



# A simple approach to estimate daily loads of total, refractory, and labile organic carbon from their seasonal loads in a watershed

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## Abstract

Loads of naturally occurring total organic carbons (TOC), refractory organic carbon (ROC), and labile organic carbon (LOC) in streams control the availability of nutrients and the solubility and toxicity of contaminants and affect biological activities through absorption of light and complex metals with production of carcinogenic compounds. Although computer models have become increasingly popular in understanding and management of TOC, ROC, and LOC loads in streams, the usefulness of these models hinges on the availability of daily data for model calibration and validation. Unfortunately, these daily data are usually insufficient and/or unavailable for most watersheds due to a variety of reasons, such as budget and time constraints. A simple approach was developed here to calculate daily loads of TOC, ROC, and LOC in streams based on their seasonal loads. We concluded that the predictions from our approach adequately match field measurements based on statistical comparisons between model calculations and field measurements. Our approach demonstrates that an increase in stream discharge results in increased stream TOC, ROC, and LOC concentrations and loads, although high peak discharge did not necessarily result in high peaks of TOC, ROC, and LOC concentrations and loads. The approach developed herein is a useful tool to convert seasonal loads of TOC, ROC, and LOC into daily loads in the absence of measured daily load data.

**Keywords** Daily load · Labile carbon · Method · Organic carbon · Refractory carbon

## Introduction

Agricultural, forest, industrial, and urbanization practices are in some cases responsible for excess nutrients (e.g., nitrogen

and phosphorus) and toxic chemicals discharged from terrestrial sources into streams and rivers, resulting in stream eutrophication, oxygen deficit, and contamination (Jackson and Pringle 2010). The fate, transport, and load of naturally occurring total organic carbon (TOC) play a pivotal role in management of eutrophication and remediation of contaminants. TOC is generally considered to be an important parameter of river water quality (Ouyang 2003; Ouyang et al. 2006). It contributes significantly to acidity of natural waters through organic acids (Eshleman and Hemond 1985; Kerekes et al. 1986), biological activities through absorption of light, and water chemistry through complexation of metals and production of carcinogenic compounds with chlorine. In addition, by forming organic complexes, TOC can influence nutrient availability and control the solubility and toxicity of contaminants (Moore 1989). Elevated TOC concentration in soils, sediments, and streams has been attributed to diverse inputs from throughfall, stemflow, inappropriate animal waste applications and disposal, forest clear cutting, agricultural practices, and different land use patterns (Moore and Jackson 1989). Furthermore, degradation, re-polymerization, and oxidation of litter and soil organic matter are also a major organic carbon

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source (Dunnivant et al. 1992; Grant 1997). TOC in rivers comes both from allochthonous sources (e.g., land use pattern and forest clear cutting) and from autochthonous sources (e.g., in situ production by phytoplankton and macrophytes). The net transport of TOC through a river represents the balance between the allochthonous inputs, the autochthonous production, the consumption during biological respiration, and the burial in sediments (Maki and Hermansson 1994).

Traditionally, TOC is divided into two groups: dissolved organic carbon (DOC) and particulate organic carbon (POC). DOC is a strong complexing agent for toxic metals, such as iron, copper, aluminum, zinc, and mercury (Ouyang 2012). It can also increase the weathering rate of minerals and increase solubility and thus mobility and transport of many metals and organic contaminants (Drever 1988). DOC has been linked to acidification processes and to heterotrophic productivity and respiration in small streams, which are important in influencing rates of C cycling and CO<sub>2</sub> emissions (Dalzell et al. 2005). POC is a landmark feature of some rivers (Trefry et al. 1992) and can act as a carrier to transport contaminants along rivers, thus decomposition of POC associated with contaminants in water columns and sediments plays an important role in river water quality (Ouyang 2003).

Biologically, TOC in natural water is often categorized, with respect to bacterial degradability, into labile and refractory organic carbon (ROC). Labile organic carbon (LOC) consists of dissolved organic C, which ranges from 0.1 to 5 mg/L in interstitial waters (Hendrickson et al. 2007). It can be readily utilized as an energy and C source by heterotrophic microorganisms (Johns and Skogley 1994). ROC decomposes slowly, primarily in the sediments, and may contribute to sediment oxygen demand years after decomposition. In general, LOC can be utilized in a short timeframe relevant to water quality processes, whereas ROC decomposes very slowly and is essentially inert (Wetzel and Likens 1990). In order to accurately estimate eutrophication and oxygen deficit of streams and rivers, LOC must be distinguished from ROC as the latter is in an inactive form, which may delay eutrophication and oxygen deficit (Hendrickson et al. 2007).

In recent years, several studies have been conducted to estimate the TOC export in stream systems. Gorniak (2017) examined the spatial and temporal patterns of TOC along the Vistula River in Central Europe. This author demonstrated that TOC export in wet years is five times higher than in dry years and argued that river flooding and droughts play an important role in TOC load to the southern Baltic Sea. Zhang and Blomquist (2018) investigated the spatial and temporal patterns of organic carbon export to the Chesapeake Bay for the period from 1984 to 2016. These authors found that TOC export is dominated by DOC in most of the tributaries. These studies have provided valuable insights into our understanding of TOC and DOC in riverine ecosystems. Additionally, several mathematical models have also been

introduced to describe the fate, transport, and load of TOC in watershed ecosystems (Jenkinson and Rayner 1977; van Veen et al. 1984; Grant 1997; Li et al. 1997). Today, the most commonly used model to estimate soil carbon (C) and nutrient cycles is the CENTURY model and later DayCent model (Parton et al. 1987, 1994). CENTURY is a general model of plant-soil nutrient cycling that can be used to simulate organic C and nutrient dynamics for different types of ecosystems, including grasslands, agricultural lands, forests, and savannas. It consists of a soil organic matter/decomposition sub-model, a water budget model, a grassland/crop sub-model, a forest production sub-model, and several management and event scheduling functions. CENTURY simulates the flow of organic C, nitrogen (N), phosphorus (P), and sulfur (S) through the model's compartments. This model, however, does not include TOC and nutrient loads from watersheds into tributary or river ecosystems. DAYCENT is the daily time-step version of the CENTURY biogeochemical model and simulates fluxes of C and N among the atmosphere, vegetation, and soil (Parton et al. 1994).

