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Use of water quality surrogates to estimate total phosphorus concentrations in Iowa rivers

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ABSTRACT

Study region: The study was focused on total phosphorus (TP) concentrations measured in rivers in Iowa, a Midwestern state located in the central United States.

Study focus: Accurate measurement of TP concentrations in rivers is needed to quantify loads and evaluate the progress of nutrient reduction strategies. We evaluated the relation of water quality surrogates, turbidity, orthophosphorus (OP), chlorophyll a, chloride and discharge to TP concentrations at 43 different river monitoring sites over a 15-year period.

New hydrological insights for the region: TP concentrations were highly correlated to turbidity (0.78 ± 0.20) and OP (0.69 ± 0.13) across all sites and less correlated to chlorophyll a (0.07 ± 0.15), chloride (−0.10 ± 0.24) and discharge (0.41 ± 0.23). When the regression models included OP as a variable, the mean r^2 for all 43 sites was 0.90 ± 0.08 and ten of the 43 sites had r^2 values greater than 0.95. When OP was excluded in the regression model, the overall mean r^2 values decreased to 0.72 ± 0.14 and for six of the river sites, the r^2 value decreased by 50%. Other variables (discharge, chlorophyll a, chloride) were included in the regression equations on a case-by-case basis. Including OP in the regression models was critically important for rivers draining the tile-drained Des Moines Lobe region.

1. Introduction

Nutrient enrichment of rivers and streams from excessive nitrogen (N) and phosphorus (P) concentrations and loads is impacting local and regional water bodies in the United States (Russell et al., 2008; Turner et al., 2008) and around the world (Diaz, 2001). In response to Mississippi River hypoxia and the need to achieve a 45% reduction in nitrogen and phosphorus delivered to the Gulf of Mexico (USEPA, 2008), states of the Upper Mississippi River Basin (UMRB) are developing strategies focused on prevention of nutrient transport to the region's streams (e.g., Iowa (INRS, 2013), Ohio (ONRS, 2013), Illinois (INLRS, 2014) and Minnesota (MNRS, 2014). An important factor in evaluating the progress of nutrient reduction strategies is being able to accurately quantify nutrient loads. Stakeholders, such as state and federal agencies, agricultural interests, environmental organizations, are asking that progress toward achieving reductions be quantified on a regular basis.

Quantifying nitrate-nitrogen reductions in Midwestern rivers is relatively straightforward since nitrate concentrations can be adequately characterized by regular grab sampling (Jiang et al., 2014; Tiemeyer et al., 2010) or with the use of NO_3-N sensors (Davis et al., 2014; Feng et al., 2013). In contrast, total phosphorus (TP) concentrations and loads are difficult to measure with much certainty. TP includes both the P attached to soil particles and soluble P present in water (typically orthophosphorus or OP). TP

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concentrations change rapidly with discharge (Quilbé et al., 2006; Johnes, 2007; Dermars et al., 2005), and grab sampling is often not sufficient to capture the variability in TP concentration patterns (Jones et al., 2012). Sensor technology has not been developed yet to measure continuous TP concentrations in rivers (Warwick et al., 2013). Methods are needed to assist with estimation of TP concentrations in streams that bridge the gap between periodic grab sampling typically used at most sites today and continuous sensor measurements that may be developed at some point in the future.

Surrogates have potential utility in estimating chemical concentrations in rivers when high frequency measurements of commonly measured water quality parameters are related to the chemical of interest. For example, turbidity has been utilized as a surrogate to estimate total suspended sediment (TSS) concentrations in rivers (e.g., Gippel, 1995; Grayson et al., 1996; Christianson et al., 2002; Tomlinson and De Carlo, 2003; Jones and Schilling, 2010; Rügner et al., 2013). Turbidity refers to the measurement of the optical scattering of light passing through a water sample due to suspension of colloidal or suspended particles in the water. Rügner et al. (2013) compiled literature on TSS-turbidity measurements and found a linear relationship showing that 1 NTU (Nepheolmetric Turbidy Unit) corresponded to approximately 1–2 mg/l suspended solids, although the relation of TSS to turbidity can be site-specific (Grayson et al., 1996; Christianson et al., 2002; Tomlinson and De Carlo, 2003) and dependent on the source of sediment (Gippel 1995). Turbidity has also shown promise as a surrogate for TP concentrations in natural and agricultural watersheds (Grayson et al., 1996; Kronevang et al., 1997; Stubblefield et al., 2007; Jones et al., 2011). Among the first to report on the relation, Grayson et al. (1996) found that turbidity explained 70–90% of the variation in TP concentration in one rural Australian watershed. The relation of turbidity to TP may be more complex in urban watersheds due to additive factors associated with urban stormwater sources (Viviano et al., 2014). Nonetheless, researchers have found statistically significant correlations between TP and turbidity in a wide range of watersheds with different characteristics and differing turbidity and TP values (Jones et al., 2011).

Most of the research documenting the use of surrogates to estimate TP concentrations have focused on a small number of intensely monitored sites for limited time periods. For example, Grayson et al. (1996) evaluated the relation of TP to turbidity in one 5000 km^2 watershed for three different months over two years and Stubblefield et al. (2007) focused on a spring snowmelt period in two < 30 km^2 subalpine watersheds for a three year period. More recently, Jones et al. (2011) evaluated two locations within the 740 km^2 Little Bear River watershed in Utah for a 2.5 year period. In this study, we expanded the assessment by evaluating the relation of water quality surrogates to TP concentrations at 43 different river monitoring sites in Iowa over a 15-year period. In addition to using turbidity, our study included OP, chlorophyll a, chloride and discharge as potential surrogates. Each of these potential surrogates are capable of being monitored continuously in rivers with sensors and thus could be deployed in the future to help estimate river TP concentrations.

The objectives of our study were to: 1) evaluate the relation of TP concentrations to individual water quality surrogates at 43 river monitoring sites in Iowa; 2) develop a regression model using combined surrogates that best estimates TP concentrations in various Iowa rivers; and 3) assess the similarities and differences among the various river-specific models based on watershed and ecoregion characteristics to gauge the suitability of using surrogates to estimate TP concentrations in Iowa rivers.

2. Methods and materials

2.1. Monitoring data

TP concentrations and other water quality surrogates were measured at an approximate monthly frequency at 43 ambient river monitoring sites located across Iowa (Fig. 1). Although monthly measurements are not ideal to characterize a parameter like TP that varies during hydrologic events, this sampling frequency was established by the Iowa Department of Natural Resources for their ambient river monitoring program. At all monitoring sites, this scheduled sampling frequency ensured that considerably more samples were collected during low to medium flow conditions than during occasional high flow conditions. All the ambient monitoring sites evaluated in this study were specifically located to be beyond the extent of urban areas when the statewide ambient program was established (IDNR, 2000), although this has not been verified with field studies. There were occasional months of missing data, but the sample size ranged from approximately 81–147 for all river monitoring sites.

