Improving Riverine Constituent Concentration and Flux Estimation by Accounting for Antecedent Discharge Conditions

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Abstract

Regression-based approaches are often employed to estimate riverine constituent concentrations and fluxes based on typically sparse concentration observations. One such approach is the recently developed WRTDS (“Weighted Regressions on Time, Discharge, and Season”) method, which has been shown to provide more accurate estimates than prior approaches in a wide range of applications. Centered on WRTDS, this work was aimed at developing improved models for constituent concentration and flux estimation by accounting for antecedent discharge conditions. Twelve modified models were developed and tested, each of which contains one additional flow variable to represent antecedent conditions and which can be directly derived from the daily discharge record. High-resolution (~ daily) data at nine diverse monitoring sites were used to evaluate the relative merits of the models for estimation of six constituents – chloride (Cl), nitrate-plus-nitrite (NO_x), total Kjeldahl nitrogen (TKN), total phosphorus (TP), soluble reactive phosphorus (SRP), and suspended sediment (SS). For each

site-constituent combination, 30 concentration subsets were generated from the original data through Monte Carlo subsampling and then used to evaluate model performance. For the subsampling, three sampling strategies were adopted: (A) 1 random sample each month (12/year), (B) 12 random monthly samples plus additional 8 random samples per year (20/year), and (C) flow-stratified sampling with 12 regular (non-storm) and 8 storm samples per year (20/year). Results reveal that estimation performance varies with both model choice and sampling strategy. In terms of model choice, the modified models show general improvement over the original model under all three sampling strategies. Major improvements were achieved for NO_x by the long-term flow-anomaly model and for Cl by the ADF (average discounted flow) model and the short-term flow-anomaly model. Moderate improvements were achieved for SS, TP, and TKN by the ADF model. By contrast, no such achievement was achieved for SRP by any proposed model. In terms of sampling strategy, performance of all models (including the original) was generally best using strategy C and worst using strategy A, and especially so for SS, TP, and SRP, confirming the value of routinely collecting stormflow samples. Overall, this work provides a comprehensive set of statistical evidence for supporting the incorporation of antecedent discharge conditions into the WRTDS model for estimation of constituent concentration and flux, thereby combining the advantages of two recent developments in water quality modeling.

Keywords

River flux estimation; flow anomalies; antecedent discharge; nutrients; sediment; river water quality monitoring.

1. Introduction

In many river monitoring programs, flow discharge is usually recorded daily but water quality constituent concentration has been historically sampled at low frequency, and rarely at more than a few times each month. In the United States, there are numerous locations where the U.S. Geological Survey and others have maintained long-term records of flow every fifteen minutes for decades, but where water quality sampling has been far less frequent. For example, even at sites of comparatively long-term monitoring, such as in tributaries of the Chesapeake Bay, where there is a roughly 30-year record of water quality sampling, the number of annual samples has typically ranged between 20 and 50, usually comprising at least 12 regular monthly samples and 8 targeted stormflow samples (Chanat *et al.*, 2016; Zhang *et al.*, 2016a). Water quality monitoring data at many other discretely sampled locations generally have even lower temporal resolutions. In using such sparse data toward load estimation, it is important to make best possible estimates of concentration for each day in the record, thus enabling calculation of daily flux (“load”) as the product of daily concentration and daily discharge. From a management perspective, such daily estimates and their temporal aggregates (monthly, seasonal, or annual averages) play an essential role toward assessment against regulatory standards (*e.g.*, maximum concentration levels), establishment and assessment of restoration targets (*e.g.*, total maximum daily loads), calibration of watershed models, and evaluation of long-term trends in surface water quality (Bowes *et al.*, 2008; Shenk and Linker, 2013; Stow and Borsuk, 2003; Zhang *et al.*, 2015).

Over the last few decades, alternative regression-based approaches have been developed by various investigators, including but not limited to, Cohn *et al.* (1992); Cohn *et al.* (1989); Crowder *et al.* (2007); Dolan *et al.* (1981); Johnes (2007); Kronvang and Bruhn (1996); Park and

Engel (2015); and Stenback *et al.* (2011). These approaches generally estimate daily concentrations and fluxes based on modeled relations between observed concentration and some set of explanatory variables, which typically include time, discharge, and season. With these covariates, a single regression model is usually established for the entire record based on common assumptions of homoscedasticity of model errors and fixed relations between concentration and each covariate. These assumptions, however, can be frequently violated in reality – see examples in Hirsch *et al.* (2010).

With consideration of the above limitations, Hirsch *et al.* (2010) developed a method called “Weighted Regressions on Time, Discharge, and Season (WRTDS)”. Similar to the prior approaches, WRTDS makes use of time, discharge, and season as explanatory variables but has a major distinction in that it develops a separate regression model for each day in the record. For each day, it re-evaluates the dependencies of concentration on time, discharge, and season based on data deemed to be most relevant to the day of estimation (Hirsch and De Cicco, 2015; Hirsch *et al.*, 2010). Consequently, WRTDS can better represent the temporally varying seasonal and discharge-related patterns and is more resistant to problems of flux-estimation bias than prior methods (Hirsch, 2014; Moyer *et al.*, 2012). Since its publication in 2010, WRTDS has been applied in a suite of large-scale studies (Chanat *et al.*, 2016; Corsi *et al.*, 2015; Hirsch, 2012; Medalie *et al.*, 2012; Moyer *et al.*, 2012; Murphy *et al.*, 2014; Pellerin *et al.*, 2014; Sprague *et al.*, 2011; Zhang *et al.*, 2016a; Zhang *et al.*, 2013; Zhang *et al.*, 2015; Zhang *et al.*, 2016b).

