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LETTER

Diminishing marginal effect in estimating the dissolved organic carbon export from a watershed

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Abstract

Dissolved organic carbon (DOC) can be initially moved from soils to inland waters with surface runoff, and then mineralized, buried, or eventually delivered to the coastal ocean. This land-to-ocean phase of the DOC flux must be accounted for to comprehensively understand the global carbon cycle. To estimate the terrestrial-aquatic DOC leaching, calculating the product of the riverine DOC concentration and the corresponding river discharge measured at the watershed outlet is a common method. However, it is challenging to frequently and exactly record riverine DOC concentrations, thus the relationship between DOC concentrations and discharges (C-Q relationship) are established and used to interpolate the time-series of DOC concentrations. We found that the widely used time-dependent and time-independent C-Q regression models are weak in representing their altered relationship when the discharge is extremely high, which was named as diminishing marginal effect. In this study, we evaluated the performance of two C-Q regression models and discussed possible reasons for the diminishing marginal effect. We suggest that repeated and long-term measurements of the DOC concentration are required to adequately analyze their relationships, especially during the early spring and seasons with heavy precipitations.

Introduction

The lateral carbon flux from terrestrial ecosystems to aquatic ecosystems is a critical component of the global carbon cycle [1], which contains a significant fraction (~30%) of dissolved organic carbon (DOC) [2]. Soil DOC is primarily created by the incomplete degradation of soil organic matter, exuded by roots, or moved along with the washout of organic compounds in vegetation throughfall [3]. The DOC can be initially moved with surface runoff from soils to inland waters. In aquatic ecosystems, a part of this terrestrially derived DOC can be mineralized and released to the atmosphere or buried in sediments, the remainder will be eventually delivered to the coastal ocean [4]. Recent studies suggest that an annual 165 Tg C DOC is ultimately delivered to coastal oceans [5–7]. Therefore, accurate estimates of the DOC export and dynamics from a landscape are essential to assessing the carbon budget from watershed to global scales.

Using the product of the riverine DOC concentration and the corresponding river discharge measured at the watershed outlet is a common way to calculate the total quantity of DOC exported from a watershed e.g., [8, 9]. The river discharge can be constantly recorded by measuring the stream velocity and cross-sectional area at the watershed outlet. To obtain riverine DOC concentrations, *in situ* measurements e.g., [10] and remote sensing images e.g., [11] are widely used; however, it is difficult to frequently and exactly record riverine DOC concentrations. This is because *in situ* water samples are initially collected from the river and then their DOC concentrations need to be measured in the laboratory, which is cost- and labor- intensive. Riverine DOC concentrations also can be inferred with remote sensing images through using the relationship between riverine

Table 1. The paired DOC concentrations and discharges of six watersheds used to assess the performance of the Weighted Regressions on Times, Discharges, and Season model (WRTDS) and the power-law regression model (PL) during high discharge events.

Watershed	Location		Drainage area km^2	Data period	Samples	References
	Latitude	Longitude				
Apalachicola	29°56'57″N	85°00'56″W	49,727	2014–2018	68	USGS02359170
Brazos	29°20'58″N	95°34'56″W	117,427	2015–2018	46	USGS08116650
Lena	66°46'36″N	123°22'00″E	2,490,000	2003–2019	75	ArcticGRO
McDonalds	39°53'06″N	74°30'19″W	6.0	2010–2018	200	USGS1466500
Naguabo	18°16'38″N	65°47'09″W	3.2	1994–1997	40	USGS50075000
Santee	33°9'25″N	79°45'46″W	1.6	2014–2016	156	USDA Forest service

DOC concentrations and riverine chromophoric dissolved organic matter concentrations; however, the atmospheric condition and limited images conspire to limit the number of inferred riverine DOC concentrations [11]. Therefore, by exploring the relationship between recorded riverine DOC concentrations and discharge amounts (C-Q relationship) to build a regression model, the time-series of DOC concentrations can be interpolated to align with the frequency of recorded discharges. In addition, hydrological-biogeochemical models are C-Q relationship-based models to estimate the DOC export from a drainage basin e.g., [12, 13]. Hydrological-biogeochemical models have the ability to simulate the river discharge at fine temporal resolutions (e.g., daily) by incorporating observed meteorological data, land cover type, and topographic information of the study area, and then they estimate the daily riverine DOC concentrations by using an established C-Q regression model [14]. Therefore, a comprehensive understanding of the C-Q relationship is critical for accurately and reliably interpolating the time-series of DOC concentrations and estimating the total DOC export from a watershed.