The surficial geology of Iowa is dominated by Pleistocene glacial deposits consisting of fine-textured glacial till and loess of varying ages (Prior, 1991). The Wisconsin-age Des Moines Lobe represents the most recent glacial advance into Iowa around 12,000 years ago (Fig. 1). The low-relief topography of the Des Moines Lobe region stands in contrast to hillslope dominated terrain found throughout the state. The average watershed area for the 43 sites was approximately 3000 km^2 and areas ranged from 89 km^2 (Bloody Run) to 20,155 km^2 (Cedar River at Conesville) (Table 1).

All surface water samples were collected as unfiltered grab samples at fixed monitoring sites following an EPA-approved Quality Assurance Project Plan. All samples were analyzed by the State Hygienic Laboratory using EPA-approved standard methods. Sample collection methods and laboratory analytical procedures were unchanged during the monitoring period. All water quality data were obtained from the Iowa Department of Natural Resources Iowa STORET/WQX Water Quality Database (https://programs.iowadnr.gov/iastoret/). Stream discharge data was obtained from U.S. Geological Survey gages that are co-located with the Iowa DNR monitoring sites.

2.2. Statistical methods

We used Pearson correlation analysis (SPSS 21.0) to evaluate the degree of correlation between TP concentrations and water quality surrogates (OP, turbidity, chlorophyll A, chloride and discharge). Multiple linear regression was then used to develop an

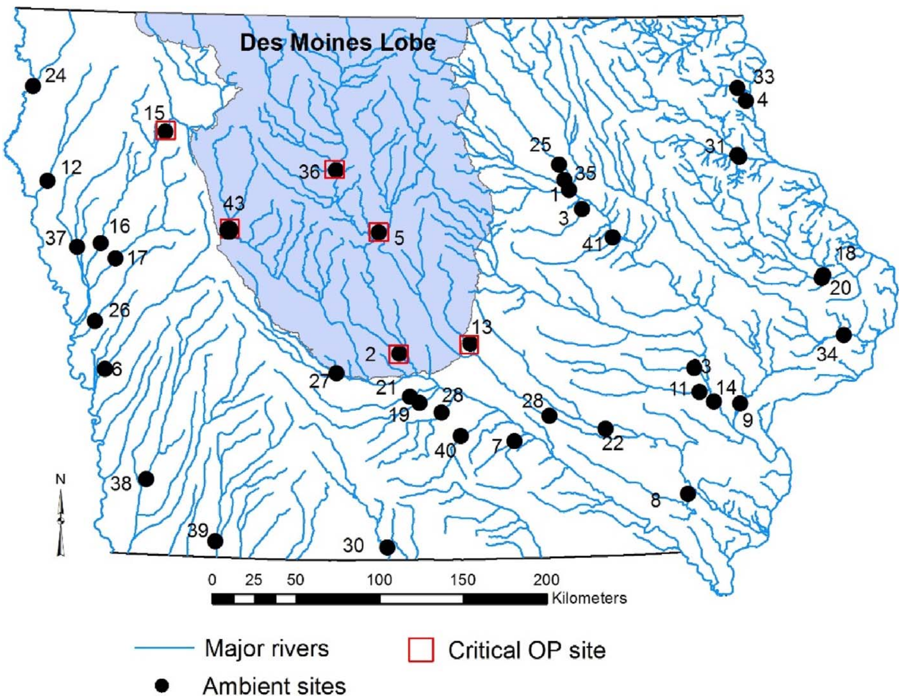

Fig. 1. Location of river monitoring sites evaluated in this study and identification of those sites where OP was critically important for estimation of TP concentrations. Numbers correspond to site locations in Table 1.

equation for each ambient river monitoring site that best estimated TP concentrations at a site using the surrogate variables. Stepwise procedures (SPSS 21.0) were used that added or removed variables in the model according to their significance in the presence of the other variables. The final selection of a regression model explained the most variability in TP concentration with the fewest number of explanatory variables (Schilling and Wolter, 2005).

The general form of multiple regression is:

$$Y_{predicted} = \alpha + \beta_1{*}X_1 + \beta_2{*}X_2 + \beta_3{*}X_3 + \cdots\cdots + \beta_k{*}X_k$$

where, $Y_{predicted}$ is the predicted value of the dependent variable Y, α is the constant or Y intercept, $\beta_1 - \beta_k$ are the slope coefficients and $X_1 - X_k$ are independent variables that explain or predict the variance in Y. Root mean square error (RMSE) is frequently used to evaluate the difference between values predicted by a model and measured values. The RMSE of a model prediction with respect to the estimated variable X model is defined as the square root of the mean squared error:

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{n} (X_{obs,i} - X_{pre,i})^2}{N}}$$

where, N is the number of samples, X_{obs}, i is observed TP concentrations and $X_{pre,i}$ is predicted TP concentrations at time i.

3. Results

3.1. TP concentrations

Mean TP concentrations across the 43 rivers ranged from 0.09 to 0.65 mg/l from 2000 to 2015 (Fig. 2) with concentrations generally higher in western Iowa rivers than those in eastern Iowa. In western Iowa rivers, mean TP concentrations tend to be greater than 0.3 mg/l, as typified by the Boyer River (0.65 mg/l, No. 6), Floyd River (0.62 mg/l, No. 12) and West Nishnabotna River (0.38 mg/l; No. 38). Eastern Iowa rivers typified by Bloody Run Creek (0.09 mg/l, No. 4), Upper Iowa River (0.16 mg/l, No. 32) and Volga River (0.17 mg/l, No. 33) tend to be less than 0.2 mg/l. However, TP concentrations greater than 1 mg/l were occasionally measured at all sites (Fig. 2).

3.2. Correlation of TP concentrations to individual surrogates

TP concentrations were best correlated to turbidity compared to other water quality surrogates (Fig. 3) with a mean correlation coefficient of 0.78 ± 0.20 and a range of 0.2–0.96 (Table 1). Approximately one-third of the monitoring sites (14 of 43) had correlation coefficients greater than 0.9 for turbidity, whereas five sites (12%) had coefficients less than 0.5. OP concentrations were

Table 1
Summary of 43 river monitoring stations evaluated in this study and the correlation of various surrogates to TP concentrations.

