Environ Monit Assess (2021) 193: 422
https://doi.org/10.1007/s10661-021-09199-4

A flow-weighted approach to generate daily total phosphorus loads in streams based on seasonal loads

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Received: 10 March 2021 / Accepted: 7 June 2021 / Published online: 15 June 2021

Abstract Phosphorus (P) is an essential nutrient for all forms of life but its over-enrichment can result in eutrophication of surface waters. For many watersheds around the world, some seasonal total P (TP) load datasets may exist but the continuous and multi-year daily TP concentrations and/or load datasets are not available due to the lacks of in situ P sensor measurement, time-consuming, and budget constraint. Traditionally, the seasonal TP loads are normally obtained with measuring daily TP concentrations for a couple of times within a season in a watershed, and then these daily TP concentrations along with their respective daily discharges are used to calculate the seasonal TP loads for the watershed. However, without the continuous and multi-year daily TP load dataset, development of total maximum daily load (TMDL) and calibration of watershed models for TP cannot be achieved. A flow-weighted method was developed (with detailed procedures) here to generate the daily TP loads based on the seasonal loads. The method was rigorously validated using the measured daily TP datasets from three different US Geological Survey gage stations. With very good statistical comparisons between the method predicted and field measured TP loads, we demonstrated that the flow-weighted method herein is a useful tool to disaggregate the seasonal TP loads into the daily TP loads when the measured daily TP data are not available while the TMDL development and model calibrations/validations are inevitable.

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Keywords Daily load · Flow-weighted method · Seasonal load · Total phosphorus

Introduction

Eutrophication of surface waters with excess nutrients is an issue of increasing environmental concern worldwide. Phosphorus (P) is an essential nutrient for all forms of life, but its over-enrichment can result in eutrophication of surface waters (Cui et al., 2015; Mueller & Helsel, 1996; Ouyang et al., 2013). Anthropogenic activities such as fertilizer application, dairy production, wastewater treatment, and industrial practices that use P for cleaning are the major sources of excess P entering into the surface waters (Domagalski et al., 2021; Ouyang et al., 2018). Disparate to the nitrogen, most surface waters have very low P concentrations due to its low water solubility, and a small increase in P concentrations could result in eutrophication of surface waters. Phosphorus in excess can lead to adverse environmental problems such as harmful algal blooms, low dissolved oxygen, fish kills, and loss of biodiversity in streams (Ouyang et al., 2006). Phosphorus enrichment in surface waters can also impair the uses of water for drinking, industry, agriculture, and recreation. To date, the commonly used approach to determine P concentration in streams is to manually collect samples and send them to a laboratory for analysis because there are no sensors and probes commercially available for real-time and/or in situ P measurements. As a result, the long-term and continuous measured daily total P (TP) concentrations in most watersheds around the world are not available although these daily concentrations and loads are essential to develop total maximum daily load (TMDL) for the P impaired watersheds.

Numerous mathematical models have been developed and applied to predict the fate, transport, and load of P and other nutrient species in watershed ecosystems (Arnold et al., 2015). Among the different models, AnnAGNPS (Ann-Agricultural Non-Point Source Pollution Model; Binger et al., 2015), APEX (Agricultural Policy Environmental eXtender; Williams & Izaurralde, 2006), HSPF (Hydrological Simulation Program-FORTRAN; Bicknell et al., 2001), SPARROW (SPAtially Referenced Regressions on Watershed attributes; Schwarz et al., 2006), and SWAT (Soil and Water Assessment Tool; Arnold et al., 2012) are the most commonly used watershed models. Although these models are the critical tools for estimating P status in watersheds, the applicability of these models depends on the availability of the long-term and continuous daily TP concentration and/or load datasets for model calibrations and validations. Unfortunately, these daily datasets are not available for most watersheds in the world, especially in the developing countries. For many watersheds, only seasonal TP load data may exist because of time-consuming and cost-prohibitive as well as the lack of in situ sensor for field P measurements. The seasonal TP loads are normally obtained with measuring TP concentrations for a couple of times within a season in a watershed. These daily TP concentrations are then multiplied with their respective daily discharges to yield the daily TP loads. The seasonal TP load is finally obtained by multiplying the average daily TP load by days for a given season.

A flow-weighted average is the average of a quantity after weighted proportional to a corresponding flow rate. For instance, if the daily TP concentrations are measured continuously from a stream, their flow-weighted mean TP concentration is the sum of the products of each measured daily TP concentration times its respective stream flow rate, and then divided by the sum of the measured flow rates. The flow-weighted approach has been used to calculate the average concentrations of water quality constituents in streams for years (Bhadha et al., 2017; Cassidy et al., 2018; Sether et al., 2004). For example, Sether et al. (2004) used the flow-weighted average nutrient and sediment concentrations to estimate the constituent loads in the Upper Red River at Pearley, Minnesota, USA, while Cassidy et al. (2018) assessed the efficacy of flow-weighted composite sampling approaches for TP in Norway, Sweden and Denmark. In addition, Aulenbach et al. (2016) developed approaches to estimate stream solute loads from five diverse small watersheds, Kerr et al. (2016) estimated stream solute loads using fixed frequency sampling regimes, and Li et al. (2019) proposed the sampling strategies and estimation algorithms to estimate total nitrogen load in a small agricultural watershed. Although these studies provide very useful information on the

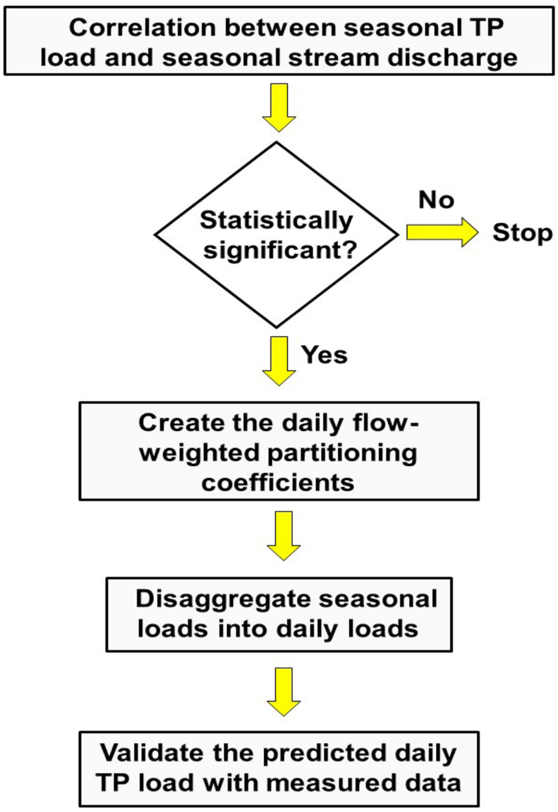

Fig. 1 A schematic diagram showing the four steps in developing the flow-weighted method

applications of the flow-weighted or similar computational method, a literature search reveals that no study has been devoted to partitioning the seasonal TP loads into the daily TP loads.

The goal of this study is to develop a computational method for generating daily TP loads from its seasonal loads using a flow-weighted approach. This method is essential for watershed TMDL development as well as for watershed model calibrations and validations when the multiple years and continuous measured daily TP concentrations and loads are absent. Such an absence is a rule rather than an exception for most watersheds in the world. The specific objectives were as follows: (1) test if the seasonal stream discharges are proportional to the seasonal TP loads for watersheds of interest using statistical analyses (this assumption is a prerequisite for applying this method); (2) determine the daily flow-weighted partitioning coefficients from daily and seasonal discharges; (3) disaggregate the seasonal TP loads into the daily TP loads using the daily flow-weighted partitioning coefficients; (4) validate the method using the measured daily TP datasets, and (5) apply the method to predict the daily TP loads for a location where the multiple-year and continuous measured daily TP loads are not available.