Recent studies indicate that the C-Q relationship can be modified by various watershed characteristics, including the composition of land cover types, topography and terrain, climate change, soil available nitrogen, sulfur deposition, disturbances, and other factors that affect the biogeochemical processes regulating DOC production and terrestrial-aquatic leaching [15–17]. It has been widely recognized that DOC exports from a watershed are highest during storm events, which can contribute to more than 40% of its annual DOC export [18–20]. Therefore, in this study, we assessed the performance of two commonly used C-Q regression models and commented on their limitations during high discharge events. In addition, we discussed the potential mechanisms for the altered C-Q relationship when the discharge is extremely high.

Method

Regression models

The two regression models generally used to describe the C-Q relationship are based on time-dependent and time-independent C-Q relationships. A typical model based on the time-dependent C-Q relationship is the Weighted Regressions on Times, Discharges, and Season model (WRTDS, equation (1)) [21]. The WRTDS model allows for maximum flexibility in representing the long-term trend, seasonal components, and discharge-related patterns of the riverine DOC concentration [21]. The power-law model (PL, equation (2)) is a popular model based on the time-independent C-Q relationship [22]. The PL model has the ability to incorporate the effects of available solute DOC in the soil as well as watershed characters such as permeability and porosity in estimating the riverine DOC concentration [22].

$$C = e^{\alpha+\theta_1 \ln(Q)+\theta_2 t_y+\theta_3 \sin(2\pi t_m)+\theta_4 \cos(2\pi t_d)+\varepsilon} \tag{1}$$

$$C = \mu Q^{\sigma} \tag{2}$$

where C is the riverine DOC concentration and Q is the river discharge. t_y is the order of the year, t_m is the order of the month (i.e., 1, 2, 3 … 12), and t_d is the day of year (i.e., 1, 2, 3 … 365 or 366). Parameters θ_1, θ_2, θ_3, θ_4, and α are fitted coefficients, and ε is the unexplained variation in equation (1). Parameter μ represents the function of solute, and the power-law exponent σ depends on the watershed permeability and porosity in equation (2) [22].

Watersheds and measurements

To discuss the C-Q relationship and evaluate the performance of the WRTDS and PL regression models when the river discharge is extremely high, we used recorded riverine DOC concentrations and corresponding river discharges of six watersheds (table 1). Locations of these six watersheds range from tropical region (Naguabo watershed) to arctic area (Lena watershed) (figure 1). They are greatly different in size. Santee watershed has the

Figure 1. Locations of the six watersheds.

minimum size of 1.6 km^2 and Lena watershed has the maximum size of 2,490,000 km^2. The paired DOC concentrations and discharges were intensively sampled spanning from 3 years (Santee watershed) to 8 years (McDonalds watershed). In these relatively short periods, the six watersheds had no obvious changes of land cover type [23]. Besides the Lana watershed, the other five watersheds (i.e., Apalachicola watershed, Brazos watershed, McDonalds watershed, Naguabo watershed, Santee watershed) are close to oceans; therefore, they experienced high discharge events due to heavy precipitation associated with storms. Large snow melts during the spring introduced anomaly high discharges in Lana watershed. Consequently, the six watersheds span a considerable diversity of size, land cover, climatic conditions, topography, and other environmental characteristics.

Results

Monotonic regression models

To observe the relationship between riverine DOC concentrations and river discharges, partial derivatives of the WRTDS and PL regression models were calculated, respectively (equations (3) and (4)). To simplify equation (3) and make it easier to read, we used t to represent the time effect on DOC concentrations. We calculated the partial derivative other than the derivative; therefore, this simplification does not influence analyzing the monotonic relationship between riverine DOC concentrations and river discharges. Because the river discharge (Q) has a value that is always larger than 0, partial derivatives of the WRTDS and PL regression models can be larger or smaller than 0, which indicates that the riverine DOC concentrations and river discharges are monotonically positively- or negatively- correlated.