No.	STORET Number	Station Name	Water-shed area (km^2)	n	Correlation with TP concentrations				
					Turbidity	Chl a	Cl	OP	Dis-charge
1	10070001	Beaver Creek (Cedar Falls)	1021	133	0.86	0.00	0.05	0.75	0.54
2	10770001	Beaver Creek (Grimes)	957	138	0.60	0.01	0.22	0.86	0.39
3	10070004	Black Hawk Creek (Waterloo)	845	147	0.87	0.05	-0.21	0.63	0.60
4	10220003	Bloody Run Creek Site #1 (BR01)	89	125	0.45	0.07	0.05	0.71	-0.03
5	10400001	Boone River (Stratford)	2299	122	0.61	0.07	0.13	0.84	0.33
6	10430001	Boyer River (Missouri Valley)	2357	134	0.24	0.07	0.32	0.71	-0.21
7	10630002	Cedar Creek (Bussey)	963	122	0.96	0.10	-0.01	-	0.58
8	10440001	Cedar Creek (Oakland Mills)	1381	132	0.73	0.15	-0.18	0.74	0.33
9	10700001	Cedar River (Conesville)	20155	123	0.20	0.44	0.46	0.27	-0.13
10	10090001	Cedar River (Janesville)	4329	103	0.83	0.05	-0.41	0.61	0.56
11	10920001	English River (Riverside)	1624	129	0.90	0.07	-0.12	0.64	0.52
12	10750001	Floyd River (Sioux City)	1624	144	0.39	0.07	0.27	0.63	-0.15
13	10500001	Indian Creek (Colfax)	1026	134	0.51	0.12	0.09	0.75	0.24
14	10580002	Iowa River (Lone Tree)	11104	93	0.68	0.04	-0.16	0.70	0.27
15	10180001	Little Sioux River (Larrabee)	4801	101	0.85	0.33	-0.40	0.59	0.34
16	10970001	Little Sioux River (Smithland)	6944	102	0.95	0.01	-0.40	0.52	0.59
17	10670002	Maple River (Mapleton)	1669	126	0.94	0.06	-0.24	0.79	0.56
18	10490002	Maquoketa River (Maquoketa)	2478	82	0.92	0.01	-0.07	0.70	0.74
19	10910001	Middle River (Indianola)	1267	116	0.93	0.23	-0.54	0.78	0.49
20	10490001	North Fork Maquoketa River (Hurstville)	1527	135	0.88	0.16	0.12	0.82	0.50
21	10910002	North River (Norwalk)	905	119	0.75	0.08	0.14	0.69	0.41
22	10540001	North Skunk River	1650	125	0.95	0.11	-0.46	0.63	0.51
23	10520001	Old Mans Creek (Iowa City)	522	120	0.76	0.09	0.15	0.80	0.43
24	10840001	Rock River (Hawarden)	4369	107	0.92	0.01	-0.40	0.77	0.51
25	10120001	Shell Rock River (Shell Rock)	4484	95	0.80	0.15	-0.38	0.73	0.61
26	10430002	Soldier River (Pisgah)	1057	124	0.96	0.13	-0.39	0.73	0.25
27	10250001	South Raccoon River (Redfield)	2539	111	0.83	0.02	-0.05	0.72	0.56
28	10910003	South River (Ackworth)	1229	95	0.90	0.06	-0.03	0.67	0.58
29	10620001	South Skunk River (Oskaloosa)	4248	133	0.78	0.10	-0.11	0.53	0.39
30	10270001	Thompson Fork (Davis City)	1801	82	0.96	0.12	-0.24	0.65	0.68
31	10220001	Turkey River (Garber)	4023	101	0.92	0.15	-0.14	0.82	0.60
32	10030001	Upper Iowa River (Dorchester)	1988	81	0.86	0.25	0.03	0.71	0.60
33	10220002	Volga River (Elkport)	1043	102	0.91	0.32	0.01	0.79	0.68
34	10820001	Wapsipinicon River (De Witt)	6047	80	0.89	0.40	-0.26	0.55	0.31
35	10070003	West Fork Cedar River (Finchford)	2203	111	0.84	0.10	-0.25	0.74	0.50
36	10460001	West Fork Des Moines River Humboldt)	6017	96	0.82	0.43	-0.46	0.48	0.30
37	10970002	West Fork Ditch (Hornick)	1042	131	0.96	0.04	0.09	0.78	0.48
38	10650001	West Nishnabotna River (Malvern)	2509	124	0.83	0.18	-0.16	0.40	0.64
39	10730001	West Nodaway River (Shambaugh)	2047	127	0.85	0.14	-0.18	0.69	0.61
40	10630003	Whitebreast Creek (Dallas)	931	58	0.89	0.10	-0.38	0.59	0.14
41	10070002	Wolf Creek (La Porte City)	844	112	0.82	0.04	0.00	0.68	0.48
42	10030002	Yellow River (Volney)	566	126	0.66	0.11	0.17	0.91	0.31
43	10810001	North Raccoon River (Sac City)	1813	147	0.38	0.11	0.17	0.87	0.11

also highly correlated with TP (0.69 ± 0.13) with a similar range (0.27–0.91) as turbidity. Seven of the 43 sites had correlation between TP and OP greater than 0.8 (16%) and only three sites had correlation less than 0.5. Twelve sites (28%) had a higher degree of correlation between TP and OP than TP and turbidity.

In contrast, TP concentrations were not correlated to chlorophyll a (0.07 ± 0.15) or chloride (−0.10 ± 0.24). The correlation of TP concentrations to discharge (0.41 ± 0.23) was moderately correlated, but it ranged from negative (−0.21) to highly positive (0.74).

3.3. Multiple linear regression models

Two multiple linear regression models were developed for each of the 43 monitoring sites (Table 2). One model included OP as a potential surrogate in the regression equation and a second model was developed without using OP as a variable. This was done so that the effects of OP on TP estimation could be better evaluated.

Results indicate that TP concentrations in Iowa rivers can be estimated very well using water quality surrogates of turbidity, OP, chlorophyll a, chloride and discharge (Table 2). When OP was included in the regression equations, the lowest coefficient of determinism (r^2) was 0.72 and the mean r^2 for all 43 sites was 0.90 with an average RMSE of 0.08. Astoundingly, ten of the 43 sites had r^2 values greater than 0.95. All but one of the equations included both turbidity and OP in the regression (Whitebreast Creek was the lone exception), and one of these two variables was identified as the best predicting term in nearly all the equations. Other