Ouyang (2003) investigated the dynamic load of TOC from the Deep Creek Watershed into the Lower St. Johns River (LSJR), FL, USA, using the modified St. Johns River Watershed Assessment Model. Simulations showed that rainfall events have decisive effects on TOC load into St. Johns River. Effects of rainfall events on daily changes of TOC are minimal in winter but are profound in late summer. Results suggest that TOC load into the river is not only a rainfall-driven but also a temperature-driven biological process. Shih et al. (2010) applied Spatially Referenced Regression on Watershed Attributes (SPARROW) model to estimate the sources, transport, and fate of the long-term mean annual load of TOC in streams of the conterminous USA. These authors argued that stream photosynthesis is the largest source of the TOC yields exported to the coastal waters, while the terrestrial sources are dominant in all other regions used in their study. Although the DayCent and other models have improved our understanding of soil C and nutrient cycles in grasslands, agricultural lands, forests, and savannas and TOC load in streams and rivers, these models do not account for LOC and ROC cycles and loads in streams, which is a prerequisite for accurately estimating eutrophication and oxygen deficit of surface waters.

There are currently very few measured daily loads of LOC and ROC in watersheds and only seasonal loads of TOC are measured for certain watersheds due to a variety of reasons including time and expense constraints. The seasonal loads are obtained by measuring TOC concentrations seasonally for several locations within a watershed and couple times within a season and then averaged and multiplied with seasonal discharge to obtain the seasonal loads. The goal of this study was to develop a simple cost-effective method to estimate daily load of TOC, LOC, and ROC from seasonal loads. Our

specific objectives are to (1) determine the daily partitioning coefficients of TOC, ROC, and LOC loads based on daily water discharge and seasonal discharge. These coefficients are then used to convert seasonal TOC, ROC, and LOC loads into their daily loads; (2) validate this conversion method using the measured TOC, ROC, and LOC data; and (3) apply the method to predict daily loads of TOC, ROC, and LOC in watersheds from their seasonal loads. The seasons are referred to spring from March to May, summer from June to August, fall from September to November, and winter from December to February in this study.

## Materials and methods

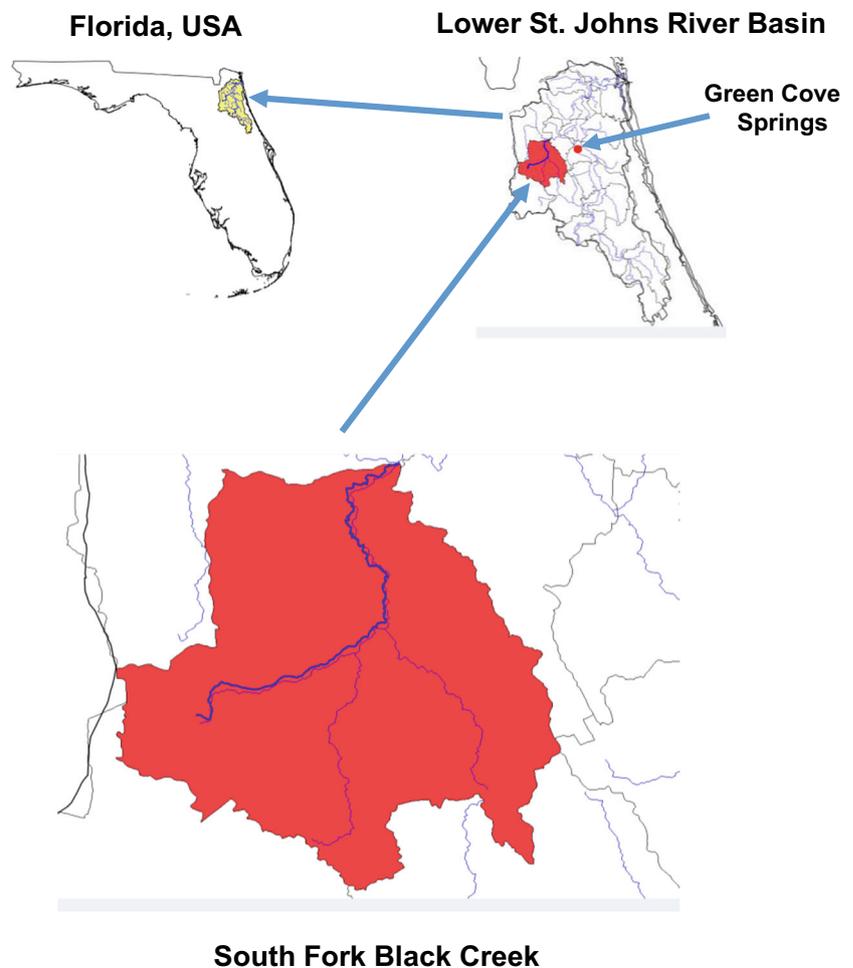
### Study site

Based on the data availability, the Lower St. Johns River Basin (LSJRB) was selected for the purpose of this study, which is located in northeast FL between 29 and 30° north latitude and between 81 and 82° west longitude (Fig. 1). This basin area is approximately 2800 mi.<sup>2</sup> and the counties that

have the majority of their area within the basin boundary are Duval, Clay, St. Johns, Putnam, Flagler, and Volusia. The drainage area of this basin is about 2200 mi.<sup>2</sup>. Major land uses are forestry and agriculture, rapidly transitioning to urban with intense urbanization in the downstream area.