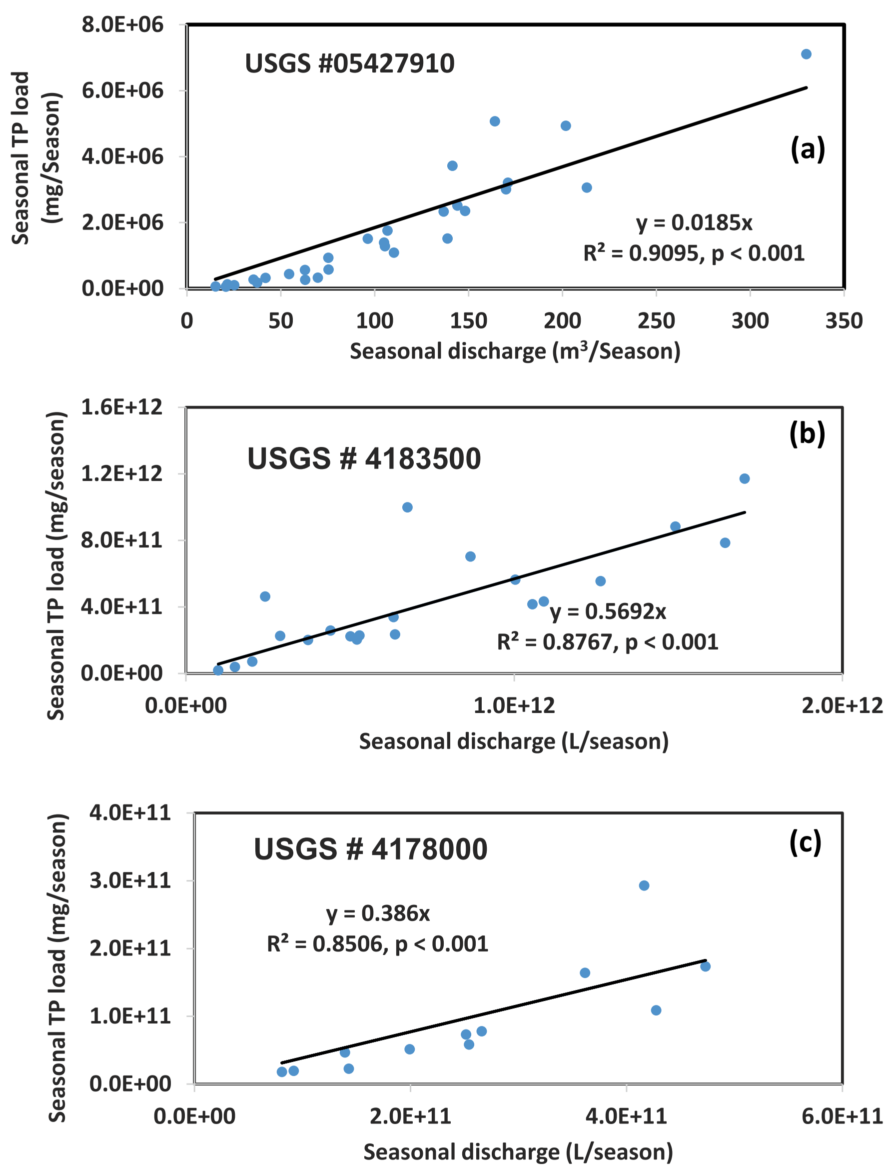

Fig. 2 Correlations between the seasonal discharges and the seasonal TP loads at the three USGS gage stations

Table 1 Excel spreadsheet calculations of daily partitioning coefficients and daily TP loads based on seasonal TP loads for the fall season at USGS #05427910

Date	Measured dally discharge (m^3/s)	Measured dally discharge volume (L)	Season	Measured seasonal discharge volume (L)	Dally flow-weighted partitioning coefficient	Measured seasonal TP load (mg)	Predicted dally TP load (mg)
9/1/2012	0.337407407	2.92E+07	Fall 2012	3.62E+09	8.06E−03	3.42E+08	2.75E+06
9/2/2012	0.355185185	3.07E+07			8.49E−03		2.90E+06
9/3/2012	0.377777778	3.26E+07			9.03E−03		3.08E+06
9/4/2012	0.381481481	3.30E+07			9.12E−03		3.11E+06
9/5/2012	0.381481481	3.30E+07			9.12E−03		3.11E+06
9/6/2012	0.353333333	3.05E+07			8.44E−03		2.88E+06
9/7/2012	0.320740741	2.77E+07			7.66E−03		2.62E+06
9/8/2012	0.324814815	2.81E+07			7.76E−03		2.65E+06
9/9/2012	0.407407407	3.52E+07			9.73E−03		3.33E+06
9/10/2012	0.403703704	3.49E+07			9.65E−03		3.30E+06
9/11/2012	0.418518519	3.62E+07			1.OOE−02		3.42E+06
9/12/2012	0.374074074	3.23E+07			8.94E−03		3.05E+06
9/13/2012	0.304814815	2.63E+07			7.28E−03		2.49E+06
9/14/2012	0.316296296	2.73E+07			7.56E−03		2.58E+06
9/15/2012	0.313333333	2.71E+07			7.49E−03		2.56E+06
9/16/2012	0.322962963	2.79E+07			7.72E−03		2.64E+06
9/17/2012	0.281111111	2.43E+07			6.72E−03		2.29E+06
9/18/2012	0.276296296	2.39E+07			6.60E−03		2.26E+06
9/19/2012	0.377777778	3.26E+07			9.03E−03		3.08E+06
9/20/2012	0.312592593	2.70E+07			7.47E−03		2.55E+06
9/21/2012	0.308888889	2.67E+07			7.38E−03		2.52E+06
9/22/2012	0.325185185	2.81E+07			7.77E−03		2.65E+06
9/23/2012	0.311851852	2.69E+07			7.45E−03		2.55E+06
9/24/2012	0.341111111	2.95E+07			8.15E−03		2.78E+06
9/25/2012	0.32	2.76E+07			7.65E−03		2.61E+06
9/26/2012	0.31037037	2.68E+07			7.42E−03		2.53E+06
9/27/2012	0.29	2.51E+07			6.93E−03		2.37E+06
9/28/2012	0.312592593	2.70E+07			7.47E−03		2.55E+06
9/29/2012	0.301111111	2.60E+07			7.19E−03		2.46E+06
9/30/2012	0.325925926	2.82E+07			7.79E−03		2.66E+06
10/1/2012	0.303703704	2.62E+07			7.26E−03		2.48E+06
10/2/2012	0.307407407	2.66E+07			7.35E−03		2.51E+06
10/3/2012	0.335555556	2.90E+07			8.02E−03		2.74E+06
10/4/2012	0.335555556	2.90E+07			8.02E−03		2.74E+06
10/5/2012	0.346296296	2.99E+07			8.27E−03		2.83E+06
10/6/2012	0.338148148	2.92E+07			8.08E−03		2.76E+06
10/7/2012	0.324444444	2.80E+07			7.75E−03		2.65E+06
10/8/2012	0.407407407	3.52E+07			9.73E−03		3.33E+06
10/9/2012	0.392592593	3.39E+07			9.38E−03		3.21E+06
10/10/2012	0.341481481	2.95E+07			8.16E−03		2.79E+06
10/11/2012	0.353703704	3.06E+07			8.45E−03		2.89E+06
10/12/2012	0.332592593	2.87E+07			7.95E−03		2.72E+06
10/13/ 2012	0.448148148	3.87E+07			1.07E−02		3.66E+06