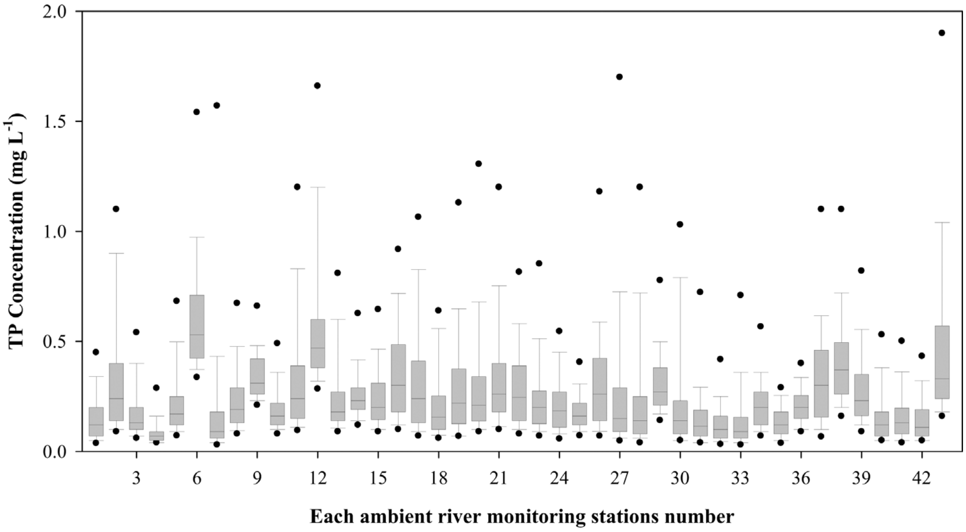

Fig. 2. Distribution of TP concentration in 43 ambient river monitoring sites in Iowa watershed. This box-plot shows the 25th, 50th, and 75th (black line) percentiles; the whiskers indicate the 10th and 90th percentiles; the circles represent the 5th and 95th percentiles.

variables (discharge, chlorophyll a, chloride) were included in the regression equations on a site-specific basis, but it is difficult to generalize on their overall contribution. Chlorophyll a was selected as a variable for 27/43 sites, chloride was selected for 12/43 sites and discharge was selected for 4/43 sites.

Excluding OP from the regression equations decreased the mean r^2 value from 0.90 to 0.72 and increased the RMSE to 0.14 among all sites (Table 2). In particular, for some monitoring sites, the decrease in model performance without OP was substantial. For example, for the monitoring site on the North Raccoon River at Sac City (site no. 43), the r^2 value decreased from 0.89 with OP to 0.18 without OP (Fig. 2). Likewise, the r^2 values decreased 50% at five other sites and the average decrease for these six poorly performing sites was from an r^2 with OP of 0.87 to a value of 0.37 without including OP. This indicates that including OP concentrations in TP estimation is critically important for some sites.

For the other sites, the drop-off in model performance without including OP was not as great. For example, the r^2 value for the English River decreased from 0.94 to 0.89 without including OP in the model (Fig. 4). The decrease in r^2 values from models with or without OP was less than 10% for 21 sites and the decrease was less than 20% for approximately 75% of the sites. Comparing the regression models for the same site with or without OP, the coefficient weight on the turbidity term typically increased slightly without using OP in the model (approximately 0.001–0.003 increase). Interestingly, the use of discharge in the regression models

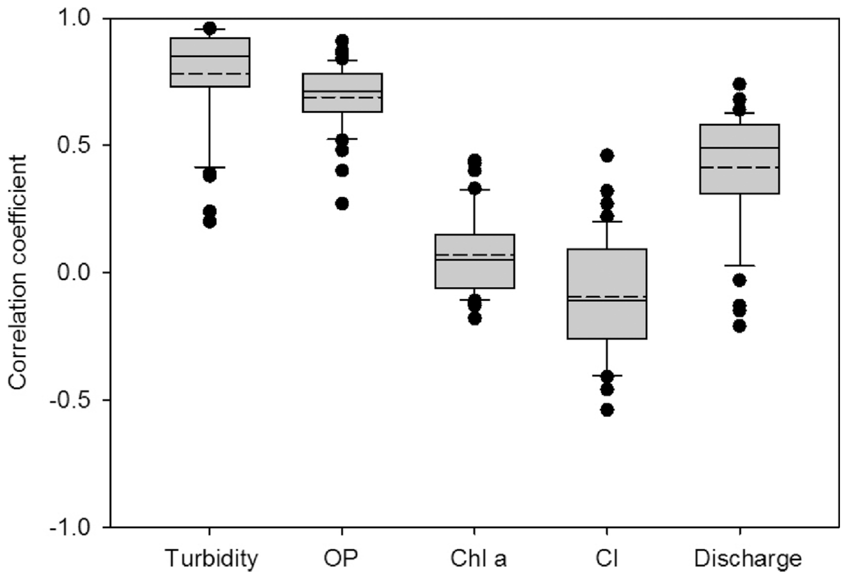

Fig. 3. Box plot of correlation coefficients associated with the relation of various surrogates and total phosphorus concentrations for the 43 river monitoring sites. Box plot notation same as Fig. 2.

Table 2
Multiple linear regression equations, R^2 and RMSE comparing measured and surrogate-estimated TP concentrations.