In support of a water management plan developed by the St. Johns River Water Management District (SJRWMD) of FL, some seasonal loads of TOC data from field measurements for the LSJRB are available. In this study, two different study sites, namely the South Fork Black Creek (SFBC) watershed and Green Cove Springs monitoring station within the LSJRB (Fig. 1), were selected because there were sufficient measured TOC, ROC, and LOC data availability for method development and validation. The discharges were measured from the stream gage stations (station IDs: BSF and Green Cove Spring 73644) that were initiated by the JSRWMD, whereas the TOC, ROC, and LOC concentrations from 1996 to 2012 used in this study were sampled by the SJRWMD field crews and analyzed at the SJRWMD laboratory in Palatka, FL. The surface water sampling and analysis procedures are in compliance with the Standard Operation Protocols developed by US-EPA (<https://water.usgs.gov/>

**Fig. 1** Location of the study area showing the lower St. Johns River Basin, South Fork Black Creek watershed, and Green Cove Springs water quality monitoring station



[owq/methods.html](#)). It should be noted that the TOC, ROC, and LOC were not measured continuously from 1996 to 2012. Most of the water quality data are available at <https://www.sjrwmd.com/data/water-quality/> or upon request to SJRWMD.

### Method development

To convert seasonal loads of TOC, ROC, and LOC into their daily loads, we first obtained daily partitioning coefficients. This was accomplished by assuming a similar time series pattern for the daily hydrograph as that of the daily pollutograph within the same season for a given watershed. In other words, daily percentages of water discharge are assumed to be proportional to daily loads of TOC, ROC, and LOC within the same season and watershed. Equations used for calculating seasonal discharge and daily partitioning coefficients are given as:

$$S_D = \sum_n^i D_i \tag{1}$$

$$P_i = D_i/S_D \tag{2}$$

where  $S_D$  is the seasonal discharge ( $m^3$ /season),  $i$  is the specific date,  $n$  is the number of dates in a season,  $D$  is the daily discharge ( $m^3$ /day), and  $P$  is the partitioning coefficient. By summing up the daily water discharges within a season for a given watershed, we obtained the seasonal water discharge for that watershed. We then divided each daily water discharge by that seasonal water discharge to obtain the daily partitioning coefficients for that season.

Once the daily partitioning coefficients were obtained, daily loads of TOC, ROC, and LOC were calculated by multiplying seasonal loads of TOC, ROC, and LOC by the daily partitioning coefficients, assuming a similar time series pattern for the daily hydrograph as that of the daily loading-graph within the same season and watershed. Equations used for calculating daily load of TOC, ROC, and LOC are given below:

$$L_i = P_i S_L \tag{3}$$

where  $L$  is the daily load ( $g$ /day) and  $S_L$  is the seasonal load ( $g$ /season). After daily loads of TOC, ROC, and LOC are calculated, their daily concentrations can be obtained using the following equation:

$$C_i = L_i/D_i \tag{4}$$

where  $C$  is the concentration of TOC, ROC, or LOC ( $mg/L$ ) at the  $i^{th}$  date.

Table 1 shows calculations of daily partitioning coefficients and daily TOC loads for the SFBC watershed from January 1, 1997 to February 5, 1997. Values in columns B, C, and E were from field measurements, whereas values in columns D and F

were calculated. Daily partitioning coefficients in column D were obtained by dividing column B (daily discharge) by column C (seasonal discharge), while daily TOC loads in column F were obtained by multiplying column D (daily partitioning coefficients) by column E (seasonal TOC load). To avoid a long list, only the first seasonal conversion was presented in Table 1. After daily TOC, ROC, and LOC loads were calculated, their daily concentrations were obtained from Eq. (4).

## Results and discussion

### Method validation

**Daily concentration comparison** Comparisons of method predictions with field measurements for TOC, ROC, and LOC concentrations were performed to develop user confidence in this method (Figs. 2, 3 and 4). The daily measured TOC, ROC, and LOC concentrations for certain dates were obtained from the SFBC watershed in the LSJRB. A statistical analysis of the method predictions and field measurements for TOC concentrations yielded the correlation coefficient ( $R^2$ ) = 0.612,  $p$  value < 0.001, and RMSE (root mean square error) = 0.025  $mg/L$  (Fig. 2a). Similar results were obtained for ROC and LOC. That is, the statistical parameters were  $R^2$  = 0.692,  $p$  value < 0.001, and RMSE = 0.017  $mg/L$  for ROC (Fig. 3a) and  $R^2$  = 0.763,  $p$  value < 0.001, and RMSE = 0.024  $mg/L$  for LOC (Fig. 4a). The method predictions agreed reasonably well with field measurements for this highly non-linear and dynamic watershed. A graphic comparison of the peaks and valleys of TOC, ROC, and LOC concentrations between method predictions and field measurements yielded a good match between timing and magnitude of signal (Figs. 2b, 3b and 4b). It should be noted that an outlier with a measured value of 2.5  $mg/L$  for LOC was observed in Fig. 4a We attributed this to certain hydrological and meteorological circumstances. This value is within the range of 5  $mg/L$  for LOC with undeveloped land use reported by Hendrickson et al. (2007) at the similar location.