Table 1 (continued)

Date	Measured dally discharge (m^3/s)	Measured dally discharge volume (L)	Season	Measured seasonal discharge volume (L)	Dally flow-weighted partitioning coefficient	Measured seasonal TP load (mg)	Predicted dally TP load (mg)
10/14/2012	1.144444444	9.89E+07			2.73E−02		9.34E+06
10/15/2012	1.088888889	9.41E+07			2.60E−02		8.89E+06
10/16/2012	0.625925926	5.41E+07			1.50E−02		5.11E+06
10/17/2012	0.574074074	4.96E+07			1.37E−02		4.69E+06
10/18/2012	0.844444444	7.30E+07			2.02E−02		6.89E+06
10/19/2012	0.740740741	6.40E+07			1.77E−02		6.05E+06
10/20/2012	0.633333333	5.47E+07			1.51E−02		5.17E+06
10/21/2012	0.562962963	4.86E+07			1.35E−02		4.60E+06
10/22/2012	0.614814815	5.31E+07			1.47E−02		5.02E+06
10/23/2012	0.7	6.05E+07			1.67E−02		5.71E+06
10/24/2012	0.655555556	5.66E+07			1.57E−02		5.35E+06
10/25/2012	0.681481481	5.89E+07			1.63E−02		5.56E+06
10/26/2012	0.740740741	6.40E+07			1.77E−02		6.05E+06
10/27/2012	0.633333333	5.47E+07			1.51E−02		5.17E+06
10/28/2012	0.6	5.18E+07			1.43E−02		4.90E+06
10/29/2012	0.577777778	4.99E+07			1.38E−02		4.72E+06
10/30/2012	0.514814815	4.45E+07			1.23E−02		4.20E+06
10/31/2012	0.496296296	4.29E+07			1.19E−02		4.05E+06
11/1/2012	0.5	4.32E+07			1.19E−02		4.08E+06
11/2/2012	0.481481481	4.16E+07			1.15E−02		3.93E+06
11/3/2012	0.47037037	4.06E+07			1.12E−02		3.84E+06
11/4/2012	0.459259259	3.97E+07			1.10E−02		3.75E+06
11/5/2012	0.459259259	3.97E+07			1.10E−02		3.75E+06
11/6/2012	0.492592593	4.26E+07			1.18E−02		4.02E+06
11/7/2012	0.462962963	4.00E+07			1.11E−02		3.78E+06
11/8/2012	0.496296296	4.29E+07			1.19E−02		4.05E+06
11/9/2012	0.440740741	3.81E+07			1.05E−02		3.60E+06
11/10/2012	0.485185185	4.19E+07			1.16E−02		3.96E+06
11/11/2012	0.681481481	5.89E+07			1.63E−02		5.56E+06
11/12/2012	0.874074074	7.55E+07			2.09E−02		7.14E+06
11/13/2012	0.592592593	5.12E+07			1.42E−02		4.84E+06
11/14/2012	0.548148148	4.74E+07			1.31E−02		4.47E+06
11/15/2012	0.52962963	4.58E+07			1.27E−02		4.32E+06
11/16/2012	0.503703704	4.35E+07			1.20E−02		4.11E+06
11/17/2012	0.462962963	4.00E+07			1.11E−02		3.78E+06
11/18/2012	0.459259259	3.97E+07			1.10E−02		3.75E+06
11/19/2012	0.474074074	4.10E+07			1.13E−02		3.87E+06
11/20/2012	0.481481481	4.16E+07			1.15E−02		3.93E+06
11/21/2012	0.47037037	4.06E+07			1.12E−02		3.84E+06
11/22/2012	0.52962963	4.58E+07			1.27E−02		4.32E+06
11/23/2012	0.411111111	3.55E+07			9.82E−03		3.36E+06
11/24/2012	0.437037037	3.78E+07			1.04E−02		3.57E+06
11/25/2012	0.451851852	3.90E+07			1.08E−02		3.69E+06
11/26/2012	0.422222222	3.65E+07			1.01E−02		3.45E+06

Table 1 (continued)

Date	Measured daily discharge (m^3/s)	Measured daily discharge volume (L)	Season	Measured seasonal discharge volume (L)	Daily flow-weighted partitioning coefficient	Measured seasonal TP load (mg)	Predicted daily TP load (mg)
11/27/2012	0.414814815	3.58E+07			9.91E−03		3.39E+06
11/28/2012	0.437037037	3.78E+07			1.04E−02		3.57E+06
11/29/2012	0.422222222	3.65E+07			1.01E−02		3.45E+06
11/30/2012	0.414814815	3.58E+07			9.91E−03		3.39E+06

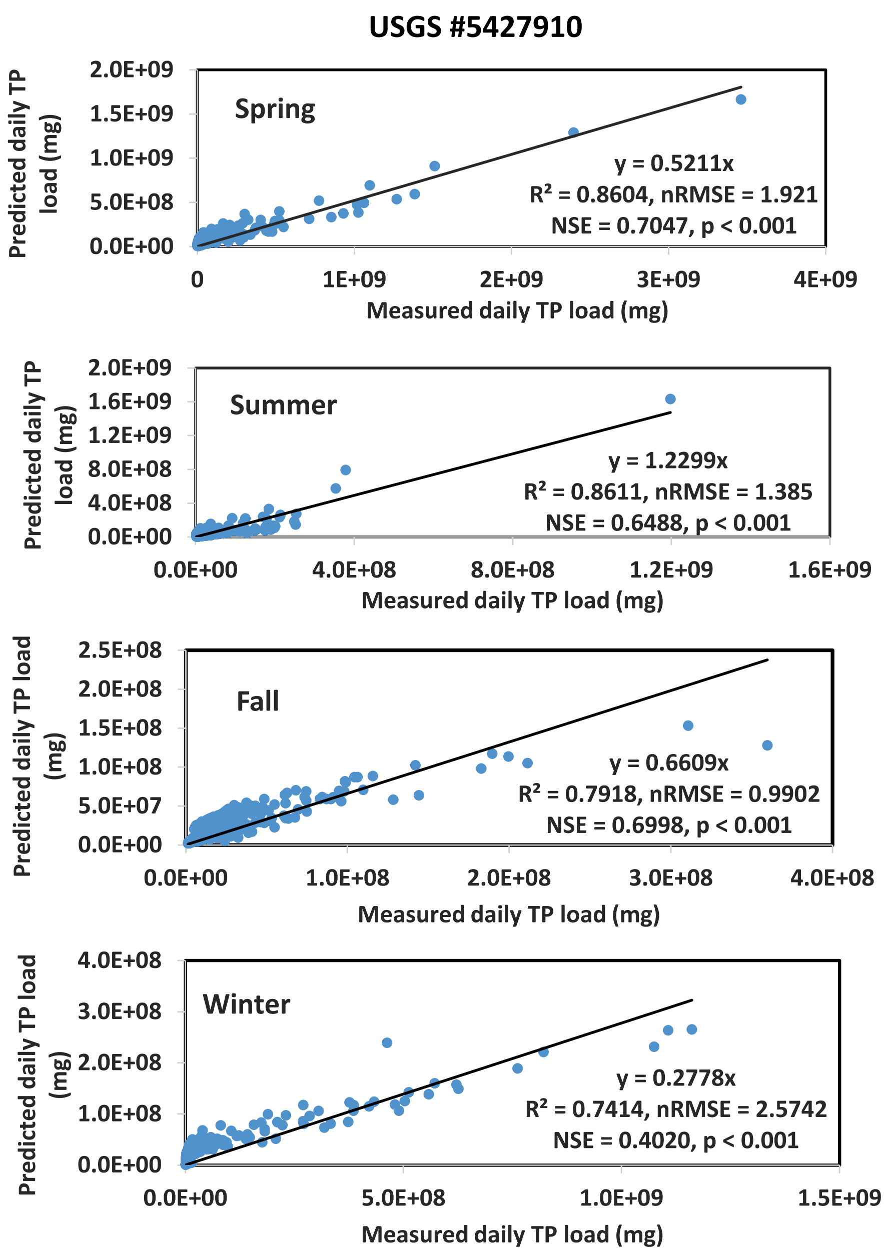

Fig. 3 Seasonal comparisons of the daily TP loads between the method predictions and the field measurements at USGS #05427910