$$\frac{\partial C}{\partial Q} = e^{\alpha+\theta t+\varepsilon} \cdot \theta_1 \cdot Q^{\tau-1} \tag{3}$$

$$\frac{\partial C}{\partial Q} = \mu\sigma Q^{\sigma-1} \tag{4}$$

where C is the riverine DOC concentration and Q is the river discharge. Parameters $\alpha, \theta, and\, \tau$ are fitted coefficients, t represents the time effect on DOC concentrations $(\theta_1 \ln(Q) + \theta_2 t_y + \theta_3 \sin(2\pi t_m) + \theta_4 \cos(2\pi t_d))$, and ε is the unexplained variation for the partial derivative of the WRTDS regression model (equation (3)). Parameter μ represents the function of solute, and the power-law exponent σ depends on the watershed permeability and porosity for the partial derivative of the PL regression model (equation (4)) [22].

DOC concentrations and discharges

By plotting the paired riverine DOC concentration and river discharge as well as the grouped average DOC concentration (figure 2, The grouped average DOC concentration is the average DOC concentration within a bin of discharges.), we found that riverine DOC concentrations and river discharge amounts are initially

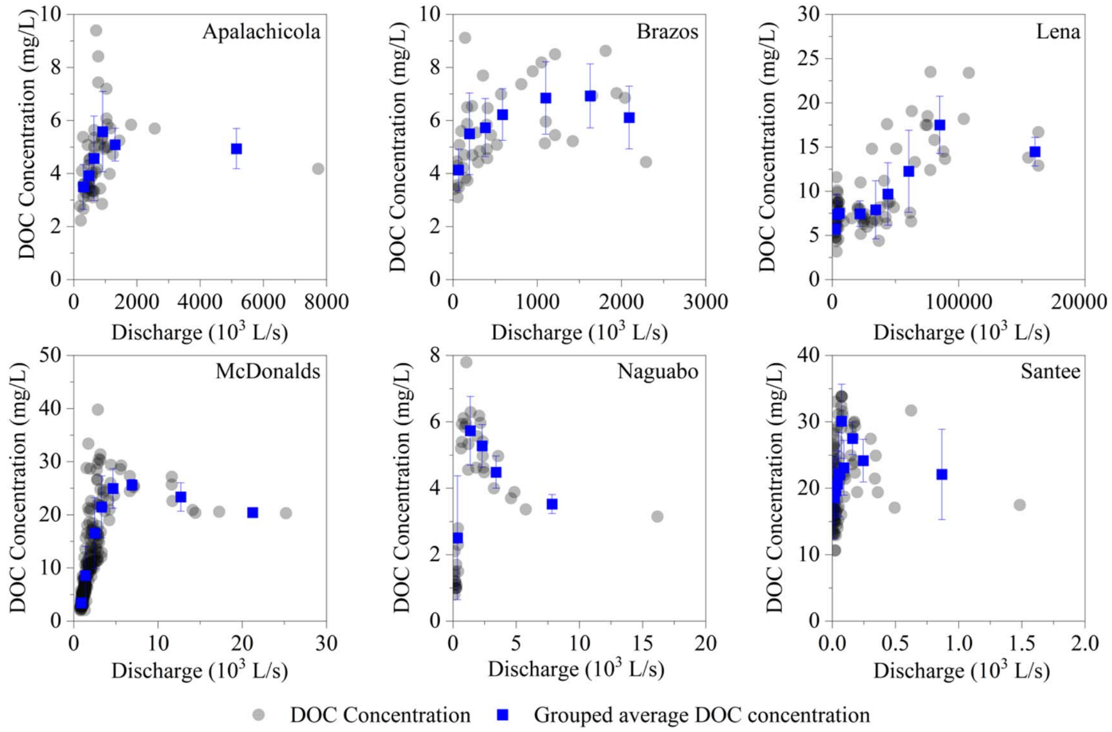

Figure 2. The pattern between paired riverine DOC concentration and river discharge of the six watersheds. Note that the grouped average DOC concentration is the average DOC concentration within a bin of discharges and the error bar represents one standard deviation.

positive-correlated. However, when the river discharge exceeds a certain value, the DOC concentrations were no longer positively correlated with discharges, instead decreasing to lower levels. We define this phenomenon as the diminishing marginal effect, which is the shifting of the C-Q relationship from a hydrology-driven pattern to a soil DOC production-driven pattern. WRTDS and PL regression models have the exponential transformation to constrain the influence of high discharges on estimating the DOC concentration; however, it is insufficient to model the C-Q relationship when river discharges are extremely high. Therefore, the DOC concentration during high discharge events will be overestimated by using a regression model, which is developed without adequate DOC concentrations sampled in extremely high discharges.