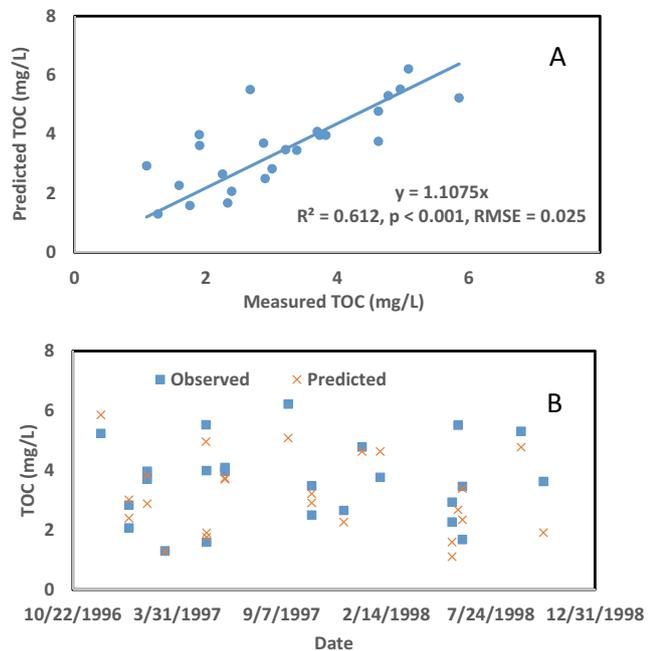
**Daily load comparison** A comparison of method predictions with field measurements for TOC, LOC, and ROC loads was also performed to further validate the method (Figs. 5 and 6). Measured data were from the SFBC watershed within the LSJRB basin. Much better statistical results were obtained for this comparison as compared to the case of TOC, ROC, and LOC concentrations. The values of  $R^2$  and RMSE were 0.991 and 0.006 for TOC, 0.992 and 0.006 for ROC, and 0.862 and 0.005 for LOC (Fig. 5), supporting the conclusion that the method predicted daily TOC, ROC, and LOC loads were in good agreement with the field measurements. The close agreement of peaks and valleys of TOC, ROC, and LOC loads between method predictions and field

**Table 1** Calculations of daily partitioning coefficients and daily TOC loads for the South Fork Black Creek watershed

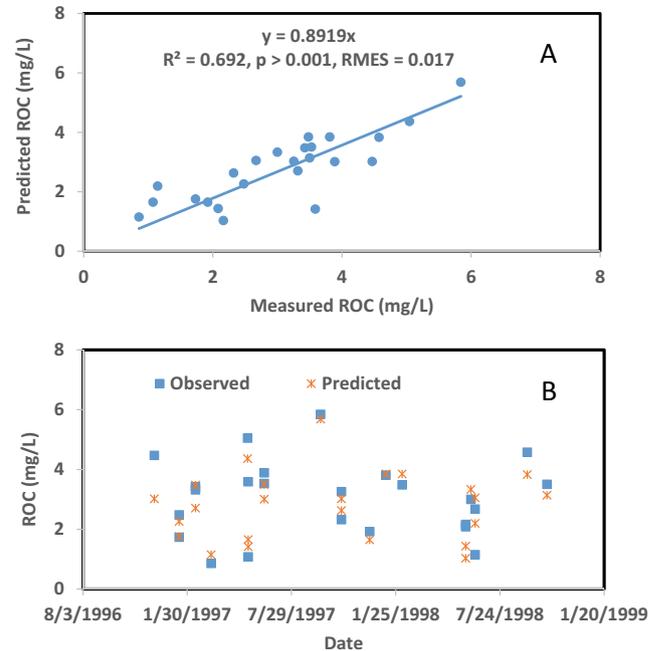
A Date	B Daily discharge (m <sup>3</sup> /day)	C Seasonal discharge (m <sup>3</sup> /season)	D Daily partitioning coeff.	E Seasonal TOC (g/season)	F Daily TOC load (g/day)
1/1/1997	56,235.68	14,784,467.07	0.0038037	5,119,150.3	19,471.71
1/2/1997	53,986.96		18,693.09		
1/3/1997	52,486.34		18,173.5		
1/4/1997	52,486.34		18,173.5		
1/5/1997	53,237.39		18,433.55		
1/6/1997	65,233.5		22,587.23		
1/7/1997	61,484.16		21,289.01		
1/8/1997	59,985.02		20,769.93		
1/9/1997	53,986.96		18,693.09		
1/10/1997	53,611.43		18,563.06		
1/11/1997	94,101.65		32,582.88		
1/12/1997	74,231.33		25,702.74		
1/13/1997	62,235.21		21,549.06		
1/14/1997	47,237.85		16,356.2		
1/15/1997	42,738.94		14,798.44		
1/16/1997	32,617.49		11,293.87		
1/17/1997	50,613.14		17,524.9		
1/18/1997	66,734.13		23,106.82		
1/19/1997	45,738.71		15,837.12		
...	...	...	...	...	...
2/1/1997	78,356.2	...	0.0052999	...	27,130.98
2/2/1997	58,110.35	...	0.0039305	...	20,120.82
2/3/1997	43,864.04	...	0.0029669	...	15,188.01
2/4/1997	37,865.98	...	0.0025612	...	13,111.17
2/5/1997	47,987.42	...	0.0032458	...	16,615.74
...	...	...	...	...	...

measurements further support our conclusion (Fig. 6). To further test the method predictions against the field

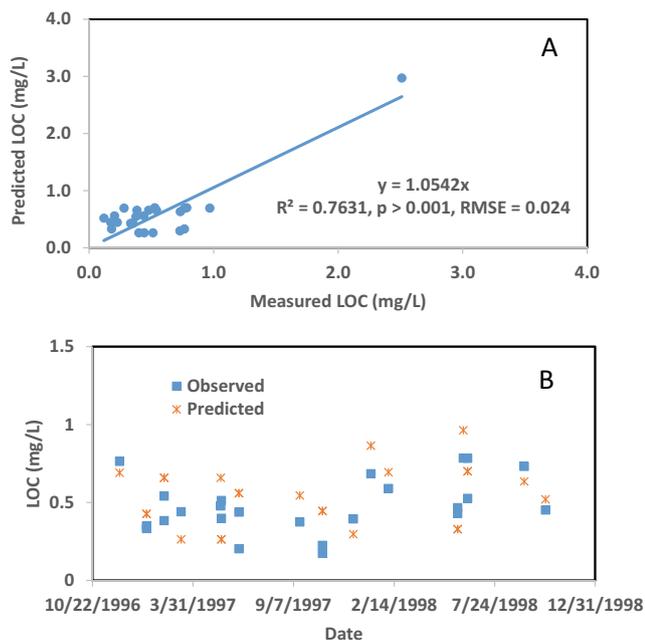
measurements (24 data points), the relative percentage difference (RPD) was used in this study (Fig. 5). RPD is the