Materials and methods

Study site

Three US Geological Survey (USGS) gage stations were selected for method development and validations. They are the USGS #05427910 at Sixmile Creek in Waunakee, Wisconsin, (https://waterdata.usgs.gov/wi/nwis/uv?site_no=05427910); USGS #04183500 at Maumee River in Antwerp, Ohio (https://waterdata.usgs.gov/nwis/inventory/?site_no=04183500&agency_cd=USGS); and USGS #4178000 at St. Joseph River near Newville, Indiana (https://waterdata.usgs.gov/nwis/inventory/?site_no=04178000). These national high priority gage stations were selected simply because they have multi-year and continuous measured daily TP concentration data available, which are crucial for method validations in this study. Additionally, the

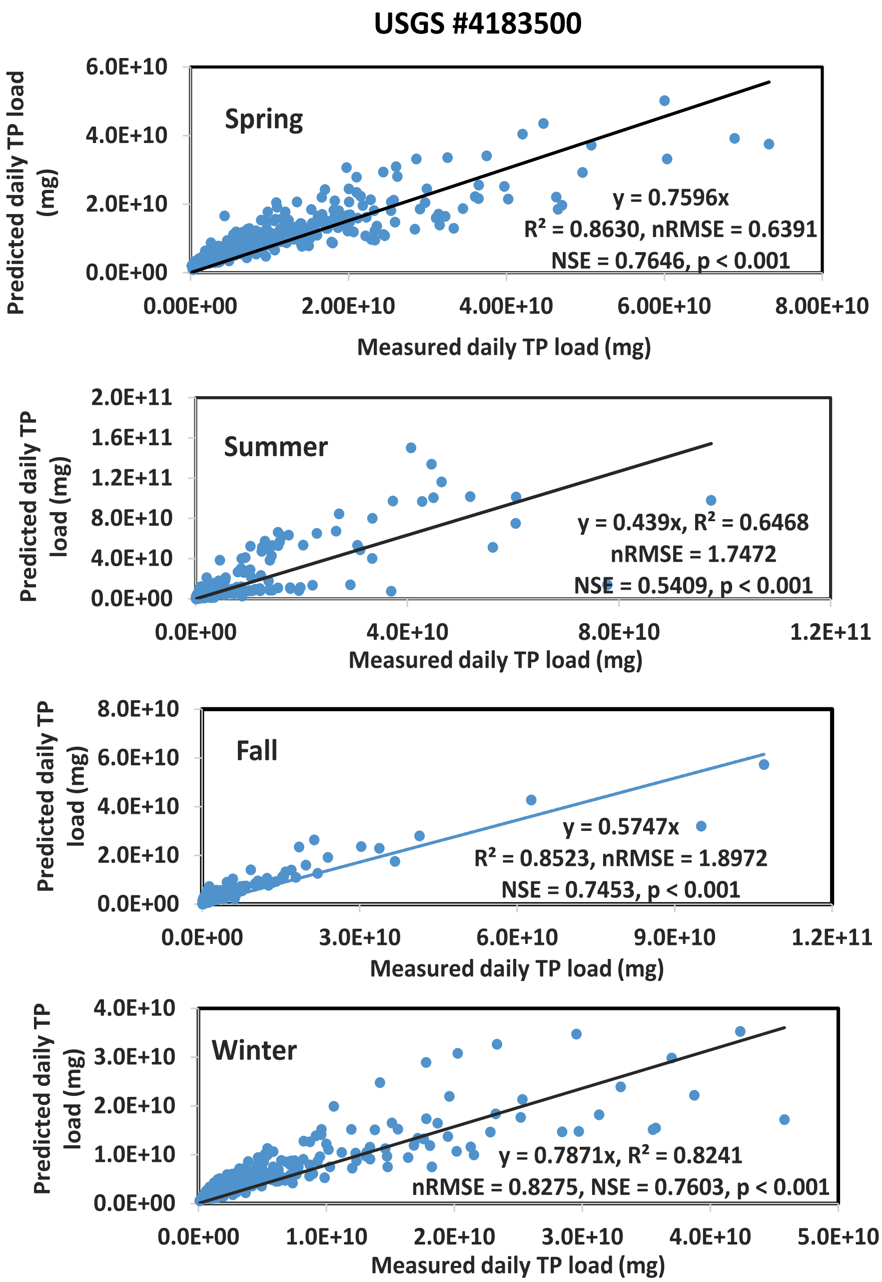

Fig. 4 Seasonal comparisons of the daily TP loads between the method predictions and the field measurements at USGS #04183500

USGS #07288500 (https://waterdata.usgs.gov/usa/nwis/uv?site_no=07288500) in the Big Sunflower River watershed (BSRW), Sunflower, MS, was selected for method application. This watershed is an intensive crop production area in mid-south USA, and its major water quality concerns are excess nutrients, organics, low dissolved oxygen, suspended solids, and pathogens (MDEQ, 2003; Ouyang et al., 2018). The reason for using this gage station is partially because there are some seasonal TP load data available from our measurements and partially because the water quality in the BSRW may be impaired (Ouyang et al., 2018).

Method development

To generate the daily TP loads from the seasonal TP loads, the following four steps are employed in this study (Fig. 1).

