted r^2 shows. In a less drained watershed (site T2, 21% drained), the model failed to capture the flux peaks. In a moderately drained watershed (site T7, 44% drained), the model performed well although slightly underestimating the high flow events. The model prediction was strongest in the highly drained site T10 (75% drained), although a significant underprediction was observed in January 2005 when high streamflow occurred with an observed monthly nitrate-N concentration of 2.2 mg/l, which is much lower than the modeled value 6.8 mg/l. A similar high flow event and underprediction was also observed in June 2010.

Modeling Nitrate-N Load

The model developed for these 22 watersheds was then extended to predict monthly average FWMC for any Indiana watershed based on the percentage that is tile-drained. The NPS nitrate-N concentrations increased significantly with increasing tile DA, as shown in Figure 7. These estimates of FWMC can be used for any watershed in Indiana or similar areas if the percentage of tile drainage can be estimated.

Making estimates of nitrate-N load rather than FWMC is less straightforward, as streamflow varies by year, by region, and for each watershed. Using the range of unit streamflow among all the investigated basins (annual average streamflow divided by watershed area), a likely range of nitrate-N load is shown in Table 8.

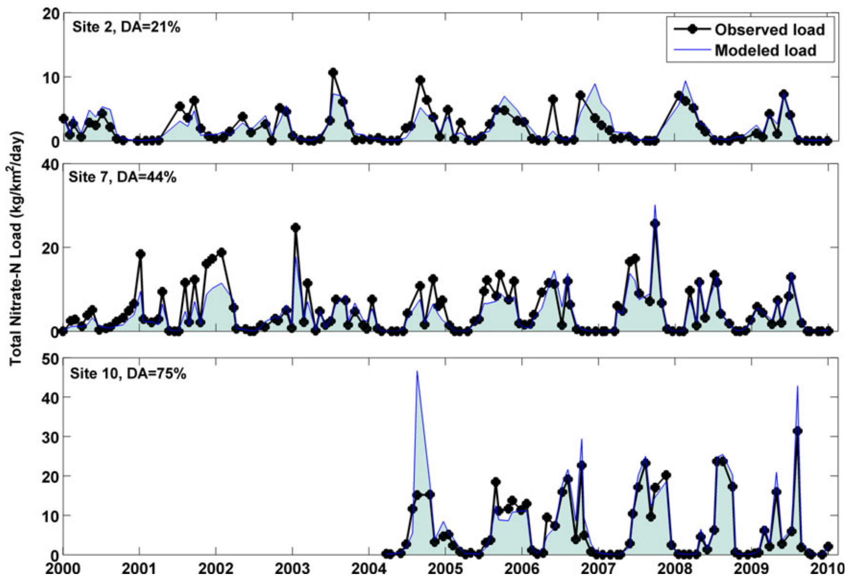

FIGURE 6. Observed (circle lines) and Modeled (shaded area) Nitrate-N Load for Selected Datasets.

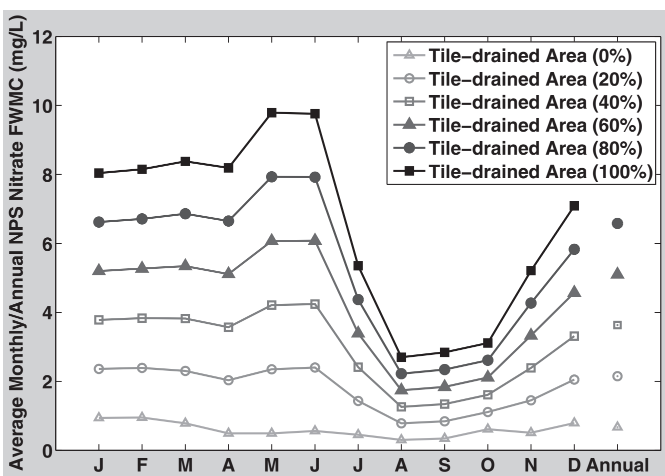

FIGURE 7. Modeled Average Monthly/Annual Nitrate-N Flow-Weighted Mean Concentration (FWMC) from Nonpoint Source (NPS) for Various Percentages of Drained Area.