Although WRTDS represents an advance relative to prior approaches, it is of course eligible for further improvement. In this context, the original authors suggested that additional explanatory variables, perhaps especially those that can account for watershed wetness conditions, may further enhance the model (Hirsch *et al.*, 2010). Mechanistically, antecedent

conditions can influence both the momentum and pathways of constituent transport from watershed to stream. In a relatively dry watershed, particulate constituents tend to be kept locally and dissolved constituents may enter the subsurface near their point of application or generation. When the watershed becomes wetter, particulate constituents can be more easily mobilized with surface runoff and dissolved constituents can be more efficiently flushed to stream due to saturation of subsurface storage (Cirimo and McDonnell, 1997; Dupas *et al.*, 2015; Inamdar *et al.*, 2004). In the last two decades, an extensive set of literature has documented the effects of antecedent condition on riverine export of constituents, including nitrogen (Biron *et al.*, 1999; Davis *et al.*, 2014; Macrae *et al.*, 2010; Murphy *et al.*, 2014; Turgeon and Courchesne, 2008), phosphorus (Ide *et al.*, 2008; Macrae *et al.*, 2010; McDowell and Sharpley, 2002; Warner *et al.*, 2009), suspended sediment (Gray *et al.*, 2015; McDowell and Sharpley, 2002), and dissolved organic carbon (Biron *et al.*, 1999; Turgeon and Courchesne, 2008). Of special relevance to the current work, Vecchia (2003) has developed the flow anomaly concept for quantification of antecedent discharge conditions, which has been subsequently used and refined in numerous analyses of surface water quality (Ryberg and Vecchia, 2014; Vecchia, 2005; Vecchia *et al.*, 2009; Vecchia *et al.*, 2008). In the context of WRTDS, Murphy *et al.* (2014) have previously considered Vecchia's approach, but that work was a preliminary effort of limited scope and depth, with evaluation of only a limited set of antecedent condition variables and with a particular focus on nitrate transport.

The overall objective of the study described here was to substantially expand upon the work of Murphy *et al.* (2014) by developing and rigorously testing several alternative statistical models that build on the WRTDS model by also accounting for antecedent discharge conditions, thereby providing improved estimation of riverine concentration and flux. For method

transferability, we focused on variables that can be directly derived from the daily river discharge record, since such record is typically available regardless of watershed characteristics or geographical regions. These variables include flow anomalies on various temporal scales (Ryberg and Vecchia, 2014; Vecchia *et al.*, 2009), average discounted flow (Wang *et al.*, 2011; Wang and Tian, 2013), base-flow index (Lyne and Hollick, 1979; Nathan and McMahon, 1990), and flow gradient (see **Section 2**). Six constituents were evaluated, namely, chloride (Cl), nitrate-plus-nitrite (NO_x), total Kjeldahl nitrogen (TKN), total phosphorus (TP), soluble reactive phosphorus (SRP), and suspended sediment (SS), using high-resolution (nearly daily) data at nine diverse monitoring sites (**Section 3.1**). For each site-constituent combination, concentration subsets were generated through Monte Carlo subsampling, which was conducted based on three different sampling strategies to mimic common monitoring practice (**Section 3.2**). Finally, model estimates were compared with observations to evaluate the performance of the original and modified models (**Section 3.3**).

2. Statistical Models: Original and Modified WRTDS

The original WRTDS model uses the following principle equation (Hirsch *et al.*, 2010):

$$\ln(C) = \beta_0 + \beta_1 t + \beta_2 \ln(Q) + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) + \varepsilon \quad (1)$$

where C is constituent concentration, t is time in decimal years, Q is daily discharge, β_i are fitted coefficients, and ε is the error term. On the right side of the equation, the 2nd and 3rd terms represent time and discharge effects, respectively, while the 4th and 5th terms represent seasonal effects. The $\ln(C) \sim \ln(Q)$ relationship is adopted for three reasons. First, it provides a generally better fit than a linear relationship. Second, the residuals from this model are more nearly normal and homoscedastic. Third, it avoids the possibility of obtaining negative values for estimated concentration (Hirsch and De Cicco, 2015). For each day in the record, WRTDS develops one

separate regression model to estimate concentration and flux. First, it pre-screens the entire concentration data set and selects at least 100 samples that are sufficiently “close” to the estimation day in three dimensions, *i.e.*, time, season, and discharge. For these three dimensions, default half-window widths are 7 years, 0.5 year, and 2 natural log units, respectively. Second, the selected samples are used to build a weighted regression model based on **Equation 1**. Third, the fitted coefficients are used to estimate $\ln(C)$ on the estimation day by substituting known values of t and Q , which is then transformed to concentration in real space using a proper bias correction factor. (Note that the set of fitted model coefficients is unique for each day of estimation.) Finally, the estimated C is multiplied by daily Q to calculate daily flux. Full details of the above estimation process are described in Hirsch and De Cicco (2015).

To account for antecedent discharge conditions, we modified **Equation 1** by adding one of several alternative flow variables. For model parsimony, only one new variable was added in each modified model, as represented by X in **Equation 2**:

$$\ln C = \beta_0 + \beta_1 t + \beta_2 \ln Q + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) + \beta_5 X + \varepsilon \quad (2)$$

The alternative variables for X include flow anomalies (FA) on various temporal scales, average discounted flow (ADF), base-flow index (BFI), and flow gradient (dQ/dt), all of which can be directly derived from the daily discharge record. These terms are defined below in **Equations 3-15**. In general, antecedent discharge variables quantified at a river monitoring site (*i.e.*, the outlet of a watershed) can be used as a proxy for antecedent moisture conditions across the watershed by amalgamating highly variable soil water and groundwater storage conditions caused by spatially varying climatic, hydrogeologic, and land use conditions across the watershed (Murphy *et al.*, 2014). Depending upon the characteristics of the watershed and the water quality variable of interest, one might expect different timescales of antecedent condition to be relevant, such that

different model selections may be more appropriate for different constituent-watershed combinations.

The FA term quantifies how different (how “anomalous”) the antecedent discharge conditions actually are for the selected temporal scale of the FA term and for the given day on which the analysis is conducted. For any given day, the FA term can be defined with the following general form (Ryberg and Vecchia, 2014; Vecchia *et al.*, 2009):

$$FA(t) = X_{T_1}(t) - X_{T_2}(t) \quad (3)$$

where $X_{T_1}(t)$ and $X_{T_2}(t)$ are averages of log-transformed daily discharge for periods of T_1 and T_2 preceding a given day t , with T_1 as the shorter of the two periods. With this definition, a positive value of FA corresponds to a situation in which the shorter-term (more recent) period has been “wetter” (has experienced more average rainfall and riverflow) than the longer-term (precedent) period. In this work, flow anomalies were quantified for varying groups of temporal scales using the *R* package “*waterData*” (Ryberg and Vecchia, 2014), which are described below and should be interpreted with the general definition in **Equation 3**.