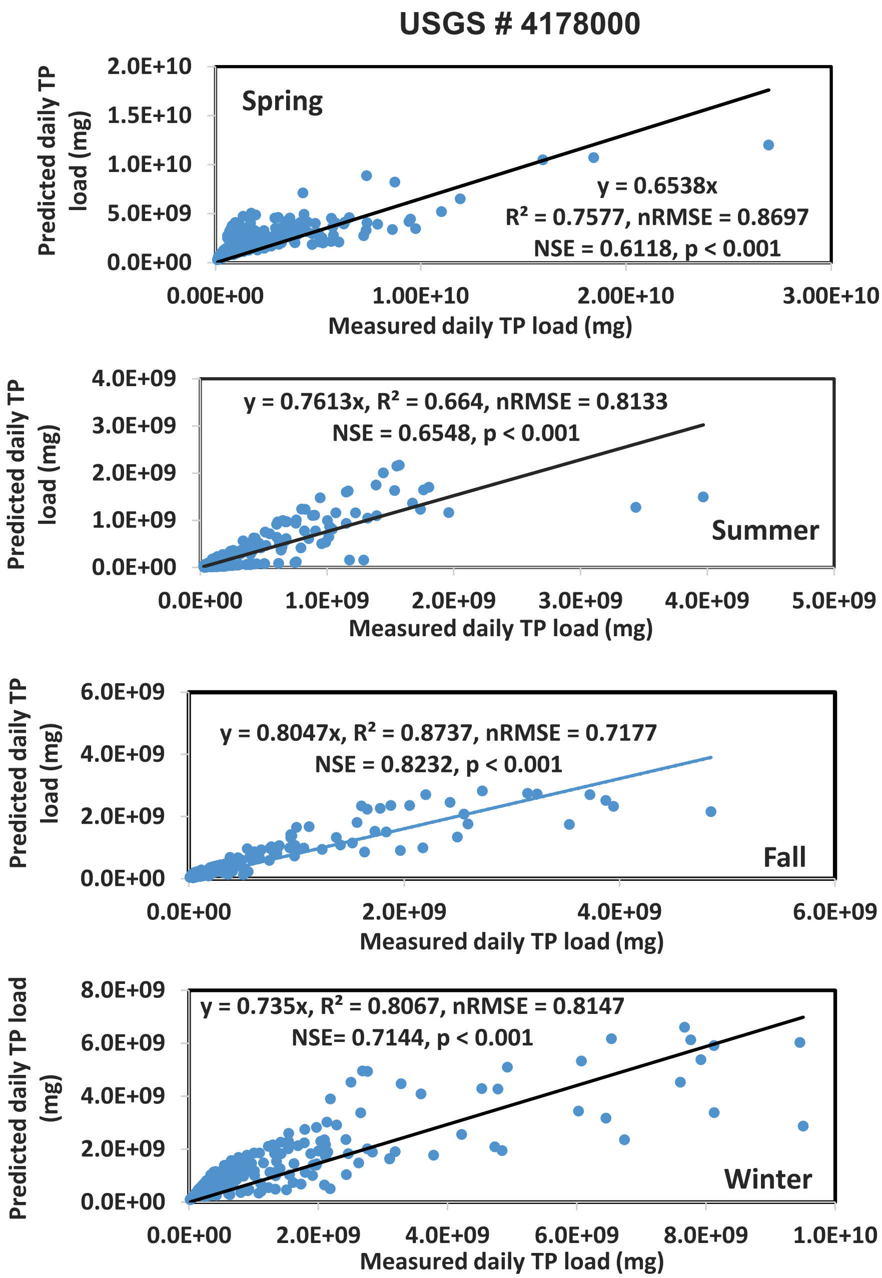

Fig. 5 Seasonal comparisons of the daily TP loads between the method predictions and the field measurements at USGS #04178000

1. Check the relationship between the seasonal stream discharge and the seasonal TP load in a dataset. The major assumption is that the seasonal TP load is proportional the seasonal stream discharge, which is a prerequisite for applying the flow-weighted method developed in this study. In particular, we assume that a linear correlation exists between the seasonal stream discharge and the seasonal TP load within the same season for a given watershed. The linear correlation is estimated using the traditional statistical measures such as coefficient of determination (R^2) and p value. Figure 2 shows the linear correlations between the seasonal stream discharges and the seasonal TP loads for the three gage stations. With the values of R^2 ranged from 0.85 to 0.91 and p values < 0.001, it is apparent that the linear correlations exist between the seasonal stream discharges and the seasonal TP loads in the datasets for those three gage stations.

2. Create the daily flow-weighted partitioning coefficients. Once the relationship between the seasonal stream discharge and the seasonal TP load has been determined to be acceptable for a dataset, the daily flow-weighted partitioning coefficients are calculated by the following: (a) summing up the daily discharge volume within a season for a given watershed to obtain the seasonal discharge volume for that watershed using Eq. (1):

$$D_{season} = \sum_i^n D_{daily}^i \tag{1}$$

and (b) dividing each daily discharge volume by the seasonal discharge volume to obtain the daily flow-weighted partitioning coefficients for that season as:

$$F_i = \frac{D_{daily}^i}{D_{season}} \tag{2}$$

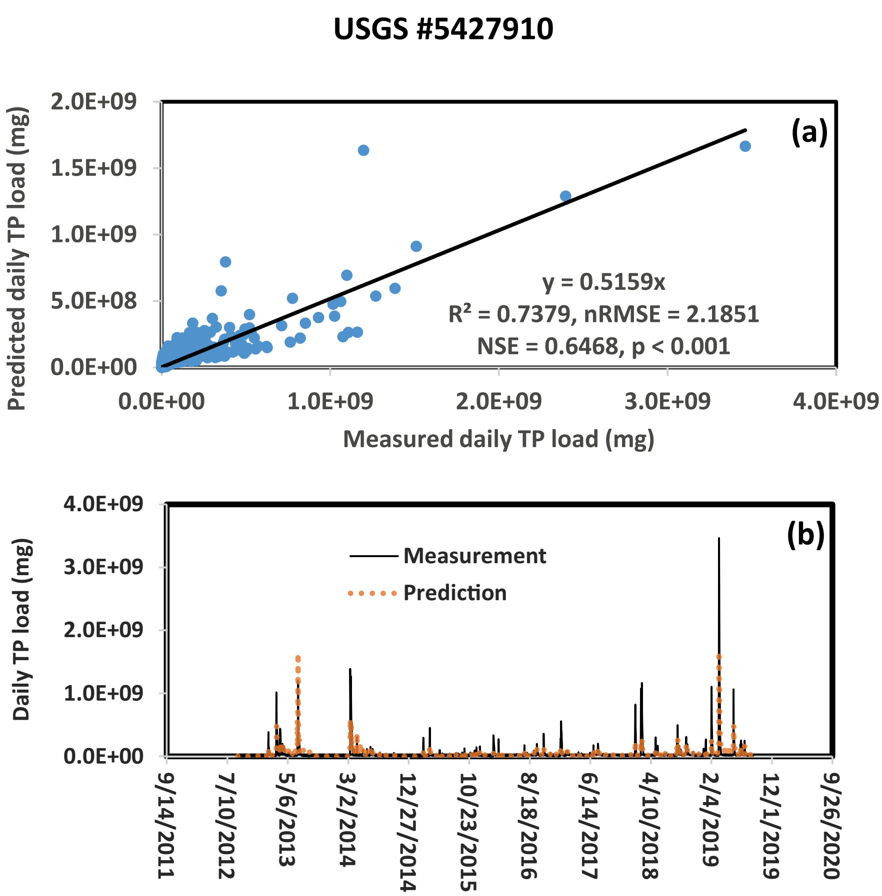

Fig. 6 Comparisons of the predicted and measured daily TP loads (**a**) and a time series plot of the predicted and measured daily TP loads (**b**) at the multi-year scale for USGS #05427910

where D_{season} is the seasonal discharge volume (L), D_{daily} is the daily discharge volume (L), i is the specific date, n is the number of dates in a season, and F is the flow-weighted partitioning coefficient. Table 1 shows the results of the flow-weighted partitioning coefficients for the fall season at the USGS #05427910, which were calculated in an Excel spreadsheet. The row values in column 3 ("Measured daily discharge volume") were obtained by multiplying the respective row values in column 2 ("Measured daily discharge") with 86,400 (seconds in a day) and 1000 (converted from m^3 to L). The value in column 5 ("Measured seasonal discharge volume") was the sum of column 3 for the entire fall season. The row values in column 6 ("Daily flow-weighted partitioning coefficient") were calculated by dividing the respective row values in column 2 with the value in column 5 using Eq. (2).