The portion of nitrate-N flux that could be attributed to tile drainage was also investigated by subtracting an assumed background nitrate-N from the estimated total NPS nitrate-N concentration. The NPS nitrate-N concentration from the case of no tile drainage (DA = 0%) in the annual regression model was used as the background (0.67 mg/l). This intercept parameter (β_0) was not significant in the models, which was one source of uncertainty in this assumption. Another is that the observed range of DA used in model development was 8% to 75%, so predictions for watersheds with >75% DA may not be reliable. Other studies have found that nitrate-N background concentration varies based on the regional conditions of soil, climate, land use, nitrogen storage, and other factors. Helsel (1995) found a background nitrate-N concentration of 0.7 mg/l for the forested streams, Dubrovsky and Hamilton (2010) used a background concentration for total nitrogen of 0.58 mg/l in studying the national riverine nutrients, and Hubbard *et al.* (2010) observed that the background nitrate-N concentration ranged from 0.17 to 1.30 mg/l in studying the nitrate-N dynamics of a third-order stream in Wyoming. Although highly uncertain, the background concentration of 0.67 mg/l is consistent with these

TABLE 8. Annual Nitrate-N Yield Prediction for Different Drained Area Percentages Based on the Annual Tile Drainage Model.

Drained Area Percentage		**0%**	**20%**	**40%**	**60%**	**80%**	**100%**
Predicted annual nitrate-N FWMC (mg/l)		0.67	2.15	3.63	5.10	6.58	8.05
Estimated NPS nitrate-N yield (kg/ha/yr)	Min (lowest flow year)	0.7	2.4	4.0	5.7	7.3	8.9
	Mean (mean flow year)	2.5	8.1	13.6	19.1	24.7	30.2
	Max (highest flow year)	4.4	14.2	23.9	33.6	43.4	53.1
Potential percentage of NPS nitrate-N load from tile drains (%)		0	69	81	87	90	92

Note: FWMC, flow-weighted mean concentration; NPS, nonpoint source.

other estimates and was used for estimating the potential percentage of NPS nitrate-N at the watershed scale that could be attributed to tile drainage, also shown in Table 8.

SUMMARY AND DISCUSSION

This article examined the statistical relationship between subsurface tile drainage and nitrate-N concentrations in watersheds across Indiana. The results indicate that a strong linear relation exists between the flow-weighted nitrate-N concentration from NPS and tile DA percentage. The relation is strong for the annual model and for monthly models from December to July. It is weaker but still statistically significant from September to October when the drain flow is low. On the basis of the relationship determined in this study, the watershed-scale NPS nitrate-N load can be estimated based only on the percent of drained land in the watershed.

There are many uncertainties in the model, including the fact that only one factor was included in the regression, and that other NPSs such as atmospheric deposition also contribute to nitrate-N loads but were not included. Other studies have used annual flow or other additional variables in the regression models, which resulted in a stronger correlation coefficient but required more inputs that may not be available. In addition, the model is also limited by the uncertainty in the nitrate-N load estimates, due both to the infrequent (mostly once per month) sampling, and to the uncertainty of the measurements processes. Harmel *et al.* (2006) found that estimated uncertainty from the cumulative effects of measurement error is likely ranging from 8 to 69% for small watersheds. The point source estimates were limited by the fact that effluent concentrations for nitrate-N were based on literature values since measured information is rarely available from permitted facilities. These different sources of uncertainty could lead to estimation biases in FWMC and also could diminish the significance of the linear relationship.

These predictions could be used as a simple yet effective tool to estimate nitrate-N concentrations in unmonitored watersheds in Indiana and similar areas. If the estimated concentrations are converted to loads, they can be compared with target nitrate-N loads to provide a basis for estimating the amount and type of conservation activities needed to achieve water quality goals.

SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

Data S1. Uncertainty analysis, regression diagnostics, and testing watersheds map.

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