**Fig. 2** Comparison of TOC concentrations between the method predictions and the field measurements at the South Fork Black Creek watershed



**Fig. 3** Comparison of ROC concentrations between the method predictions and the field measurements at the South Fork Black Creek watershed



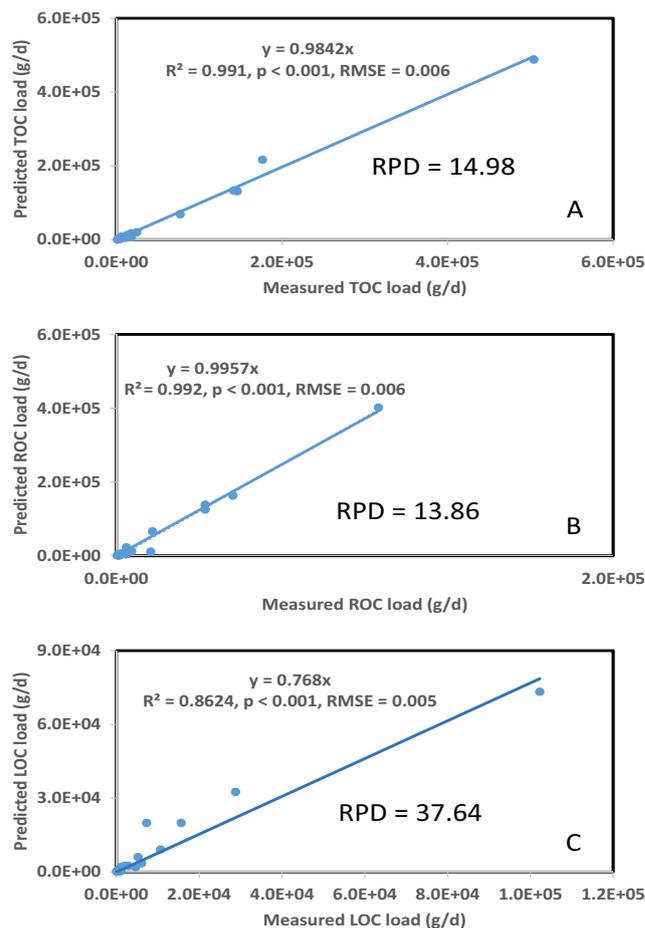
**Fig. 4** Comparison of LOC concentrations between the method predictions and the field measurements at the South Fork Black Creek watershed

absolute value of the difference between each method prediction and each field measurement multiplied by 100. The median RPD is then used for comparison between the method predictions and the field measurements (Christensen et al. 2000; Ryberg 2007). Figure 5 shows that the simple approach predicted TOC and ROC much better than LOC because the former two had low RPDs. Overall, the simple method developed in this study is a useful approach for converting seasonal loads of TOC, ROC, and LOC to daily loads when measured data are not available.

For a rigorous validation of the method, another set of data from a different study site, namely the Green Cove Springs water quality monitoring station (Fig. 1), was used. This site has measured data for seasonal and some daily TOC (but not LOC and ROC) concentrations as well as daily stream discharge from 2009 to 2011. Comparisons of the measured and predicted TOC concentrations are given in Fig. 7. With the very good  $R^2$  value, low  $p$  value, small RMSE, and low RPD, we concluded that the method predicted the daily TOC concentrations very well.

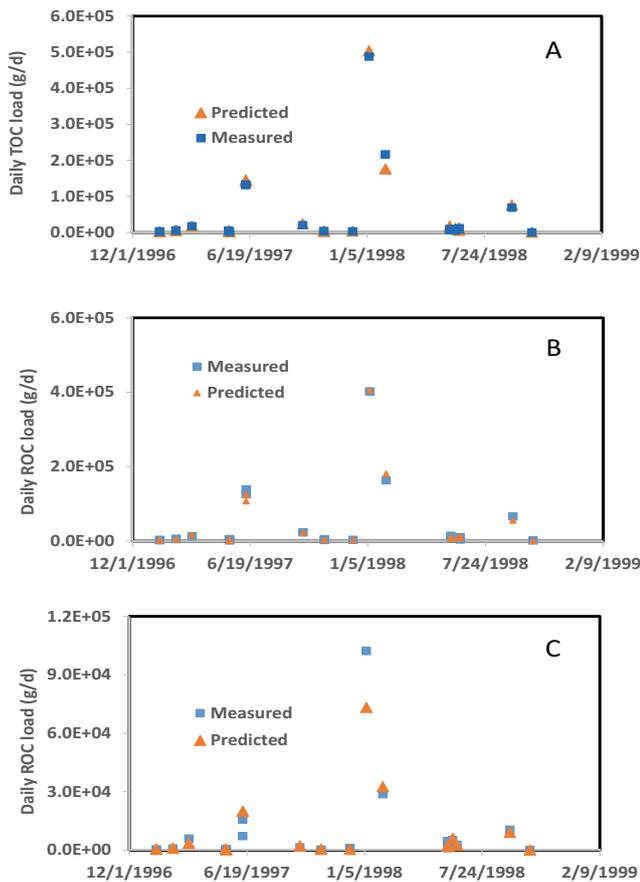
### Method application

**Daily variations of TOC, ROC, and LOC concentrations** Daily discharges as well as daily TOC, ROC, and LOC concentrations at the SFBC watershed outlet are shown in Fig. 8. Daily



**Fig. 5** Comparisons of TOC, ROC, and LOC loads between the method predictions and the field measurements at the South Fork Black Creek watershed. RPD is the relative percentage difference