Long-term FA (preceding 1-year vs. entire period):

$$LTFA(t) = X_{1\text{ year}}(t) - X_{\text{entire period}} \quad (4)$$

Mid-term FA (preceding 1-month vs. preceding 1-year):

$$MTFA(t) = X_{1\text{ month}}(t) - X_{1\text{ year}}(t) \quad (5)$$

Short-term FA (current day vs. preceding 1-month):

$$STFA(t) = X_{\text{current day}}(t) - X_{1\text{ month}}(t) \quad (6)$$

Annual FA (preceding 1-year vs. preceding 5-year):

$$AnnualFA(t) = X_{1\text{ year}}(t) - X_{5\text{ year}}(t) \quad (7)$$

Seasonal FA (preceding quarter-year vs. preceding 1-year):

$$SeasonFA(t) = X_{1/4\ year}(t) - X_{1\ year}(t) \quad (8)$$

Daily FA (current day *vs.* preceding quarter-year):

$$DailyFA(t) = X_{current\ day}(t) - X_{1/4\ year}(t) \quad (9)$$

100-day FA (preceding 100-day *vs.* entire period):

$$FA100(t) = X_{100\ day}(t) - X_{entire\ period} \quad (10)$$

10-day FA (preceding 10-day *vs.* preceding 100-day):

$$FA10(t) = X_{10\ day}(t) - X_{100\ day}(t) \quad (11)$$

1-day FA (current day *vs.* preceding 10-day):

$$FA1(t) = X_{current\ day}(t) - X_{10\ day}(t) \quad (12)$$

(Note that the term $X_{entire\ period}$ is not a function of t , *i.e.*, temporally invariant.) For the work described herein, all of these alternative FA terms (**Equations 4-12**) were considered in order to test which would most appropriately represent antecedent conditions for the various constituents in a given watershed. For each FA term, a daily-step time series was quantified for the period of record, as illustrated with the Maumee River record in **Fig. 1b-1j**. (This is one of the nine monitoring sites examined in this work, as described further in **Section 3.1**.)

The ADF term was originally proposed by Wang *et al.* (2011) to incorporate the influence of historical flows into flux estimation:

$$ADF(t) = \frac{\sum_{j=1}^J d^{t-t_j} Q_{t_j}}{\sum_{j=1}^J d^{t-t_j}} \quad (13)$$

Where J is the maximum number of daily discharge observations in the record, t is the day of estimation, t_j is a historical day relative to t (*i.e.*, $t_j < t$), $t - t_j$ is the lag time between t and t_j ($1 \leq j \leq J$), and d is the discounting rate. In this work, d was taken to be 0.95 per day (~0.5 per fortnight). This term aims to capture the integrated effect of all past flows in terms of flushing

and exhaustion, with higher weights assigned to more recent flows than those that occurred long time ago (Wang *et al.*, 2011; Wang and Tian, 2013). An example time series of ADF is given in **Fig. 1k** for Maumee River. So far, the development and application of ADF has been limited to sediment (Wang *et al.*, 2011; Wang and Tian, 2013; Wang *et al.*, 2015). In this work, we seek to compare the effectiveness of ADF and the other antecedent discharge terms for six common water quality constituents. Operationally, the logarithmic form of ADF was taken as the X term in **Equation 2**.

The next candidate term for X in **Equation 2** is dQ/dt , which is simply the first derivative of the daily discharge series at the day of interest:

$$dQ/dt(t) = Q_t - Q_{t-1} \quad (14)$$

An example time series of dQ/dt is given in **Fig. 1l** for Maumee River. This term may be effective in capturing the effect of hysteresis, *i.e.*, concentration may vary significantly depending on whether the sampling is occurring on the rising or falling limb of the hydrograph (Bierozza and Heathwaite, 2015; Evans and Davies, 1998).

The last candidate term, BFI, is simply the ratio of baseflow to total stream flow:

$$BFI(t) = BF(t)/Q(t) \quad (15)$$

where $BF(t)$ is the baseflow on day t , which was calculated using the Lyne-Hollick filter method (Lyne and Hollick, 1979; Nathan and McMahon, 1990) through the *R* package “*EcoHydRology*” (Fuka *et al.*, 2014). An example time series of BFI is given in **Fig. 1m** for Maumee River.

Operationally, the logarithmic form of BFI was taken as the X term in **Equation 2**. As a measure of the slow continuous contribution of groundwater, BFI may be effective in capturing dynamics of subsurface solute transport, particularly Cl and NO_x (Böhlke and Denver, 1995; Harman, 2015; Kirchner *et al.*, 2001; Sanford and Pope, 2013).

3. Data and Analysis

3.1. Testing Sites and Data

The main body of our work used the above described models with high-resolution (nearly daily) water quality concentration data for several tributaries to Lake Erie and Ohio River, as obtained from the National Center for Water Quality Research at Heidelberg University, Ohio, USA (National Center for Water Quality Research, 2015). Nine sites with at least 15 years of samples were selected, including Maumee River, Scioto River, Great Miami River, Sandusky River, River Raisin, Cuyahoga River, Grand River, Honey Creek, and Rock Creek (**Table 1**). These sites have all been frequently sampled and cover a wide range of drainage area ($34.6 \sim 6,330 \text{ mi}^2$), agriculture land (30.4% $\sim$ 89.9%), wooded land (7.3% $\sim$ 50.1%), and urban land (0.6% $\sim$ 9.6%), thus allowing a cursory test of the extent to which each model's results are site-specific or more generally applicable and also providing an initial consideration of the effect of watershed size and characteristics on model selection. Although it was beyond our scope to rigorously investigate the general applicability of the findings, our selection of a suite of different watersheds does at least provide some assurance that the findings are not strictly limited to a single watershed or watershed type.

For each site, concentration data were compiled for six water quality constituents, namely, Cl, NO_x, TKN, TP, SRP, and SS. For each site-constituent combination, the original concentration data were imported from pre-prepared files using the *R* package “*dataRetrieval*” (Hirsch and De Cicco, 2015). In some cases, non-positive concentration values were recorded due to a combination of very small true (but unknown) concentrations plus random instrument errors (Dr. Laura Johnson, personnel communication). These values were removed from the data sets, because (1) these values make no physical sense and (2) the original and modified WRTDS

models can never generate negative estimates due to the logarithmic operation (**Equation 1**). For days with multiple concentration measurements, their median value was used. The average number of sampled days ranges between 256 and 349 per year. (See details in **Table 2**.) In addition, daily river discharge data at each site were directly imported from the U.S. Geological Survey National Water Information System (U.S. Geological Survey, 2015) using the *R* package “*dataRetrieval*” (Hirsch and De Cicco, 2015). Time series of the proposed flow variables were calculated using the respective equations and associated *R* packages, as described in **Section 2**.