Model performance

To evaluate the performances of the two regression models, we estimated the fitted coefficients of the WRTDS and PL regression models. A bootstrapping estimation method was employed. First, for each watershed, twenty paired DOC concentrations and discharges were randomly selected from its records pool and applied to estimate these fitted coefficients. Secondly, the first step was repeated 50 times, thus each coefficient was estimated 50 times. Third, each coefficient was the mean value of its 50 estimates. Then, the parameterized WRTDS model and PL model together with the recorded discharges was used to estimate the riverine DOC concentration. The total DOC export was thus calculated as the product of the riverine DOC concentration and the corresponding river discharge. The paired DOC exports estimated with measured data and modeled results by using the WRTDS or PL regressing model were compared, respectively (figure 3). The results suggest that when discharges are extremely high, DOC exports from a watershed estimated through using the WRTDS or PL regression model are typically higher than exports calculated with measured DOC concentrations (figure 3); therefore, using the WRTDS or PL regression model to estimate DOC exports potentially introduces overestimates for high discharge events.

Discussion

Most current approaches for estimating DOC export from a watershed typically assume that terrestrially derived DOC is the only source in inland waters and that streams or rivers act as passive pipes that simply deliver the total amount of it unaltered directly to the coastal ocean [4]. Therefore, the diminishing marginal effect can be caused by three mechanisms controlling DOC leaching from soils to inland waters. First, precipitation immediately

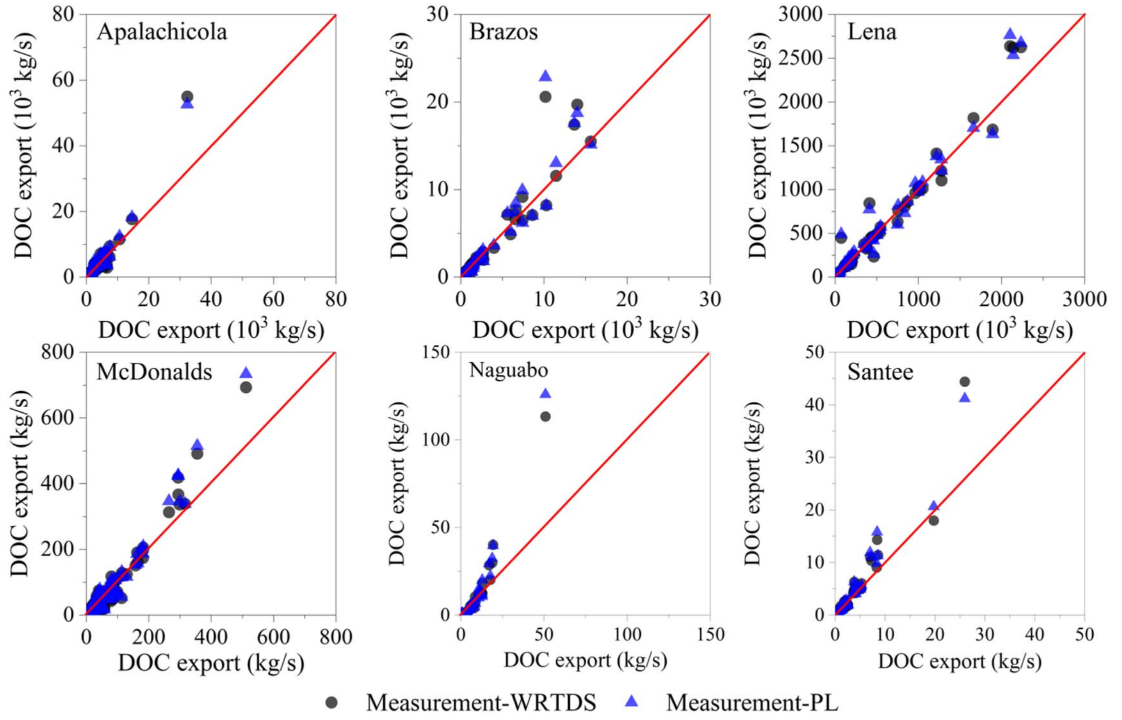

Figure 3. Paired DOC exports estimated with measured data and modeled results by using the WRTDS or PL regressing model.