No.	Station Name	Regression Equation	R^2	RMSE
1	Beaver Creek (Cedar Falls)	Y = 0.018 + 0.003*(T) + 0.902*(OP) + 0.001*(CA)	0.90	0.10
		Y(no OP) = 0.05 + 0.004*(T) + 0.001*(A)	0.85	0.14
2	Beaver Creek (Grimes)	Y = 0.017 + 0.002*(T) + 1.050(OP)	0.96	0.07
		Y(no OP) = 0.056 + 0.003*(T) + 0.002*(CL)	0.35	0.26
3	Black Hawk Creek (Waterloo)	Y = − 0.009 + 0.003*(T) + 0.908*(OP) + 0.001*(CL) + 0.001(CA)	0.84	0.08
		Y(no OP) = 0.075 + 0.003*(T) + 0.002*(CA)	0.63	0.12
4	Bloody Run Creek	Y = 0.021 + 0.002*(T) + 0.761*(OP)	0.81	0.03
		Y(no OP) = 0.051 + 0.004*(T)	0.57	0.05
5	Boone River (Stratford)	Y = 0.017 + 0.001*(T) + 1.079*(OP) + 0.001*(CA)	0.96	0.05
		Y(no OP) = −0.062 + 0.003*(T) + 0.007*(CL)	0.34	0.22
6	Boyer River (Missouri Valley)	Y = 0.115 + 0.002*(T) + 0.894*(OP) − 0.003*(D)	0.85	0.23
		Y(no OP) = 0.098 + 0.003*(T) + 0.019*(CL) − 0.001(CA) − 0.006(D)	0.81	0.29
7	Cedar Creek (Bussey)	Y(no OP) = 0.023 + 0.002*(T)	0.95	0.32
8	Cedar Creek (Oakland Mills)	Y = 0.024 + 0.002*(T) + 0.990*(OP) + 0.001*(CL)	0.90	0.10
		Y(no OP) = 0.121 + 0.002*(T) + 0.001*(CA)	0.79	0.12
9	Cedar River (Conesville)	Y = 0.027 + 0.002*(T) + 0.706*(OP) + 0.002*(CL)	0.79	0.10
		Y(no OP) = 0.073 + 0.002*(T) + 0.005*(CL)	0.76	0.08
10	Cedar River (Janesville)	Y = 0.031 + 0.002*(T) + 0.931*(OP) + 0.001*(CA)	0.72	0.06
		Y(no OP) = 0.108 + 0.004*(T)	0.52	0.10
11	English River (Riverside)	Y = 0.028 + 0.002*(T) + 0.983*(OP) + 0.001*(CL) − 0.001*(D)	0.94	0.09
		Y(no OP) = 0.117 + 0.002*(T)	0.88	0.12
12	Floyd River (Sioux City)	Y = −0.002 + 0.003*(T) + 1.065*(OP) + 0.001*(CA)	0.86	0.15
		Y(no OP) = 0.157 + 0.003*(T) + 0.003*(CL) − 0.005*(D)	0.70	0.23
13	Indian Creek (Colfax)	Y = 0.015 + 0.002*(T) + 1.000*(OP) + 0.001*(CA)	0.96	0.05
		Y(no OP) = 0.082 + 0.003*(T) + 0.002*(CL) − 0.003*(D)	0.54	0.16
14	Iowa River (Loan Tree)	Y = −0.018 + 0.002*(T) + 0.970*(OP) + 0.001*(CA) + 0.001*(CL)	0.94	0.04
		Y(no OP) = 0.161 + 0.002*(T)	0.85	0.07
15	Little Sioux River (Larrabee)	Y = 0.019 + 0.002*(T) + 0.970*(OP) + 0.001*(CA)	0.87	0.07
		Y(no OP) = 0.098 + 0.003*(T)	0.46	0.14
16	Little Sioux River (Smithland)	Y = 0.034 + 0.002*(T) + 0.892*(OP)	0.89	0.09
		Y(no OP) = 0.081 + 0.002*(T) + 0.001*(D)	0.78	0.12
17	Maple River (Mapleton)	Y = 0.015 + 0.002*(T) + 0.969*(OP) + 0.001*(CA)	0.95	0.07
		Y(no OP) = 0.058 + 0.003*(T)-0.001*(D) + 0.002*(CL) + 0.001* (CA)	0.88	0.12
18	Maquoketa River (Maquoketa)	Y = −0.041 + 0.002*(T) + 1.080*(OP) + 0.003*(CL)	0.95	0.07
		Y(no OP) = 0.067 + 0.003*(T) + 0.001*(D)	0.77	0.10
19	Middle River (Indianola)	Y = 0.028 + 0.002*(T) + 1.035*(OP) + 0.001*(CA)	0.86	0.16
		Y(no OP) = 0.138 + 0.002*(T) + 0.001*(CA) − 0.003*(CL)	0.79	0.19
20	North Fork Maquoketa (Hurstville)	Y = −0.018 + 0.003*(T) + 0.877*(OP) + 0.001*(CA) + 0.003*(CL)	0.93	0.03
		Y(no OP) = −0.047 + 0.004*(T) + 0.008*(CL)	0.85	0.16
21	North River (Norwalk)	Y = 0.015 + 0.002*(T) + 0.979*(OP) + 0.002*(CL)	0.97	0.06
		Y(no OP) = 0.020 + 0.002*(T) + 0.008*(CL)	0.68	0.20
22	North Skunk River	Y = 0.046 + 0.002*(T) + 0.791*(OP)	0.88	0.09
		Y(no OP) = 0.100 + 0.003*(T)	0.81	0.16
23	Old Mans Creek (Iowa City)	Y = −0.024 + 0.003*(T) + 1.129*(OP) + 0.002*(CL)	0.94	0.08
		Y(no OP) = 0.107 + 0.004*(T) − 0.006*(D)	0.68	0.16
24	Rock River (Hawarden)	Y = 0.032 + 0.003*(T) + 0.924*(OP)-0.001*(D)	0.92	0.06
		Y(no OP) = 0.078 + 0.003*(T)	0.72	0.10
25	Shell Rock River (Shell Rock)	Y = 0.032 + 0.002*(T) + 0.925*(OP) + 0.001*(CA)	0.83	0.04
		Y(no OP) = 0.111 + 0.004*(T)	0.47	0.09
26	Soldier River (Pisgah)	Y = 0.010 + 0.003*(T) + 0.871*(OP) + 0.002*(CA)	0.95	0.11
		Y(no OP) = 0.184 + 0.003*(T) − 0.008*(CL) + 0.003*(CA)	0.94	0.12
27	South Raccoon River (Redfield)	Y = 0.020 + 0.002*(T) + 0.889*(OP) + 0.001*(CA)	0.95	0.06
		Y(no OP) = 0.053 + 0.003*(T) + 0.001*(D)	0.90	0.15
28	South River (Ackworth)	Y = −0.003 + 0.001*(T) + 1.178*(OP) + 0.003*(CL) + 0.001*(CA)	0.98	0.08
		Y(no OP) = 0.048 + 0.003*(T) + 0.001*(CA)	0.90	0.18
29	South Skunk River (Oskaloosa)	Y = 0.014 + 0.002*(T) + 1.073*(OP) + 0.001*(CA)	0.94	0.05
		Y(no OP) = 0.104 + 0.003*(T) + 0.003*(CL)	0.82	0.10
30	Thompson Fork (Davis City)	Y = 0.049 + 0.002*(T) + 0.851*(OP)	0.85	0.13
		Y(no OP) = 0.050 + 0.003*(T)	0.78	0.26
31	Turkey River (Garber)	Y = 0.021 + 0.003*(T) + 0.925*(OP)	0.97	0.07
		Y(no OP) = 0.051 + 0.004*(T)	0.88	0.14
32	Upper Iowa River (Dorchester)	Y = 0.029 + 0.003*(T) + 0.746*(OP) + 0.001*(CA)	0.90	0.09
		Y(no OP) = −0.002 + 0.004*(T) + 0.003*(CL) + 0.001*(D)	0.77	0.11
33	Volga River (Elkport)	Y = 0.015 + 0.002*(T) + 0.830*(OP) + 0.002*(CA) + 0.001*(D)	0.95	0.05
		Y(no OP) = 0.039 + 0.004*(T)	0.86	0.13
34	Wapsipinicon River (De Witt)	Y = −0.024 + 0.002*(T) + 1.122*(OP) + 0.001*(CA) + 0.003*(CL)	0.96	0.05
		Y(no OP) = 0.073 + 0.003*(T)	0.80	0.09
35	West Fork Cedar River (Finchford)	Y = 0.023 + 0.002*(T) + 0.871*(OP) + 0.001*(CA)	0.93	0.03