3. Determine daily TP load. The daily TP loads are calculated with multiplying the seasonal TP loads by the daily partitioning coefficients as:

$$L^i_{d-TP} = F_i L_{s-TP} \quad (3)$$

where $L_{d\text{-}TP}$ is the daily TP load (mg/day) and $L_{s\text{-}TP}$ is the seasonal TP load (mg/season). The predicted daily TP loads in the fall season for USGS #05427910 are given in column 8 (last column) of Table 1. More specifically, the row values in column 8 were obtained by multiplying the value in column 7 ("Measured seasonal TP load") with the respective row values in column 6.
4. Validate the method. A validation of the method is a process by comparing the predicted daily TP loads with the measured daily TP loads for the goodness-of-fit using R^2, normalized root mean square error (nRMSE), and Nash–Sutcliff efficiency (NSE). The nRMSE normalized by mean is calculated as (Taebi & Mansy, 2017):

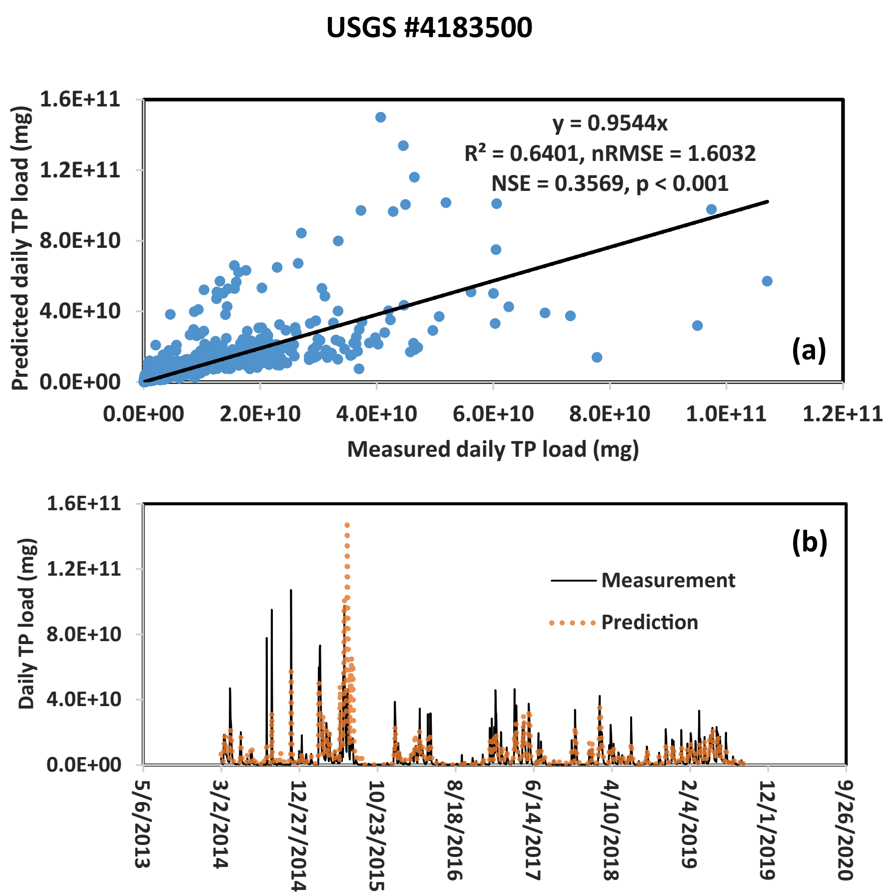

Fig. 7 Comparisons of the predicted and measured daily TP loads (**a**) and a time series plot of the predicted and measured daily TP loads (**b**) at the multi-year scale for USGS #04183500

$$nRMSE = \frac{1}{\overline{O}}\left(\sqrt{\frac{\sum_{i=1}^{n}\left(o_i - s_i\right)^2}{n}}\right) \quad (4)$$

where O_i is the field observation, S_i is the model prediction, $\overline{O}$ is the average of field observation, and n is the total number of field observations.

The NSE is given as (Nash & Sutcliffe, 1970):

$$NSE = 1 - \frac{\sum_{i=1}^{n}\left(o_i - s_i\right)^2}{\sum_{i=1}^{n}\left(o_i - \overline{o}\right)^2} \quad (5)$$

The NSE ranges from $-\infty$ to 1 with the values of 1 for a perfect fit, > 0.75 for very good fit, between 0.36 and 0.75 for a reasonable fit, and < 0.36 for unsatisfied fit of the model (Krause et al., 2005).

Two timeframes of the measured datasets were used to validate the method, one is from multiple years and the other is from different seasons. The validation results are given and discussed in the next section.

Results and discussion

Method validation with seasonal data

Comparisons of the method predicted and field measured daily TP loads within each season for USGS #5,427,910, USGS #4,183,500, and USGS #04178000 are given in Figs. 3, 4, and 5. In this study, the spring is from March to May, summer from June to August, fall from September to November, and winter from December to February. As shown on these figures, the statistical values ranged from 0.647 to 0.861 for R^2, from 0.639 to 2.574 mg for nRMSE, and from 0.402 to 0.823 for NSE, while the p values were all less than 0.001. These statistical values indicated that the flow-weighted method, in general, predicted the daily TP loads at each season reasonably

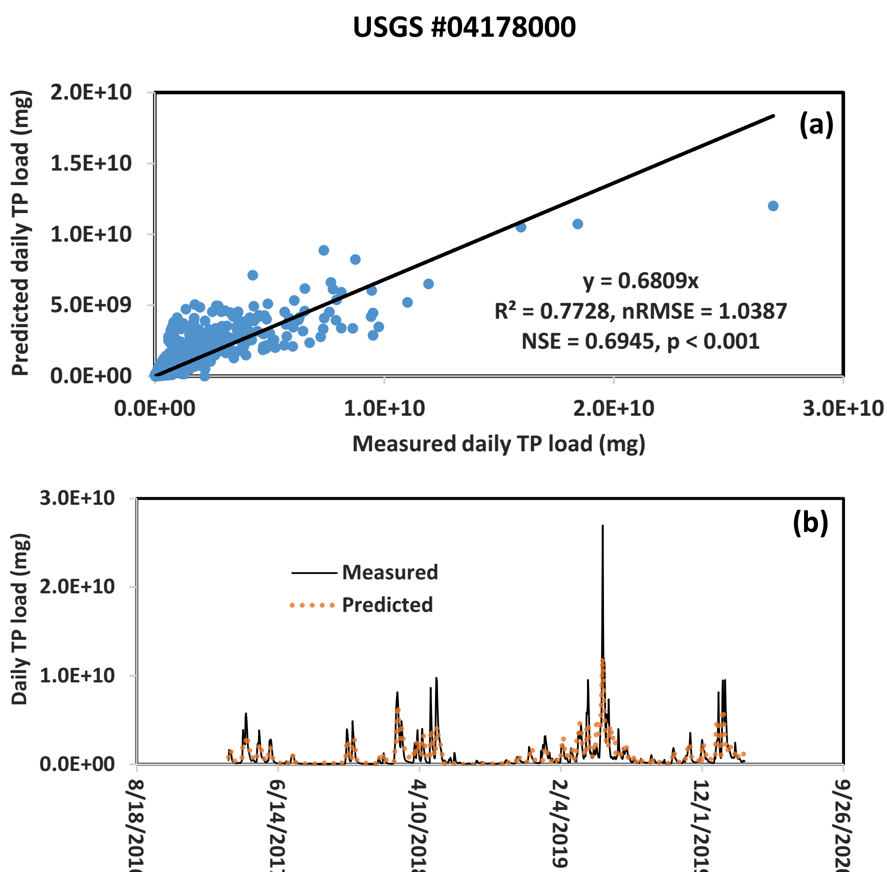

Fig. 8 Comparisons of the predicted and measured daily TP loads (**a**) and a time series plot of the predicted and measured daily TP loads (**b**) at the multi-year scale for USGS#04178000

well for all of the three gage stations used in this study.