3.2. Monte Carlo Subsampling

To mimic the roughly monthly sampling frequency in many monitoring programs, we performed Monte Carlo subsampling of the original concentration data to produce concentration subsets for subsequent model evaluation. Three common sampling strategies were considered:

- (A) One concentration sample was randomly selected for each calendar month for which concentration samples were available (*i.e.*, 12 concentration samples per year),
- (B) 12 random monthly samples plus additional 8 random samples per year (*i.e.*, 20 concentration samples per year), and
- (C) Flow-stratified sampling with 12 regular samples and 8 storm samples per year (20 concentration samples per year). Within each specific year of the record, samples with daily discharge exceeding the 90th percentile of daily discharge distribution of the year were marked as “storm sample”; all other samples were considered as “regular samples”. Because this sampling strategy has been adopted for many river monitoring sites within the Chesapeake Bay watershed (see details in Chanat *et al.* (2016)), evaluation of model performance for this sampling strategy can provide important insights toward the design and maintenance of the Chesapeake Bay watershed monitoring network and other

similarly designed monitoring programs in other watersheds.

The original concentration data and the three types of subsamples are illustrated in **Fig. 2** for NO_x in Maumee River.

To formally assign uncertainties on WRTDS estimates, one approach is to use the block-bootstrap method of Hirsch *et al.* (2015), which involves resampling (with replacement) of the original concentration data to obtain many realizations of representative sets and associated estimates. See Zhang *et al.* (2016b) for example applications. In this work, for each site-constituent combination, 30 subsets were independently generated for each of the three sampling strategies, in order to reduce the required total computational time, whilst providing a sufficient number of replicates to reasonably describe overall uncertainties in each model's performance.

3.3. Model Evaluation

With each concentration subset, the original and modified models (13 in total) were run to estimate daily concentration and flux, which was implemented in *R* using codes modified after the existing WRTDS package “*EGRET*” (Hirsch and De Cicco, 2015). These estimates were then compared against actual observations for calculation of model residuals ($Y_i^{residual}$):

$$Y_i^{residual} = Y_i^{obs} - Y_i^{est} \quad (16)$$

where Y_i^{obs} and Y_i^{est} are observed and modeled values for the i^{th} day, respectively. $Y_i^{residual}$ can be interpreted as the portion of concentration (or flux) not accounted for by a specific model. Positive and negative residuals indicate under- and over-estimation, respectively. In addition, Spearman's correlation coefficient (γ) was also quantified to examine structural relationships between the residuals from the original WRTDS model and each of the proposed flow variables (Helsel and Hirsch, 2002). Intuitively, a high correlation coefficient may imply that the associated flow variable has a high potential for improving the estimation performance.

To facilitate performance comparison among the 13 models, three common numerical measures were considered – namely, Nash-Sutcliffe efficiency (NSE), modified NSE (E), and percent bias (PBIAS), as defined below (Krause *et al.*, 2005; Moriasi *et al.*, 2007):

$$NSE = 1 - [\sum_{i=1}^n (Y_i^{obs} - Y_i^{est})^2 / \sum_{i=1}^n (Y_i^{obs} - Y_i^{mean})^2] \quad (17)$$

$$E = 1 - [\sum_{i=1}^n |Y_i^{obs} - Y_i^{est}| / \sum_{i=1}^n |Y_i^{obs} - Y_i^{mean}|] \quad (18)$$

$$PBIAS = [\sum_{i=1}^n (Y_i^{obs} - Y_i^{est}) / \sum_{i=1}^n (Y_i^{obs})] \times 100 \quad (19)$$

where Y_i^{obs} and Y_i^{est} are defined as above, Y_i^{mean} is the average of observed data in the record, and n is the total number of observations. NSE quantifies the squared difference between the estimated and observed values normalized by the variance of observations. A model that perfectly matches available observations has $NSE = 1$, with values < 0 representing inferior levels of fit (Krause *et al.*, 2005; Moriasi *et al.*, 2007). Despite being the most common measure, NSE is very sensitive to large errors (*i.e.*, large differences between estimated and observed values) due to the square operation. To deal with this issue, the second measure E uses absolute differences instead of squared differences. As with NSE, a perfectly accurate model has $E = 1$. Unless otherwise noted, results documented herein are based on E. Finally, PBIAS measures the average tendency of the estimates to be larger or smaller than observations. A perfectly accurate model has $PBAIS = 0$. In this work, for each constituent (6 in total) at each site (9 in total), the three performance measures were calculated for each model (13 in total) in each replicate run (30 for each of three considered sampling strategies).

4. Results and Discussion

This section is organized as follows. In **Section 4.1**, we describe two cases where modified models show major improvement over the original model. In **Section 4.2**, we present the overall performance of all models based on results at all nine sites. Focus here is on the effects of model

choices on estimation performance. For brevity, the presented results are associated with sampling strategy “A” unless otherwise noted. In **Section 4.3**, we elaborate the effects of sampling strategies on model performance.

4.1. Selected Cases with Major Improvement in Performance

4.1.1. Case 1: LTFA Model for NO_x Estimation in Grand River

The first case considered here is NO_x in Grand River. For this parameter, concentration residuals from the original WRTDS model appear to fluctuate around zero over time, indicating low bias for the original model (**Fig. 3a**). There exists, however, a clear negative correlation (Spearman’s $\gamma = -0.27$) between the original model residuals and LTFA values (**Fig. 3b**). In other words, large positive LTFA values correspond to negative residuals from the original model, and vice versa. Such correlation is likely reflective of a “storage-and-then-release” effect. Specifically, for days with negative LTFAs, the watershed is relatively dry in the preceding 1-year and NO_x is more likely to have accumulated during the dry period (*i.e.*, less regular “flushing”). Consequently, observed NO_x concentrations on such days tend to be higher for a given flow than those predicted by the original model (*i.e.*, positive residuals). Conversely, for days with large positive LTFAs, relatively wet watershed conditions existed in the preceding 1-year (relative to the entire record), and this likely corresponds with more regular “flushing” of NO_x and less storage. Thus, observed concentrations on these days are likely to be lower than those predicted by the original model (*i.e.*, negative residuals).

Given the above considerations, we hypothesized that the original WRTDS model can be improved by adding LTFA per **Equation 2**. This hypothesis was validated by comparing residuals of the LTFA model and those of the original model (**Fig. 3c**). A more focused look at the majority of data with residual values in the range of 0 – 2.0 mg/L (**Fig. 3d**) clearly reveals

more points below the 1:1 reference line, reflecting smaller positive residuals (*i.e.*, less under-estimation) for the LTFA model. Such improvements are achieved primarily for days with highly negative LTFAs, as shown by red (as opposed to green) colors in **Fig. 3c** and **3d**. This is consistent with the discussion above that the original model tends to under-estimate concentrations for days with strongly negative LTFAs. By taking into account the antecedent discharge effect, the LTFA model effectively alleviates that issue. Conversely, for days with positive LTFAs, the LTFA model appears to exacerbate the issue of over-estimation; however, such undesirable cases are much less frequent. Moreover, improvement with the LTFA model is reflected by the time series of annual flow-weighted concentration – compared with the original model, the LTFA model shows annual NO_x concentration estimates that follow concentration observations much more closely, with markedly improved modeling of extreme concentrations (**Fig. 3e**).