(continued on next page)

Table 2 *(continued)*

No.	Station Name	Regression Equation	R^2	RMSE
		Y(no OP) = 0.058 + 0.003*(T) + 0.001*(D)	0.67	0.05
36	West Fork Des Moines (Humboldt)	Y = 0.035 + 0.002*(T) + 0.872*(OP) + 0.001*(CA)	0.76	0.06
		Y(no OP) = 0.102 + 0.003*(T)	0.43	0.08
37	West Fork Ditch (Hornick)	Y = 0.004 + 0.002*(T) + 1.052*(OP) + 0.001*(CA) + 0.001*(CL)	0.90	0.11
		Y(no OP) = 0.077 + 0.003*(T) + 0.001*(CR)	0.82	0.12
38	West Nishnabotna River (Malvern)	Y = 0.036 + 0.002*(T) + 0.934*(OP) + 0.001*(CA)	0.91	0.10
		Y(no OP) = 0.065 + 0.003*(T) + 0.007*(CL)	0.86	0.11
39	West Nodaway River (Shambaugh)	Y = −0.017 + 0.002*(T) + 0.969*(OP) + 0.001*(CA) + 0.004*(CL)	0.95	0.06
		Y(no OP) = 0.128 + 0.003*(T) + 0.001*(CA)	0.91	0.17
40	Whitebreast Creek (Dallas)	Y = 0.056 + 0.002*(T) + 0.001*(CA)	0.85	0.08
		Y(no OP) = 0.048 + 0.002*(T) + 0.001*(CA) + 0.001*(D)	0.85	0.08
41	Wolf Creek (La Porte City)	Y = 0.021 + 0.002*(T) + 0.919*(OP) + 0.001*(CA)	0.84	0.07
		Y(no OP) = 0.063 + 0.003*(T) + 0.001*(CA)	0.70	0.09
42	Yellow River (Volney)	Y = 0.012 + 0.003*(T) + 0.951*(OP) + 0.001*(CA)	0.85	0.05
		Y(no OP) = 0.018 + 0.007*(T) + 0.002*(CL) + 0.003*(D)	0.54	0.14
43	Raccoon River (Sac city)	Y = 0.012 + 0.002*(T) + 0.989*(OP) + 0.001*(CA)	0.89	0.15
		Y(no OP) = −0.035 + 0.005*(T) + 0.009*(CL)	0.18	0.35

*Turbidity (T), Orthophosphate (OP), Discharge (D), Chloride (CL), Chlorophyll a (CA).
*Y (no OP): this regression equation does not include Orthophosphate as an independent variable.
*R^2 (Validation): validation of MLR (Multiple Linear Regression) equation from 2001 to 2015.

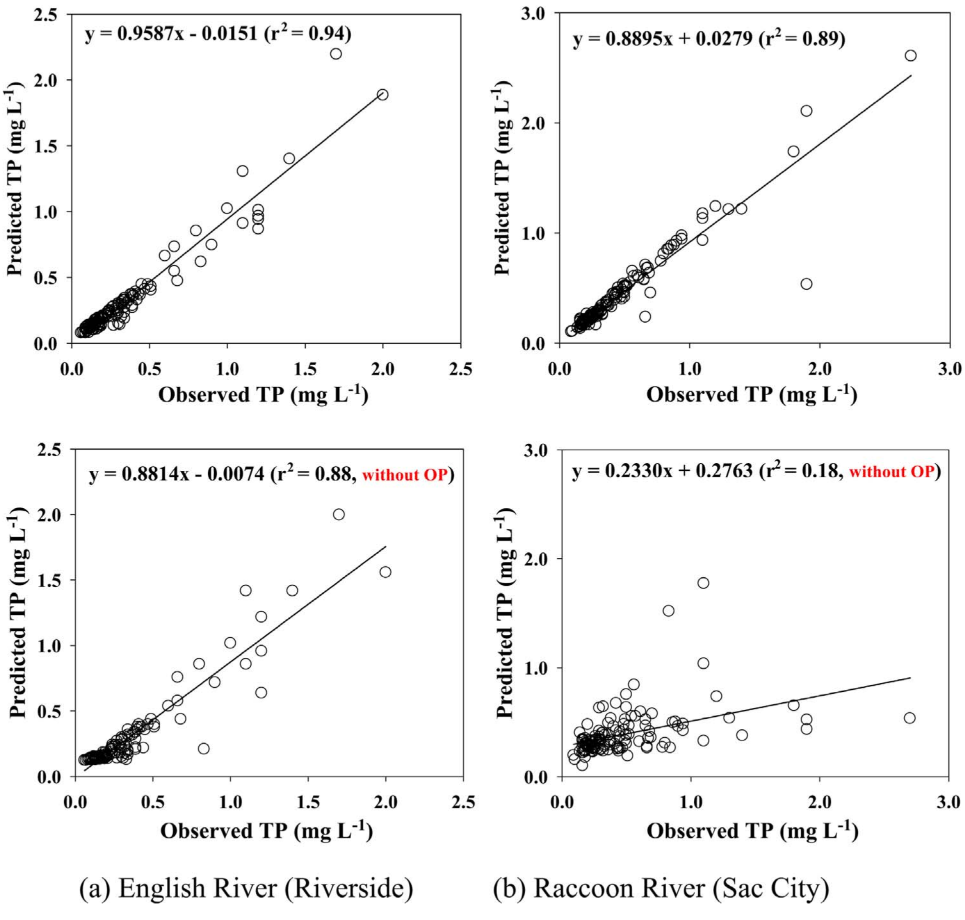

Fig. 4. Comparison of surrogate-predicted TP concentrations to measured values at two monitoring sites where inclusion of OP in the model was less important (a) and critically important (b).

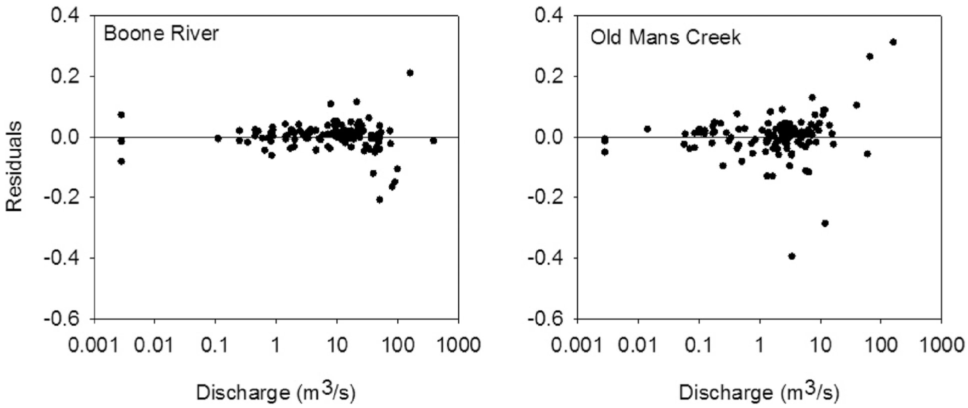

Fig. 5. Regression model residuals plotted against discharge for a Des Moines Lobe watershed (Boone River) and a southern Iowa watershed (Old Mans Creek). No systematic bias in residuals with discharge were observed in these or other rivers included in study.

increased when OP was excluded (from 4 to 10 of 43 models) and several equations had fewer terms without OP (in addition to excluding OP). Overall, the residuals from the regression models showed no systematic bias with discharge (Fig. 5), indicating that the regression models performed consistently across a range of flow conditions captured by the monthly sampling frequency.