Figures 3, 4, and 5 further reveals that the goodness-of-fit between the predicted and measured daily TP loads varied with seasons and stations. The best goodness-of-fit followed the order of spring (NSE = 0.705) > fall (NSE = 0.700) > summer (NSE = 0.645) > winter (NSE = 0.402) for USGS #5427910; spring (NSE = 0.863) > fall (NSE = 0.745) > winter (NSE = 0.760) > summer (NSE = 0.541) for USGS #4183500; and fall (NSE = 0.823) > winter (NSE = 0.714) > summer (NSE = 0.655) > spring (NSE = 0.612) for USGS #04178000. It is therefore apparent that the goodness-of-fit was site-specific and occurred depending on the amounts of TP entering into the streams. The more TP mass was in streams, the better the correlation between the stream discharge and the daily TP load would be, and thereby a better flow-weighted method prediction.

Method validation with multi-year data

To develop readers' confidences, the flow-weighted method was further validated using the multi-year measured datasets. Comparisons of the predicted daily TP loads with the measured daily TP loads from 2012 to 2019 for the three gage stations are shown in Figs. 6a, 7a, and 8a. The statistical values ranged from 0.640 to 0.773 for R^2, from 1.039 to 2.185 mg for nRMSE, from 0.357 to 0.695 for NSE, and < 0.001 for p. With these reasonably good statistical measures, we concluded that the predicted daily TP loads matched the measured daily TP loads well at the multi-year scale. A time series plot of the predicted and measured daily TP loads from 2012 to 2019 at the three gage stations are shown in Figs. 6b, 7b, and 8b. The timing and magnitude of the signals between the predicted and measured daily TP loads matched very well graphically. Results further confirmed that the flow-weighted method is feasible to generate the daily TP loads from their seasonal loads at a multi-year scale.

Comparisons of Fig. 2 with Figs. 6a, 7a, and 8a further disclose that the better correlations between the seasonal TP load and the seasonal discharge would result, in general, the better flow-weighted method predictions. For example, the value of R^2 was 0.910 between the seasonal TP load and the seasonal discharge (Fig. 2a) and was 0.738 between the predicted and measured daily TP loads (Fig. 6a) for USGS #5427910, whereas the value of R^2 was 0.877 between the seasonal TP load and the seasonal discharge (Fig. 2b) and was 0.640 (Fig. 7a) between the predicted and measured daily TP loads for USGS #4183500. Apparently, the flow-weighted method predicted the daily TP loads for USGS #5427910 ($R^2 = 0.738$) better than for USGS #4183500 ($R^2 = 0.640$). Results indicated that the accuracy of the method prediction relied on the correlation between the seasonal TP load and the seasonal discharge in the dataset.

Method application

There are currently no continuous measured daily TP concentration data available for the USGS #07288500 at the BSRW in Sunflower, MS. However, there are some sparsely and discontinuously

Table 2 Some discontinuous measured daily TP concentrations in every season from 1/1/2010 to 2/28/2011at USGS #07,288,500 in the Big Sunflower River watershed, MS. These sparse daily TP concentrations in conjunction with daily discharges were used to calculate the seasonal TP loads

Date	Season	Measured daily TP (mg/L)	Seasonal TP load (mg)
1/5/2010	Winter	0.32	1.33E+13
1/13/2010		0.41	
1/19/2010		0.39	
2/9/2010		0.25	
3/2/2010	Spring	0.27	7.10E+12
3/22/2010		0.24	
4/11/2010		0.69	
4/13/2010		0.36	
5/4/2010		0.25	
5/27/2010		0.22	
6/16/2010	Summer	0.2	4.05E+12
7/14/2010		0.22	
7/28/2010		0.29	
8/18/2010		0.24	
9/8/2010	Fall	0.3	8.55E+12
9/29/2010		0.28	
10/27/2010		0.23	
11/15/2010		0.23	
11/17/2010		0.18	
12/1/2010	Winter	0.8	5.83E+12
1/12/2011		0.18	
2/2/2011		1.29	
2/22/2011		0.27	

measured daily TP concentrations in every season for the time period from 1/1/2010 to 2/28/2011 at this station (Table 2). The sparse measured daily TP concentrations within a season were multiplied by the respective daily discharges to yield the daily TP loads. These partial daily TP loads were averaged and then multiplied by days in the season to yield the seasonal TP loads.

Figure 9a shows that a very good correlation ($R^2 = 0.918$) existed between the seasonal TP load and the seasonal discharge for the USGS #07288500. Result confirmed that this seasonal TP load dataset can be used to generate the daily TP loads according to Step 1 described in the "Method development" section. In other words, a good correlation between the seasonal TP loads and the seasonal discharges is a prerequisite to apply the flow-weighted method. The measured daily discharges and predicted daily TP loads at the USGS #07288500 are shown in Figs. 9b, c. An increase in daily discharge resulted in an increase in daily TP load. That is, the daily discharge had a very similar fluctuate pattern as that of the daily TP load. This occurred because the stream daily TP load was proportional to stream daily discharge.

Overall, the predicted daily TP loads are useful to the TMDL development and watershed model calibrations/validations. It should be pointed out that

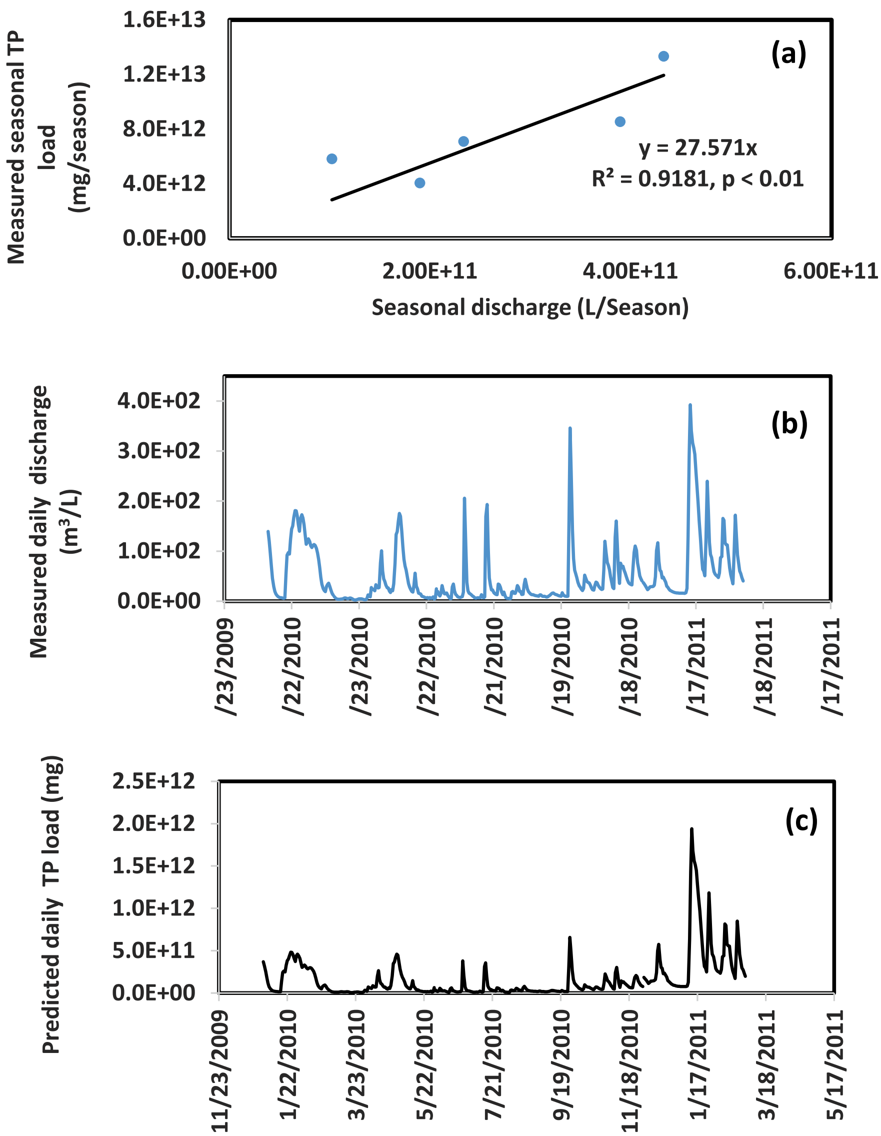

Fig. 9 Correlation of measured seasonal TP load with seasonal discharge (**a**), a time series plot of measured daily discharges (**b**), and a time series plot of predicted daily TP loads (**c**) for USGS #07288500

although the flow-weighted method developed in this study was used for generating the daily TP loads, there are potentials that the method could be applicable to generate daily sediment loads or other water quality constituents that have good correlations between their seasonal loads and the seasonal discharges. Further study is therefore warranted to tackle on this issue.