saturates surface soil in a watershed and increases surface runoff, which is the main force that transports DOC from soils to inland waters. Therefore, DOC leaching from soils to inland waters is a hydrology-driven process. When the surface runoff is sufficient and the amount of available soil DOC becomes a rate-limiting factor, the soil DOC leaching switches to a production-driven process. Second, the immediately increasing discharge caused by the heavy precipitation or snowmelt can significantly accelerate the speed of surface flow and reduce the water retention time, thus relatively less DOC can be dissolved in surface runoff and transported to inland waters [24]. The third possible reason is simply due to the dilution behavior of water associated with the substantial amounts of discharge, which leads to lower riverine DOC concentrations.

Meanwhile, the differences in watersheds including biotic and abiotic characteristics would impact the responses of DOC concentrations to high discharges geographically and hydrologically. Therefore, the diminishing marginal effect varies for different watersheds. For example, Raymond and Saiers [25] performed a meta-data analysis by integrating 30 small eastern United States forested watersheds with no wetland component and concluded an obvious increase in DOC concentration during storms and snowmelts. Yoon and Raymond [19] used measured and modeled high-resolution time-series data to explore the DOC transportation during the hurricane Irene in Esopus Creek in New York, USA. They found that the hurricane introduced a 330-fold discharge increase, but the concentration of DOC did not dilute. Therefore, diminishing marginal effect is not obvious in these watersheds. Zarnetske *et al* [26] used paired observations of DOC concentration and discharge from 1,006 watersheds in the United States to explore the DOC flux behavior. They concluded that DOC flux is transport-limited in 80% of these watersheds, which means that the DOC concentration increases with discharge. In addition, Zarnetske *et al* [26] suggested that watersheds with less than 20% wetland coverage are more likely to be source-limited. But above this threshold, watersheds are discharge-limited. Because wetlands are often assumed to be a near-infinite source of terrestrially-derived DOC in inland waters [27]. Koenig *et al* [28] analyzed high-frequency concentrations of fluorescent dissolved organic matter, which is a proxy for DOC, and discharges of 10 drainage basins in the northeastern United States and indicated that C-Q relationships cannot fully explain the variation of DOC concentrations. They reported a similar conclusion that a watershed having less wetlands exhibits a dilution response to high flows. Therefore, the diminishing marginal effect is highly correlated with the extent of wetland with the watershed, which significantly contributes to the terrestrially derived DOC in inland waters.

Wen *et al* [13] reported a dilution C-Q relationship by using measurements and model results, which means that the increasing discharge above a threshold potentially reduces the riverine DOC concentration. They suggested that the dilution C-Q relationship was caused by insufficient soil DOC content or controlled by the soil sorption ability. Wymore *et al* [29] used high-frequency sensors to sample the DOC concentrations in ten streams and rivers across central and southeastern New Hampshire, USA together with recorded discharges to observe the C-Q pattern. They identified a diluting response, which means that the DOC concentration decreases in concentration during high flow events and suggested that this diluting response is caused by the limited soil DOC. Consequently, insufficient soil DOC is the major factor that causes the diminishing marginal effect.

Conclusion

With global warming, hurricanes and other extreme precipitation events are projected to increase in the future [30, 31]. The surges of heavy precipitations associated with these events immediately increase surface runoff. In addition, the warmer spring can increase the amount of snowmelt and greatly accelerate the surface runoff. Therefore, the diminishing marginal effect needs to be considered when applying models based on the C-Q relationship to interpolate the riverine DOC concentration and estimate the DOC export from a watershed experiencing frequently heavy precipitation events or having flood periods resulting from melting ice and snow. Otherwise, the terrestrial-aquatic DOC leaching may be overestimated. To accurately represent the C-Q relationship, repeated and long-term measurements of the DOC concentrations during high discharge events are required, which is important to reduce uncertainties introduced by the altered C-Q relationship in estimating the DOC export.

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Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: https://doi.org/https://nwis.waterdata.usgs.gov/usa/nwis/qwdata.

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