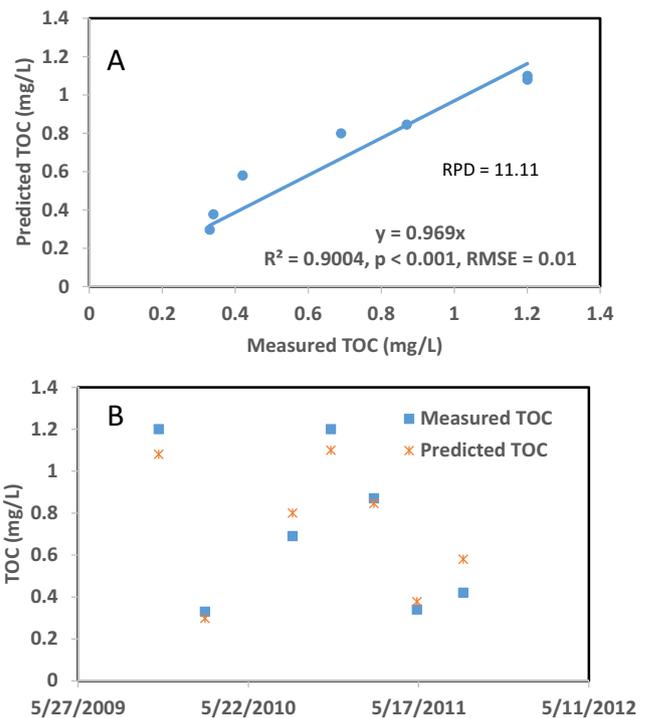
discharges were obtained from field measurements, whereas daily TOC, ROC, and LOC concentrations were calculated with the method developed in this study. In general, an increase in stream discharge (Fig. 8a) resulted in an increased stream TOC concentration (Fig. 8b). However, a comparison of the peak discharges and peak TOC concentrations showed that the greatest peak discharge did not result in the greatest TOC concentration. For example, the maximum discharge of  $5.6 \times 10^6$  m<sup>3</sup>/day occurred on February 17, 1998, while the maximum TOC concentration of 2.4 mg/L happened on November 14, 1997. The mismatch in timing of peak discharge with peak TOC concentration indicated that discharge was not the only factor affecting stream TOC content. Other factors such as land cover and season that control sources of TOC entering into the stream likely play important roles. In general, forest land produces more TOC than other land uses. Tree leaves and litters fall down to the ground during winter.



**Fig. 6** Visual comparisons of peaks and valleys for TOC, ROC, and LOC loads between the method predictions and the field measurements at selected dates at the South Fork Black Creek watershed

These organic matter break down into TOC during late summer under warmer temperature and export to streams (Ouyang 2003). In addition, antecedent discharge condition is also a driving force for TOC export to the streams. Zhang and Ball (2017) reported that incorporation of antecedent discharge conditions improves surface water quality load estimation.

Consistent results to the TOC finding were obtained for ROC and LOC (Fig. 8c, d). That is, an increase in daily stream discharge normally resulted in increased concentration of ROC and LOC in the stream, whereas a peak discharge did not necessarily translate to peak ROC and LOC contents. Patterns in concentration among TOC, ROC, and LOC were similar; increased concentrations of TOC increased concentrations of ROC and LOC in the stream because TOC consists of ROC and LOC. It should be pointed out that the concentration-discharge ( $C-Q$ ) hysteresis may also influence the peak discharge vs. the peak TOC load. The hysteresis of a variable depends not only on time or rate but also on the

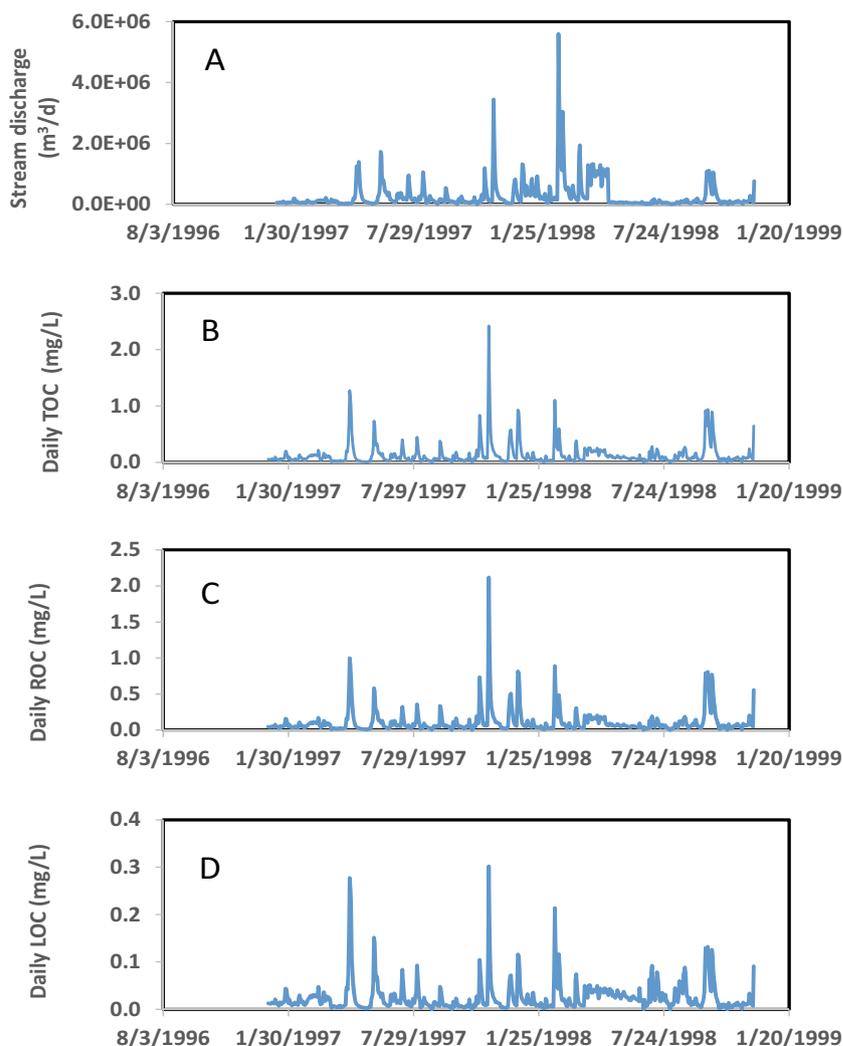


**Fig. 7** Comparisons of TOC concentrations between the method predictions and the field measurements at the Green Cove Springs. RPD is the relative percentage difference

history of variation (Williams 1989; Long et al. 2017). The  $C-Q$  hysteresis loop has been used for relating water quality constituent concentrations to stream discharge and determining if the concentrations are increased on the rising limb (clockwise) or increased on the falling limb (counterclockwise) as well as for assessing if the concentrations are increased due to flushing or decreased due to dilution (Creed et al. 2015).