Overall, the LTFA model provides major improvement over the original model for NO_x estimation in Grand River, as quantified using numerical measures in **Table 3**. Compared with the original model, the LTFA model has larger NSE and E values for both concentration and flux. In addition, the LTFA model has much a smaller absolute PBIAS for flux.

4.1.2. Case 2: STFA Model for Cl Estimation in Maumee River

The second case considered here is Cl in Maumee River. Similar to the case presented above, concentration residuals from the original model appear to fluctuate around zero (**Fig. 4a**). In this case, however, there exists a clear positive correlation ($\gamma = 0.48$) between the original model residuals and STFA values (**Fig. 4b**). In other words, negative STFAs correspond to negative residuals from the original model. Note that in the case of STFA, the comparison is between the current day (as X_{T_1} in **Equation 3**) and the monthly antecedent discharge (as X_{T_2} in **Equation 3**),

which can be contrasted with the LTFA, where the annual antecedent discharge (as X_{T_1}) is compared to the entire discharge record (as X_{T_2}). Hence, with STFA, a positive (rather than negative) residual corresponds to relatively wet day but a drier antecedent month, whereas with LTFA, negative residual corresponds to a dry antecedent year relative to the full record. As a result, the positive STFA values are what now suggest the dry antecedent conditions of a “storage-and then-release” effect, as opposed to the negative LTFA values for the NO_x case above. In particular, a negative STFA now represents a relatively wet condition in the preceding 1-month and reflects a period with sustained “flushing” or loss of storage. Consequently, observed Cl concentrations on such days tend to be lower than those predicted by the original model (*i.e.*, negative residuals). These interpretations are consistent with the case of LTFA above. Other analyses (results summarized subsequently) revealed that STFA was less effective than LTFA for estimation of NO_x at Grand River but that STFA was more effective than LTFA for estimation of Cl at Maumee. We hypothesize that such contrasts reflect differences in response times of the two different constituents in the two different watershed systems. In terms of watershed size alone, the finding might seem somewhat counter-intuitive, because Grand River is the smaller basin (**Table 1**) yet is better understood in terms of LTFA. These results suggest, perhaps not surprisingly, that parameters other than watershed size controls the time scale at which antecedent discharge is relevant toward regulating riverine concentrations. In this case, the constituent of interest (NO_x vs. Cl) is also important, and a reasonable explanation might be that Cl response is more sensitive to short-term antecedent discharge relative to the present discharge, whereas NO_x processing is more sensitive to the past-year discharge relative to the long-term record. The mechanistic underpinnings of these statistical results deserve further investigation.

As with the NO_x case presented above, the residual-STFA correlation for Cl in Maumee River led us to hypothesize that the original WRTDS model could be improved by specifically incorporating STFA per **Equation 2**. Again, the hypothesis was validated by the comparison – see **Fig. 4c-4d** – and as before, there are evidently more points below the 1:1 reference line, which represent cases where the STFA model has smaller positive residuals (*i.e.*, less model under-estimation) than the original model. Such improvements are generally achieved for days with positive STFAs, as shown with green color. Thus, the STFA model effectively improves the estimation by taking into account the antecedent discharge effect. Conversely, the STFA model appears to exacerbate the issue of over-estimation for days with negative STFAs, but again such undesirable cases are less frequent.

In addition, one can again conduct a comparison of the time series of modeled versus observed values of annual flow-weighted Cl concentration as a good overall evaluation of model performance. The results (**Fig. 4e**) reveal that the STFA model estimates follow observed annual concentrations much more closely than do the original model estimates, with markedly improved modeling of extreme concentrations. Moreover, our quantitative measures of fit for the full record again reveal that the STFA model has larger NSE and E values for both concentration and flux as well as smaller absolute PBIAS values for both concentration and flux (**Table 3**).

4.2. Performance Comparison for All Model Runs: Effects of Model Choices

Here we present the overall performance of all models based on results for all nine sites. For brevity, the presented results are associated with sampling strategy A unless otherwise noted. Conclusions are similar based on the other two sampling strategies (see **Fig. S1-S2**). For quantitative comparison with the original model, it is useful to calculate the ratio of E-values between each modified model and the original model for each replicate run and for each site (*i.e.*,

30 runs/sites x 9 sites = 270 cases). These 270 ratios are shown with boxplots in **Fig. 5**. Simple guidelines for model evaluation were developed. Specifically, the modified models are considered to show (1) major improvement, (2) moderate improvement, and (3) inferior performance, if the E-value ratio falls to the following regions: (1) ratio > 1.2 (as indicated by blue bars in **Fig. 5**), (2) $1 < \text{ratio} < 1.2$ (grey bars), and (3) ratio < 1.0 (red bars), respectively.

In addition, Spearman's γ was calculated to quantify the correlation between original model residuals and each proposed flow variable for each replicate run and for each site, which can provide some indication with respect to if a certain flow variable may improve the original model (see discussion in **Section 4.1**). For better comparison of correlation strengths, we use boxplots (**Fig. 6**) to summarize the absolute correlations (*i.e.*, $|\gamma|$) for all 270 model runs (*i.e.*, 30 runs/sites x 9 sites). In general, a flow variable with a high $|\gamma|$ may have a high potential for model improvement.

4.2.1. Constituents with Major Improvement: Cl and NO_x

The modified models show generally major improvements in the estimation of Cl and NO_x. For Cl (**Fig. 5a**), most of the modified models have E-value ratio (modified model versus original model) > 1.0, indicating that the modified models are generally effective in improving Cl estimation. Among all modified models, ADF, STFA, and FA1 show the highest E-value ratios, with about 25%-50% falling into the category of major improvement. The ADF model, in particular, provides a roughly even split between “moderate” and “major” improvement. For NO_x (**Fig. 5b**), the LTFA model shows the best overall performance, followed by AnnualFA, DailyFA, and FA100. These four models generally have E-value ratio > 1.0. Among these models, LTFA falls into the category of major improvement most frequently. Many other models,

however, show some occasions of inferior performance relative to the original model (*i.e.*, E-value ratio < 1.0), including MTFA, STFA, SeasonFA, FA1, ADF, BFI, and particularly dQ/dt .