4. Discussion

4.1. Suitability of TP surrogates

In this study, we examined the suitability of using water quality surrogates (turbidity, OP, discharge, chloride and chlorophyll a) to estimate TP concentrations in 43 Iowa rivers. The approach used in our study differs from other studies reported the literature in that we used a longer dataset (15 years), evaluated multiple sites (43) and included multiple potential surrogates (5). Results indicate that various combinations of these surrogates are capable of estimating TP concentrations with a high degree of accuracy in many Iowa rivers.

Consistent with other researchers (e.g., Grayson et al., 1996; Kronevang et al., 1997; Stubblefield et al., 2007; Jones et al., 2011), we found that turbidity is a useful surrogate to estimate TP concentrations in rivers. In our study, the correlation (r) of TP to turbidity averaged 0.78 for all 43 sites and nearly one-third of the sites had a correlation coefficient of 0.9 or above. Jones et al. (2011) reported similar degrees of correlation in two Utah watersheds (0.95 and 0.70), whereas Viviano et al. (2014) reported correlation of 0.94 in a natural Italian watershed and correlation was greater than 0.9 in Grayson et al. (1996). Hence, our study confirms that TP concentrations are also highly correlated with turbidity in Midwestern agricultural watersheds. Strong correlation of TP to turbidity was found throughout Iowa in watersheds where hillslopes have been eroded into older, fine-textured glacial deposits.

However, it was clear that in some Iowa rivers, TP concentrations could not be reliably estimated without including OP in the regression model. For six rivers, the decrease in r^2 value was greater than 0.5 in regression models with or without including OP as a variable. These rivers are all located in, or drain portions of, the recently glaciated Des Moines Lobe region of Iowa (Fig. 1). This region of Iowa is typified by widespread artificial subsurface drainage systems (tiles) that were installed in the 1800's to early 1900's to drain the wetlands, swamps and pothole depressions for crop production (Kanwar et al., 1983; Zucker and Brown, 1998; Schilling et al., 2012). Watersheds containing artificial drainage systems are susceptible to increased losses of many agricultural pollutants although much of the focus has been on NO3-N export (e.g., Baker et al., 1975; Tomer et al., 2003; Kalita et al., 2006; Schilling and Helmers, 2008). However, it is becoming increasingly recognized that subsurface tiles are also contributing to dissolved P loads in agricultural watersheds (Gentry et al., 2007; Thoma et al., 2005; Smith et al., 2015). For example, Smith et al. (2015) reported that 25–80% of the P lost from farm fields in Ohio occurred via subsurface tile. Results from our study indicate that surrogate models to estimate TP concentrations in rivers flowing through watersheds characterized by widespread tile drainage will need to include OP as a variable or else the models may be subject to considerable error.

Unfortunately, measuring OP concentrations instantaneously in rivers using sensor technology is not well-advanced. In contrast, instantaneous and continuous measurement technology for NO_3-N is mature and robust. Nitrate and nitrite ions (NOx) are very water soluble and absorb light in their unaltered form at a wavelength favorable for quantification by optical methods. Dissolved OP can be measured continuously using recently developed technology that mixes the aqueous phosphate ion with molybdate ion and Rhodamine B in an acidic solution to yield a complex that absorbs light at a usable wavelength (Benisch et al., 2011). Data obtained from a recent deployment of one such device in the effluent at the Cedar Rapids, Iowa wastewater treatment plant, compared favorably with lab-generated results obtained from effluent grab samples (Fig. 6). Successful deployment of this or other similar devices in streams would generate high frequency data and help refine a regression model that uses OP as a variable describing TP transport.

Other surrogates variably contributed to explaining TP concentrations in Iowa rivers. We initially suspected that discharge would

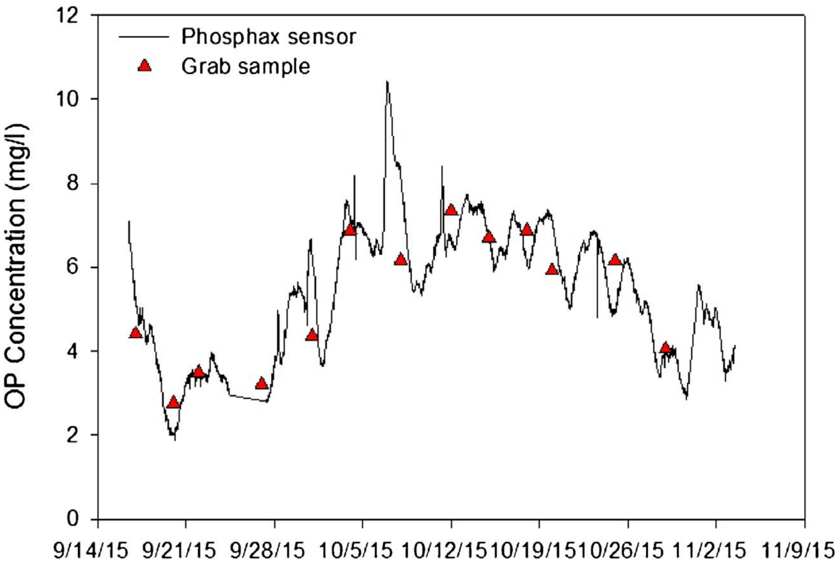

Fig. 6. Comparison of OP concentrations measured with a continuously reading Phosphax sensor to grab samples collected at the City of Cedar Rapids, IA wastewater treatment plant.

be a significant variable since discharge was an important variable in modeling TP concentration trends in Iowa rivers. Wang et al. (2016) reported that the effects of discharge could be as either seasonal or nonseasonal coefficients in their time-series models of TP concentrations. Incorporating discharge in their models allowed them to uncover the trend information hidden behind discharge-driven fluctuations. In our TP surrogate study, discharge was retained as a significant variable in only 4 of 43 models including OP and 10 of 43 models excluding OP. However, since turbidity was also correlated with discharge ($r \sim 0.6$) and actually better correlated with TP ($r = 0.78$), turbidity better captured the discharge-driven fluctuation in TP concentrations than discharge did in a regression model that included both turbidity and discharge. Model residuals showed no additional correlation with discharge when turbidity was included in the regression model (Fig. 5).