Figure 8 further revealed that the relationship among concentrations of TOC, ROC, and LOC occurred in the following order:  $TOC > ROC > LOC$ . The concentration of LOC was about an order of magnitude lower than that of ROC. For instance, the maximum concentrations of TOC, ROC, and LOC on November 14, 1997 were 2.4, 2.1, and 0.3 mg/L, respectively. This finding is consistent with results reported by Hendrickson et al. (2007) where the authors found that the concentration of LOC was an order of magnitude lower than that of ROC in forest and wetland watershed (undeveloped land). It should be pointed out that the order of ROC and LOC concentrations may vary with land uses. While the concentration of ROC was much greater than that of LOC for the undeveloped land use, the opposite was true for the historical urban land use (Hendrickson et al. 2007).

**Fig. 8** Method predictions of TOC, ROC, and LOC concentrations at the South Fork Black Creek watershed



**Daily variations of TOC, ROC, and LOC loads** Daily changes in TOC, ROC, and LOC loads through the SFBC watershed outlet along with daily stream discharge over a period from January 1, 1997 to November 30, 1998 are shown in Fig. 9. This figure illustrates that patterns of daily TOC, ROC, and LOC loads were similar to that of daily stream discharge, i.e., as daily stream discharge increased, more TOC, ROC, and LOC were transported out of the watershed outlet. However, analogous to the case of daily TOC, ROC, and LOC concentrations discussed in the previous section, the greatest peak discharge did not result in greatest loads of TOC, ROC, and LOC. For instance, the maximum discharge of  $5.6E + 06 \text{ m}^3/\text{day}$  occurred on February 17, 1998, while the maximum TOC load of  $8.3E + 06 \text{ g/day}$  occurred on November 14, 1997 (Fig. 9a, b). The mismatch of peak discharge with peak TOC load in time occurred for reasons discussed in the previous section.

A similar loading pattern was observed among TOC, ROC, and LOC (Fig. 9). In other words, an increased load of TOC did result in increased loads of ROC and LOC in the stream because TOC is the sum of ROC and LOC. The loads of TOC, ROC, and LOC occurred in the following order:  $\text{TOC} > \text{ROC} > \text{LOC}$ . Maximum loads of TOC, ROC, and LOC on November 14, 1997 were  $8.3E + 06$ ,  $7.3E + 06$ , and  $1.0E + 06 \text{ g/day}$ , respectively, for the SFBC watershed with undeveloped land use.

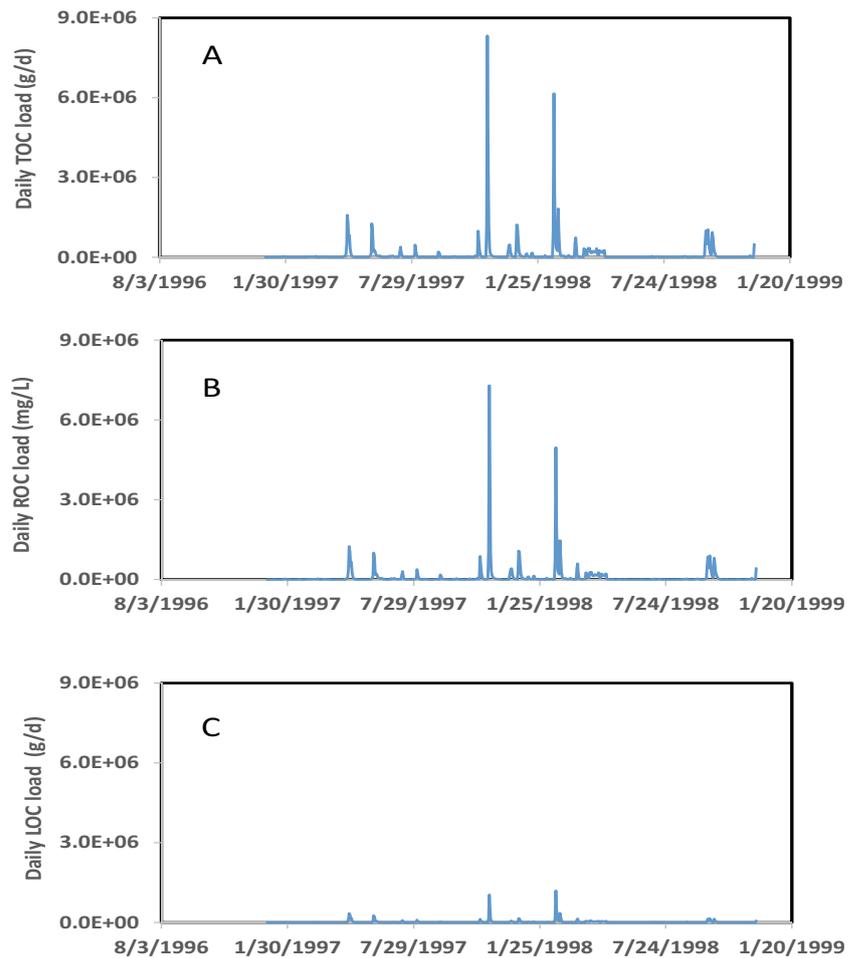
Plots of the daily TOC, ROC, and LOC loads against the daily discharge (Fig. 10) yielded the following curvilinear regression equations:

$$L_{\text{TOC}} = 2E-07D^2 + 0.2525D \tag{5}$$

$$L_{\text{ROC}} = 2E-07D^2 + 0.2169D \tag{6}$$

$$L_{\text{LOC}} = 4E-08D^2 + 0.0356D \tag{7}$$

**Fig. 9** Method predictions of TOC, ROC, and LOC loads at the South Fork Black Creek watershed



with  $R^2 = 0.7134$  for TOC, 0.6811 for ROC, and 0.8529 for LOC, these equations are presented to approximate the daily TOC, ROC, and LOC loads for a given watershed in the absence of measure daily data. Additionally, the above organic carbon loading and daily discharge relationships can also be obtained using the following formula:  $\log(\text{load}) = a + b * \log(\text{discharge})$  if this formula yields better correlations.

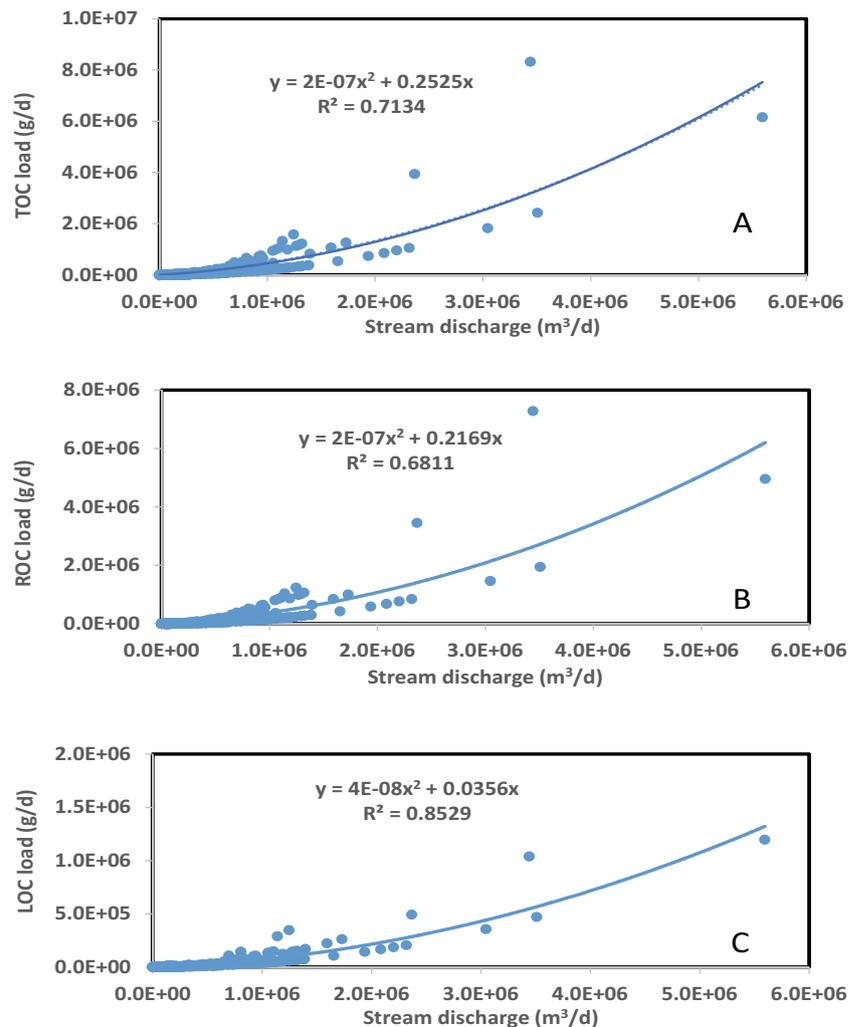
**Summary**

Very few measured daily loads of TOC, ROC, and LOC are available in most watersheds, and only seasonal load of TOC is measured for certain watersheds due to a variety of reasons with budget and time constraints being primary. However, daily loads of TOC, ROC, and LOC are needed to accurately estimate eutrophication, oxygen deficit, and pollutant remediation in streams. In this study, a simple method was developed

to convert seasonal loads of TOC, ROC, and LOC into their daily loads. This method was validated using field measured data prior to its application. Based on moderate to good values of  $R^2$ ,  $p$  value, and RMSE in comparisons, we conclude that the method developed is a useful tool for approximating daily loads of TOC, ROC, and LOC.

The method was then applied to estimate daily variations in concentrations and loads of TOC, ROC, and LOC in the SFBC watershed within LSJRB. In general, an increase in stream discharge resulted in increased stream TOC, ROC, and LOC concentrations and loads, although a high peak discharge did not necessarily result in high peak concentrations and loads of TOC, ROC, and LOC. The mismatch in timing of peak discharge relative to peaks of TOC, ROC, and LOC concentrations and loads indicates that discharge was not the only factor affecting stream TOC, ROC, and LOC loads. Loads are likely influenced by other factors such as land cover and season that control sources of TOC

**Fig. 10** Relationships of stream discharge to TOC, ROC, and LOC loads at the South Fork Black Creek watershed



entering into the stream. A curvilinear correlation existed between daily discharge and daily loads of TOC, ROC, and LOC.

The method is conceptually simple and is very easy to be adapted by users. Improvements to the method can be made by extending its validations and applications to other watersheds with the long-term measured data if the measured seasonal TOC, ROC, and LOC data are available. Although this method was developed for converting seasonal TOC, ROC, and LOC loads into their daily loads, we anticipate that the method could also be used to convert seasonal nutrient, sediment, and other water quality constituent loads into their daily loads when their daily measured loads are not available. We recommend that the method be tested in other watersheds and for other constituent loads to determine whether it is broadly applicable.

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