These results are consistent with those obtained from correlation analysis. For Cl, highest $|\gamma|$ values are associated with STFA, FA1, and ADF (**Fig. 6a**). In terms of the correlation sign, STFA consistently shows positive γ with the original model residuals (**Fig. S3a**). For NO_x , LTFA shows the highest $|\gamma|$ among all variables (**Fig. 6b**) and the γ sign is always negative (**Fig. S3b**). These γ signs are consistent with the two cases presented in **Section 4.1**.

Comparing LTFA with STFA, we observe a phenomenon previously discussed in the context of our two case examples – *i.e.*, that LTFA is more effective for NO_x estimation, whereas STFA is more effective for Cl estimation. The key distinction between these two terms lies in the temporal scale for quantification of antecedent conditions. Specifically, LTFA compares average discharges in the preceding 1-year and in the entire record (**Equation 4**), whereas STFA compares discharge on the day of estimation and average discharge in the preceding 1-month (**Equation 6**). Thus, “wet antecedence” is a wet month relative to the estimation day for STFA, but a wet year relative to the entire record for LTFA. The relatively longer temporal scale of antecedent relevance for NO_x than Cl may reflect the relevance of long-term biogeochemical processes that convert ammonia and organic nitrogen to NO_x , but will likely also reflect that NO_x is dominantly applied to pervious land through atmospheric deposition and fertilizer application, such that it is more likely to reflect transport through deep and long pathways in the groundwater system (Böhlke and Denver, 1995; Sanford and Pope, 2013). By contrast, Cl is heavily influenced by winter road salt applications in urban and suburban areas, which are either rapidly flushed to the river channel or temporally stored in the shallow groundwater system and later slowly released via baseflow (Corsi *et al.*, 2015). To verify these or other possible explanations,

further investigation is required to better understand and compare the source and fate of the two constituents in these watersheds as well as watersheds elsewhere that may have very different sizes and land uses. Additionally, it might be useful to consider alternative definitions of FA terms – *i.e.*, comparisons among several FAs that consider antecedent conditions of different durations relative to the entire record.

4.2.2. Constituents with Moderate Improvement: TKN, TP, and SS

For TKN (**Fig. 5c**), TP (**Fig. 5e**), and SS (**Fig. 5f**), the ADF model shows the best performance among all considered models, with E-value ratios that are generally > 1.0 , although a large proportion of the ratios show only moderate improvement. BFI and STFA also show improved estimation of TKN and TP. The other models, however, show some occasions of inferior performance relative to the original model. In particular, the dQ/dt model is inferior to the original model more often than not, with some E-value ratios far less than 1.0.

Again, these results are consistent with those from correlation analysis. For all three constituents (TKN, TP, and SS), ADF shows the highest $|\gamma|$ with the original model residuals (**Fig. 6c, 6e, 6f**) and the signs are generally negative (**Fig. S3c, Fig. S3e, Fig. S3f**), which is similar to the case of LTFA discussed in **Section 4.1.2** and reflective of the “storage-and-then-release” effect.

4.2.3. Constituent without Improvement: SRP

For soluble reactive phosphorus (SRP), none of the modified models shows consistent improvement over the original model (**Fig. 5d**). In fact, these models have approximately equal probability of being better or worse than the original model. As elsewhere, the results are consistent with those of the correlation analysis: these proposed variables show generally small $|\gamma|$ (**Fig. 6d**) and the correlations generally have mixed signs (**Fig. S3d**). This may indicate that

SRP transport have been more influenced by factors other than antecedent conditions, such as physico-chemical sorption and biological uptake processes in the soil horizon and in the river channel. Another possible explanation is that, among all the six constituents analyzed, SRP has the most occurrences of non-positive concentration values (ranging 0%~12% among the nine sites with a median of 7%). These values were excluded from our analysis, which may have biased the samples' probability distributions and thus the quantification of models' performance.

4.3. Performance Comparison for All Model Runs: Effects of Sampling Strategies

4.3.1. Original Model: Performance under Different Sampling Strategies

Estimation performance of the original model clearly varies with sampling strategies, as shown in **Fig. 7**. Based on E-values for concentration, estimation performance generally follows the order of strategy C > strategy B > strategy A, especially for SS and SRP (**Fig. 7a**). Based on E-values for flux, estimation performance follows the same order, with SS, TP, and SRP showing the strongest improvement with strategy C (**Fig. 7b**). Similarly, based on absolute percent bias (|PBIAS|), estimation performance for both concentration and flux also follows the same order, especially for SS, TP, and SRP (**Fig. 7c-7d**). By contrast, such improvement with strategy C is least strong for the two dissolved constituents, *i.e.*, Cl and NO_x, particularly for concentration estimation.

These results provide several important insights with respect to the effects of sampling strategy on estimation performance. First, the overall better performance with strategy B relative to strategy A illustrates the value of collecting additional water quality samples (*i.e.*, 20 vs. 12 samples per year). Second, the overall better performance with strategy C than strategy B indicates the value of routinely collecting highflow samples, assuming that the number of total samples per year is fixed (*i.e.*, 20). Consequently, strategy C always has the best estimation

performance (*i.e.*, largest E-value and smallest |PBIAS|). Therefore, increased sampling frequency and special emphasis on storm sampling should continue to be recommended for river monitoring implementation. An area where further investigation may be needed, however, is in regard to finding an optimum ratio of storm sampling versus random sampling and to searching for possible dependence of results on constituent of interest and watershed characteristics.

The results presented herein demonstrate that the effects of sampling strategy on estimation performance vary considerably with the constituent of interest. Among all six constituents considered, SS generally shows overall the least satisfactory performance (lowest E-value and highest |PBIAS| for flux) under all three sampling strategies. Following SS, TP and SRP also show large |PBIAS| values. Interestingly, these three constituents also show strong differences in estimation performance among the three sampling strategies. By contrast, Cl, NO_x, and TKN show the smallest |PBIAS| for both concentration and flux and also show very weak differences in estimation performance among the three sampling strategies. These patterns undoubtedly relate to the different mechanisms of release, transformation, and transport of these constituents. One useful measure to consider in this regard is the coefficient of variation (CV) for observed concentrations. Based on monitoring data at the nine sites, SS has the largest CV among all constituents, followed by TP and SRP (**Fig. 8**). From statistical theory, a larger CV means that accurate estimation will require a larger number of concentration samples (Haan, 2002). Also, a larger CV indicates that a better coverage of the full hydrograph (*i.e.*, both regular flow events and episodic stormflow events) may be required. This interpretation further highlights the benefits of adopting strategy C for river water quality sampling, especially for SS, TP, and SRP.