Summary

Phosphorus enrichment in surface waters can impair the uses of water for drinking, industry, agriculture, and recreation. The traditional approach to determine P concentration in streams is to manually collect samples and send them to a laboratory for analysis due to the lack of sensors for in situ P measurement, cost-prohibitive, and budget constraint. As a result, the long-term and continuous measured daily TP concentrations in most watersheds around the world are not available although these daily concentrations are essential to develop TMDL and calibrate/validate watershed models.

A flow-weighted method was developed to generate the daily TP loads from their seasonal TP loads. The method was validated at the seasonal and multi-year scales using field measured TP data from three different USGS gage stations. Based on the very good statistical comparisons, we concluded that the flow-weighted method developed in this study is capable to disaggregate the seasonal TP loads into the daily TP loads, which is a very useful tool when the measured daily TP datasets are not available but the TMDL development and model calibrations and validations are inevitable.

There is a potential to apply the flow-weighted method for generating daily sediment loads and/or other water quality constituent loads that have good correlations between their seasonal loads and the seasonal discharges. Further study is therefore warranted to tackle on this issue.

Data availability Data are available by the authors upon request.

References

Arnold, J. G., Youssef, M. A., Yen, H., White, M. J., Sheshukov, A. Y., Sadeghi, A. M., Moriasi, D. N., Steiner, J. L., Amatya, D. M., Skaggs, R. W., Haney, E. B., Jeong, J., & Arabi, & M., Gowda, P. H. . (2015). Hydrological processes and model representation: Impact of soft data on calibration. *Transactions of the ASABE, 58*(6), 1637–1660. https://doi.org/10.13031/trans.58.10726

Arnold, J. G., Moriasi, D. N., Gassman, P. W., Abbaspour, K. C., White, M. J., Srinivasan, R., Santhi, C., Harmel, R. D., Van Griensven, A., & Van Liew, M. W. (2012). SWAT: Model use calibration and validation. *Transactions of the ASABE, 55*(4), 1491–1508.

Aulenbach, B. T., Burns, D. A., Shanley, J. B., Yanai, R. D., Bae, K., Wild, A. D., Yang, Y., & Yi, D. (2016). Approaches to stream solute load estimation for solutes with varying dynamics from five diverse small watersheds. *Ecosphere*, *7*(6), e01298.

Bhadha, J. H., Sexton, A., Lang T. A., & Daroub, S. H. (2017). Capturing flow-weighted water and suspended particulates from agricultural canals during drainage events. *Journal of Visualized Experiments: JoVE*, (129). https://doi.org/10.3791/56088

Bicknell, B. R., Imhoff, J. C., Kittle, J. L., Jobes, T. H., & Donigian, A. S. (2001). Hydrological Simulation Program – FORTRAN HSPF Version 12 User's Manual. National Exposure Research Laboratory Office of Research and Development US Environmental Protection Agency Athens Georgia 30605 March 2001.

Bingner, R., Theurer, F., & Yuan, Y. (2015). AnnAGNPS technical processes Version 5.4. USDA.

Cassidy, R., Jordan, P., Bechmann, M., Kronvang, B., Kyllmar, K., & Shore, M. (2018). Assessments of composite and discrete sampling approaches for water quality monitoring. *Water Resources Management, 32*, 3103–3118.

Cui, L., Ouyang, Y., Yang, W., Huang, Z., Xu, Q., & Yu, G. (2015). Removal of nutrients from septic tank effluent with baffle subsurface-flow constructed wetlands. *Journal of Environmental Management, 153*, 33–39.

Domagalski, J. L., Morway, E., Alvarez, N. L., Hutchins, J., Rosen, M. R., & Coats, R. (2021). Trends in nitrogen phosphorus and sediment concentrations and loads in streams draining to Lake Tahoe California Nevada USA. *Science of The Total Environment*, *752*, 141815.

Kerr, J. G., Eimers, M. C., & Yao, H. (2016). Estimating stream solute loads from fixed frequency sampling regimes: The importance of considering multiple solutes and seasonal fluxes in the design of long-term stream monitoring networks. *Hydrological Processes, 30*(10), 1521–1535.

Krause, P., Boyle, D. P., Bäse, F. (2005) Comparison of different efficiency criteria for hydrological model assessment, Adv. Geosci., 5, 89-97.

Li, Y., Yen, H., Harmel, R. D., Lei, Q., Zhou, J., Hu, W., & Li, X. (2019). Effects of sampling strategies and estimation algorithms on total nitrogen load determination in a small agricultural headwater watershed. *Journal of Hydrology*, *579*, 124114.

MDEQ (Mississippi Department of Environmental Quality). (2003). Proposed TMDL for organic enrichment nutrients and sediment for the Big Sunflower River. June 2003. Mississippi Department of Environmental Quality, Office of Pollution Control, P. O. Box 10385, Jackson, Mississippi 39289.

Mueller, D. K., & Helsel, D. R. (1996). Nutrients in the Nation's water - too much of a good thing?. *US Geological Survey Circular*, *1136*.

Nash, J. E., & Sutcliffe, J. V. (1970). River flow forecasting through conceptual models part I—A discussion of principles. *Journal of Hydrology, 10*, 282–290.

Ouyang, Y., Nkedi-Kizza, P., Wu, Q. T., Shinde, D., & Huang, C. H. (2006). Assessment of seasonal variations in surface water quality. *Water Research, 40*(20), 3800–3810.

Ouyang, Y., Leininger, T. D., & Hatten, J. (2013). Real-time estimation of TP load in a Mississippi Delta stream using a dynamic data driven application system. *Journal of Environmental Management, 122*, 37–41.

Ouyang, Y., Feng, G., Parajuli, P., Leininger, T., Wan, Y., & Jenkins, J. N. (2018). Assessment of surface water quality in the Big Sunflower River watershed of Mississippi Delta using nonparametric analysis. *Water Air & Soil Pollution, 229*, 373.

Sether, B. A., Berkas, W. R., & Vecchia, A. V. (2004). *Constituent loads and flow-weighted average concentrations for major subbasins of the Upper Red River of the North Basin 1997–99*. US Department of the Interior, US Geological Survey.

Schwarz, G. E., Hoos, A. B., Alexander, R. B., & Smith, R. A. (2006). The SPARROW surface water-quality model: Theory, application and user documentation. *US Geological Survey Techniques and Methods Report Book, 6*(10), 248.

Taebi, A., & Mansy, H. A. (2017). Time-frequency distribution of seismocardiographic signals: A comparative study. *Bioengineering, 4*(2), 32. https://doi.org/10.3390/bioengineering4020032

Williams, J. R., & Izaurralde, R. (2006). The APEX model Watershed Models ed VP Singh and DK Frevert.

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