The relation of chlorophyll a to phosphorus is well established in lake environments (e.g., see recent regional assessments reported in Filstrup et al., 2014; Spears et al., 2013) and chlorophyll a was selected as a surrogate for estimating TP concentrations in 27/43 Iowa rivers. However, chlorophyll a was not well correlated to TP concentrations ($r = 0.07 \pm 0.2$) and the weight on this term in the regression models was not very high (typically 0.001) compared to other parameters included in the regression models. Likewise, chloride concentrations exhibited a wide range of correlation to TP concentrations in Iowa rivers ($r = -0.54$ to 0.46) and the mean correlation was negative ($r = -0.10$). Negative correlation implies that as TP concentrations increase, chloride concentrations decrease. This is consistent with dilution of chloride concentrations during rainfall runoff events when TP concentrations are higher (Schilling and Helmers, 2008), but the effects of runoff on TP concentrations are better captured with turbidity. Considering that chloride was added as a surrogate to capture potential impacts from wastewater treatment plants or road salt (Kelly et al., 2010), the lack of positive correlation suggests that this parameter may not be sensitive enough to capture potential influence on TP from urban sources. The monitoring sites in this study were selected to be ambient locations beyond the influence of urban areas and WWTPs (IDNR, 2000).

Overall, results from this study suggest that turbidity and OP are the dominant surrogates needed to estimate TP concentrations in Iowa rivers. Adding OP measurements to nearly all regression models improved the model fits substantially, and for rivers draining the tile-drained Des Moines Lobe region it is not possible to reliably estimate TP concentrations without including OP as a surrogate variable. Although it should come as no surprise that OP measurements are useful in estimating TP concentrations since OP comprises a portion of the TP load in all rivers, study results highlight the importance of OP contributions in tile-drained landscapes (Smith et al., 2015). For rivers flowing through watersheds with less intensive tile drainage, continuous turbidity measurements combined with other surrogates may provide a suitable proxy for TP concentration patterns.

4.2. Relation to nutrient reduction strategies

Many Midwestern U.S. states have developed strategies to reduce N and P loads exported from their states (e.g., INRS, 2013; INLRS, 2014; ONRS, 2013) and study results provide information that may assist state and federal agencies and other interested organizations in quantifying P reductions. An important first step in quantifying reductions is developing an accurate estimate of current conditions and establishing a surrogate relation between water quality variables and TP concentrations that may improve the quantification of P loads in rivers. However, progress toward meeting nutrient reduction goals is expected to be slow and gradual. If load reductions occur slowly over time, would using a method involving TP surrogates to estimate TP be better able to detect gradual changes?

Wang et al. (2016) used time-series analysis to show that TP concentrations in 12 of 40 Iowa rivers significantly decreased from 1999 to 2013 ranging from 2.6 to 7.5% per year, and as a population of 40 rivers, TP concentrations decreased at an average rate of 2.6% per year. These trends were determined based on monthly TP concentration data with a sample size ranging from 138 to 175 (Wang et al., 2016). If a surrogate relation had been developed for these rivers for the same time period using 15-min measurement frequency, the sample size would have expanded from approximately 150 samples in 14 years to more than 490,000 measurements, with the caveat that these are generally much more strongly dependent data than the monthly data. Although the regression model with or without OP explained 90 ± 8% and 72 ± 14% of the variability in TP concentrations for 43 Iowa rivers, respectively, the models were not perfect fits to the measured data. Errors in estimating TP concentrations with surrogates, even with an r^2 of 0.9, will still present challenges in trend detection if potential trends are within the range of model error. Use of the surrogate relation to estimate TP concentrations for trend detection would have to compensate for the unexplained variance in the model (i.e., error). However, the greatly expanded sample size would enhance the ability of watershed managers to detect gradual trends. In the detection of TP trends in Iowa, it is conceivable that more rivers may have shown significant trends if the sample size were larger. Although more work is needed to assess the statistical detection of trends in the presence of severe autocorrelation of 15-min data (Loftis and Ward, 1980), the use of surrogate relations to estimate TP concentrations at a finer temporal resolution would be expected to increase the potential to detect gradual trends over time.

Additionally, accurate estimation of TP loads in rivers is critically important for reasons beyond measuring progress toward meeting nutrient reduction goals. Improving TP concentration estimation will improve the ability to estimate riverine loads which are essential in the identification of sources of nutrients loads in watersheds (Robertson et al., 2009), development of waste-load allocation schemes via the Total Maximum Daily Load (TMDL) program, calibration and validation of watershed models (Gassman et al., 2007), evaluation of long-term trends in loads (Turner and Rabalais, 1991) and estimation of riverine flux to the Gulf of Mexico (Goolsby et al., 1999).

5. Conclusions

In this study, the relation of TP concentrations to water quality surrogates (turbidity, OP, discharge, chlorophyll a, and chloride) was evaluated for 43 river monitoring sites in Iowa. Two multiple linear regression models were developed for each site: one model that included OP as a potential surrogate in the regression equation and a second model developed without using OP as a variable. Overall, TP concentrations were highly correlated to turbidity (0.78 ± 0.20) and OP (0.69 ± 0.13) across all sites and less correlated to chlorophyll a (0.07 ± 0.15), chloride (−0.10 ± 0.24) and discharge (0.41 ± 0.23). Regression results indicate that various combinations of these surrogates are capable of estimating TP concentrations with a high degree of accuracy. When the regression models included OP as a variable, the mean r^2 for all 43 sites was 0.90 ± 0.08 and ten of the 43 sites had r^2 values greater than 0.95. When OP was excluded in the regression model, the overall mean r^2 values decreased to 0.72 ± 0.14 and for six of the river sites, the r^2 value decreased by 50%. Other variables (discharge, chlorophyll a, chloride) were included in the regression equations on a case-by-case basis.

Overall, turbidity and OP are the dominant surrogates needed to estimate TP concentrations in Iowa rivers. Adding OP measurements to the regression models improved the model performance for nearly all sites, but the importance of OP was particularly apparent for rivers draining the tile-drained Des Moines Lobe region. In this regions, subsurface tiles are contributing dissolved P loads to rivers that are not captured by traditional turbidity-TP relations. Future deployment of sensor technology for continuous OP measurement will substantially aid in estimation of TP concentrations and loads in rivers. When this occurs, the use of surrogate relations will improve the ability of stakeholders to estimate TP loads with greater temporal resolution and increase the potential to detect gradual improvements over time.

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