4.3.2. All Models: Performance under Different Sampling Strategies

Estimation performance of the modified models also varies with sampling strategies, as shown in **Fig. 9-10** and **Fig. S4**. For brevity, these figures only compare the median values of each performance measure based on all 270 model runs (*i.e.*, 30 runs/sites x 9 sites) for each sampling strategy. The performance measures include E-value for concentration (**Fig. 9**), E-value for flux (**Fig. S4**), and |PBIAS| for flux (**Fig. 10**).

In terms of E-values for concentration, the above-documented improvements with the modified models are observed under all three sampling strategies (**Fig. 9a-9c**). Specifically, the ADF, STFA, and FA1 models show major improvement in Cl estimation. The LTFA model shows major improvement in NO_x estimation. The ADF model shows moderate improvement for SS, TP, and TKN. By contrast, none of the modified models can effectively improve SRP estimation. Comparing the three sampling strategies directly, median E-values for concentration are generally higher for strategy B than A (**Fig. 9d**), generally higher for strategy C than B (**Fig. 9f**), and of course, generally higher for strategy C than A (**Fig. 9e**), and these are most pronounced for SS and SRP. In terms of E-values for flux, the results are similar, with SS, SRP, and TP showing considerable improvement with strategy C (**Fig. S4**).

In terms of |PBIAS| for flux, estimation performance is also generally the best under strategy C, with absolute bias consistently < 5% (**Fig. 10c**). Notably, the dQ/dt model performs much worse than the original model under sampling strategies A and B (**Fig. 10a-10b**). This candidate variable seems to be a confounding variable in the sense that it compromises the power of the original model's existing independent variables (*i.e.*, time, discharge, and season) in capturing the variability of the independent variable (*i.e.*, concentration). For SS in particular, |PBIAS| values are about 40% and 20% under strategy A and strategy B, respectively, which are much higher than those of any of the other models. Such inefficacy (high bias) disappears only under

strategy C, where routinely collected stormflow samples are available (**Fig. 10c**). Comparing the three sampling strategies directly, |PBIAS| medians for flux are generally smaller for strategy B than A (**Fig. 10d**), smaller for strategy C than A (**Fig. 10e**), and smaller for strategy C than B (**Fig. 10f**), and these patterns are most pronounced for SS, SRP, TP, and TKN (**Fig. S4**).

5. Conclusion and Final Remarks

In this work, we developed and evaluated alternative statistical models for estimation of riverine concentration and flux by accounting for antecedent discharge conditions. Results reveal that estimation performance varies with both model choice and sampling strategy. In terms of model choice, the modified models show general improvement over the original model under all three sampling strategies. Major improvements were achieved for NO_x by the LTFA model and for Cl by the ADF model and the STFA model. By contrast, no such achievement was achieved for SRP by any proposed model. In terms of sampling strategy, performance of all models (including the original) was generally best using strategy C and worst using strategy A, and especially so for SS, TP, and SRP, confirming the value of routinely collecting stormflow samples.

Accurate estimation of riverine constituent concentrations and fluxes has been an active research area for decades and will remain a critical challenge to the hydrological community (Cohn *et al.*, 1992; Cohn *et al.*, 1989; Hirsch, 2014; Hirsch *et al.*, 2010). The major contribution of this work is to provide a comprehensive set of statistical evidence for supporting the incorporation of antecedent discharge into the WRTDS model for improved concentration and flux estimation, thereby combining the advantages of these two recent developments in water quality modeling. In recognition of the need for additional future work, several limitations of this study are acknowledged. First, this study has been limited to only six constituents for nine

watersheds within a specific geographical location. Model performance may vary for constituents not covered here. In addition, more studies need to be carried in different types of watershed in other geographical regions to place these results into a more generalizable context to inform further improvement of estimation methods. (In this regard, however, there are unfortunately few (if any) data of comparable resolution and duration as the Heidelberg set studied here.) Second, all modified models contain only one additional flow variable for the sake of model parsimony. It is possible that a mixture of these flow terms can better incorporate export dynamics at different temporal scales and thus provide additional improvement. Third, this work examined three sampling strategies that are representative of common monitoring practice, but not strategies with different sampling frequencies (*e.g.*, weekly *vs.* monthly), record lengths (*e.g.*, 10 *vs.* 30 years), or proportions of routine versus storm sampling. Further understanding of these aspects can help inform the allocation of valuable (and often limited) resources toward river water quality monitoring. Fourth, in addition to the time, discharge, and season windows in the current WRTDS model, an additional window may be introduced for the new variable on antecedent discharge, such that higher weights are assigned to concentration samples that have similar antecedent discharge conditions to the estimation day. Fifth, this work is limited to consideration of WRTDS true-condition estimates. In the current WRTDS framework, there is a flow-normalization algorithm for water quality trend analysis, which is also implemented based on **Equation 1**, *i.e.*, with time, discharge, and season as model covariates but without any antecedent discharge variable. We expect that antecedent discharge variables may also be considered toward use in the flow-normalization algorithm. Last but not least, this work has focused entirely on traditional monitoring data that derive from infrequently measured water quality samples. With increasing use of new technology that allows very high-

frequency or even continuous data collection from in-situ probes, a practical challenge facing the hydrological community is how to combine the use of both traditional low-frequency data and in-situ high-frequency data toward riverine water quality analysis and load estimation. Moving forward, there is need for additional research to advance understanding on these aspects and to incorporate all available understanding into the development and upgrade of software that can be broadly applied.

Appendix A. Supplementary Material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/xxx>.

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Tables

Table 1. Details of the nine river monitoring sites.

Station Number	River site	Drainage area, mi ²	Upstream land use (percent)			
			Agricultural	Urban	Wooded	Other
04193500	Maumee River at Waterville, OH	6,330	89.9	1.2	7.3	1.6
03231500	Scioto River at Chillicothe, OH	3,854	80.2	4.6	12.9	2.3
03271601	Great Miami River below Miamisburg, OH	2,685	82.1	4.7	10.3	2.9
04198000	Sandusky River near Fremont, OH	1,251	84.1	0.9	13.0	2.0
04176500	River Raisin near Monroe, MI	1,042	79.0	2.3	14.0	4.7
04208000	Cuyahoga River at Independence, OH	707	30.4	9.6	50.1	9.9
04212100	Grand River near Painesville, OH	685	40.0	0.9	45.2	13.1
04197100	Honey Creek at Melmore, OH	149	85.6	0.6	12.5	1.3
04197170	Rock Creek at Tiffin, OH	34.6	82.0	0.9	16.1	1.0

Table 2. Temporal coverages of water quality data at the nine river monitoring sites.

