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

Keith E. Schilling[a,*], Sea-Won Kim[b], Christopher S. Jones[b]

[a] Iowa Geological Survey, 300 Trowbridge Hall, University of Iowa, Iowa City, IA, USA
[b] IIHR–Hydroscience & Engineering, University of Iowa, Iowa City, IA, USA

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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

* Corresponding author.
E-mail address: keith-schilling@uiowa.edu (K.E. Schilling).

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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