River site	First sampled day	Last sampled day	Total number of sampled days (Average number of sampled days per year)					
			Cl	NO _x	TKN	SRP	TP	SS
Maumee River at Waterville, OH	1975- 01-10	2014- 12-31	11,447 (345)	10,898 (328)	11,397 (343)	10,752 (324)	11,462 (345)	11,429 (344)
Scioto River at Chillicothe, OH	1996- 04-23	2015- 01-03	4828 (258)	4816 (258)	4812 (257)	4785 (256)	4825 (258)	4803 (257)
Great Miami River below Miamisburg, OH	1996- 04-22	2015- 04-04	6356 (335)	6357 (335)	6309 (333)	6317 (333)	6349 (335)	6333 (334)
Sandusky River near Fremont, OH	1974- 10-02	2014- 12-31	12,055 (301)	12,054 (300)	10,719 (275)	11,319 (281)	12,363 (307)	12,315 (306)
River Raisin near Monroe, MI	1982- 03-06	2014- 12-31	8,268 (281)	8,213 (279)	8,228 (280)	7,621 (259)	8,269 (281)	8,236 (280)
Cuyahoga River at Independence, OH	1981- 11-04	2014- 12-31	10,856 (327)	10,890 (329)	10,838 (327)	10,627 (321)	10,896 (329)	10,862 (328)
Grand River near Painesville, OH	1988- 02-16	2006- 08-10	5,621 (304)	5,435 (294)	5,545 (300)	4,977 (269)	5,598 (303)	5,565 (301)
Honey Creek at Melmore, OH	1976- 01-28	2014- 12-31	11,604 (342)	11,617 (343)	11,353 (342)	10,647 (314)	11,623 (343)	11,499 (339)
Rock Creek at Tiffin, OH	1982- 10-11	2014- 12-31	9,249 (349)	8,911 (336)	9,202 (347)	8,697 (328)	9,251 (349)	9,191 (347)

Table 3. Summary of cases with major improvements in model estimation performance. Each case shows results from on one selected model run.

Case	Model	Concentration			Flux		
		NSE	E	PBIAS	NSE	E	PBIAS
Grand River NO _x	Original Model	0.28	0.18	2.3	0.73	0.63	-2.2
	LTFA Model	0.41	0.27	1.7	0.83	0.71	0.83
Maumee River Cl	Original Model	0.54	0.36	0.46	0.83	0.72	1.7
	STFA Model	0.77	0.54	0.43	0.89	0.77	1.3

Figures

Fig. 1. Time series of (a) observed daily discharge and (b-m) derived antecedent discharge variables for Maumee River at Waterville, OH. Only the period of 2005-2009 is shown for visual clarity. Panel (a) is repeated in both columns to aid comparison with the derived flow variables.

Fig. 2. Example time series of (a) the original NO_x concentration data (black open circle) and (b-d) three types of concentration subsets (non-black solid circle) in Maumee River at Waterville, OH between 2005 and 2006. Panels (b), (c), and (d) correspond to sampling strategies A, B, and C, respectively. See text for details.

Fig. 3. Comparison of the original WRTDS model and the *LTFA* (*long-term flow anomaly*) model for NO_x in Grand River near Painesville, OH. (a) Time series of residuals from the original model. (b) Relationship between the original model residuals and LTFA, as modeled with LOWESS curve (green line). Spearman's correlation coefficient (γ) is shown on the plot. (c) Comparison between the LTFA model residuals and the original model residuals. (d) An enlarged view of the first quadrant of panel (c). (e) Time series of annual concentration based on observed data, the original model, and the LTFA model.

Fig. 4. Comparison of the original WRTDS model and the *STFA* (*short-term flow anomaly*) model for Cl in Maumee River at Waterville, OH. (a) Time series of residuals from the original model. (b) Relationship between the original model residuals and STFA, as modeled with LOWESS curve (green line). Spearman's correlation coefficient (γ) is shown on the plot. (c) Comparison between the STFA model residuals and the original model residuals. (d) An enlarged view of the first quadrant of panel (c). (e) Time series of annual concentration based on observed data, the original model, and the STFA model.

Fig. 5. Boxplots of the ratio between the modified Nash-Sutcliffe efficiency (E) of each modified model and E -value of the original WRTDS model for the nine study sites for (a) Cl, (b) NO_x , (c) TKN, (d) SRP, (e) TP, and (f) SS. The E -value ratios are divided into three regions: (1) major improvement (ratio > 1.2 ; blue bar), (2) minor improvement ($1 < \text{ratio} < 1.2$; grey bar), and (3) inferior performance (ratio < 1.0 ; red bar). Each boxplot represents 30 replicates at each of the nine sites (*i.e.*, 270 cases) under sampling strategy A.

Fig. 6. Boxplots of the absolute value of Spearman's correlation ($|\gamma|$) between residuals from the original WRTDS model and each of the twelve proposed flow variables. Each boxplot represents 30 replicates at each of the nine sites (*i.e.*, 270 cases) under sampling strategy A.

Fig. 7. Performance of the original WRTDS model under each of the three sampling strategies. The performance is quantified with modified Nash-Sutcliffe efficiency (E) for (a) concentration and (b) flux and with absolute percent bias (|PBIAS|) for (c) concentration and (d) flux. Each boxplot represents 30 replicates at each of the nine sites (*i.e.*, 270 cases) under each sampling strategy.

Fig. 8. Boxplots of the coefficient of variation in observed daily discharge (Q) and constituent concentration data. Each boxplot summarizes nine coefficients, each of which is based on monitoring data at one of the nine sites.

Fig. 9. Performance of the original and modified WRTDS models under the three sampling strategies. Panels (a)-(c) summarizes the performance with medians of modified Nash-Sutcliffe efficiency (E) for concentration based on 30 replicates at each of the nine sites (*i.e.*, 270 cases) under each sampling strategy. Panels (d)-(f) compares the three sampling strategies directly using ratios of E median.

Fig. 10. Performance of the original and modified WRTDS models under the three sampling strategies. Panels (a)-(c) summarizes the performance with medians of absolute value of percent bias ($|PBIAS|$) for *flux* based on 30 replicates at each of the nine sites (*i.e.*, 270 cases) under each sampling strategy. Panels (d)-(f) compares the three sampling strategies directly using ratios of $|PBIAS|$ median.