Science of the Total Environment 861 (2023) 160744

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Analysis of spatiotemporal variation in dissolved organic carbon concentrations for streams with cropland-dominated watersheds

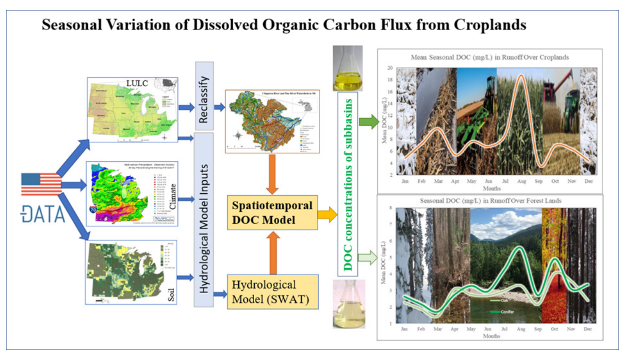
Yong Q. Tian [a,*], Qian Yu [b], Hunter J. Carrick [c], Brian L. Becker [a], Remegio Confesor [d], Mark Francek [a], Olivia C. Anderson [c]

[a] Department of Geography and Environmental Studies & Institute for Great Lakes Research, Central Michigan University, MI 48858, United States of America
[b] Department of Geosciences, University of Massachusetts-Amherst, Amherst, MA 01003, United States of America
[c] Department of Biology & Institute for Great Lakes Research, Central Michigan University, MI 48858, United States of America
[d] Environment and Natural Resources, Norwegian Institute of Bioeconomy Research, Norway

HIGHLIGHTS

- DOC concentrations in streamflow of croplands are higher than forested lands.
- Accumulation of crop residues rapidly increases DOC load in freshwater.
- Snowmelt caused alarmingly high riverine DOC concentrations in springtime.
- Spatiotemporal baseflow DOC flux is predictable by using LULC data and SWAT model.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Ashantha Goonetilleke

Keywords:
Dissolved organic carbon
Inland water
Anthropogenic activity
Crop residue management
Baseflow
Agricultural landscape
SWAT model

ABSTRACT

It remains a challenge to understand how dissolved organic carbon (DOC) is cycled from farmlands to rivers due to the complex interaction between farming practices, the baseflow hydrology of predominantly flat lowlands, and seasonal environmental influences such as snowpack. To address this, field DOC concentrations were measured monthly throughout the year at sub-basin scales across the Chippewa River Watershed, which falls within the Corn Belt of the Midwestern United States. These DOC dynamics in stream water from croplands were benchmarked against the data sampled from hilly forested areas in the Connecticut River Watershed. The Soil Water Assessment Tool (SWAT) simulation was applied to provide potential predictive variables associated with daily baseflow. Our study outlines a framework using the combination of primary field data, hydrological modeling, and knowledge-based reclassification of Land Use/Land Cover (LULC) data to analyze the viability of modeling the spatial and temporal variations of cropland stream DOC concentrations. Calibration of the SWAT model resulted in the overall daily Nash–Sutcliffe model efficiency coefficient (NSE) of 0.67 and the corresponding $R^2 = 0.89$. Our main results show: 1) baseflow DOC concentrations from croplands were substantially higher throughout the year relative to other landcover areas, especially for spring runoff/snowmelt scenarios, 2) an empirical analysis explained ~82 % of the spatial gradient of annual mean observed DOC concentrations, and 3) with the addition of hydrological simulated variables, a linear model explained ~81 % of monthly and 54 % of daily variations of observed DOC concentrations for cropland sub-basins. Our study identified key factors regulating the spatiotemporal DOC concentrations in cropland streamflow; the contribution here promotes to strengthen future analytical models that link watershed characteristics to carbon cycling processes in a large freshwater ecosystem.

* Corresponding author.
E-mail address: yong.tian@cmich.edu (Y.Q. Tian).

http://dx.doi.org/10.1016/j.scitotenv.2022.160744
Received 12 September 2022; Received in revised form 30 October 2022; Accepted 3 December 2022
Available online 7 December 2022

1. Introduction

Terrestrial organic carbon in the dissolved form (DOC) is easily transported to inland or coastal waters via hydrological processes (Dusek et al., 2017; Heppell et al., 2017). Excessive riverine carbon has a pronounced impact on aquatic ecosystems via processes such as amplifying microbial activity, diminishing the quantity and quality of light penetrating the water column, and controlling toxic metal availability (Butman and Raymond, 2011; Spencer et al., 2013; Stedmon et al., 2006). As a major use of land (Ellis et al., 2010), an agricultural landscape is a significant source of DOC into freshwater ecosystems (Bhattacharya and Osburn, 2020). Recent studies raised public health concern that rivers receiving runoff from croplands contain elevated and harmful DOC concentrations at regional and worldwide scales (D'Amario and Xenopoulos, 2015; Humbert et al., 2020; Qiao et al., 2017). DOC levels originating from croplands are often enriched in aromatic structures and exhibit high fractions of labile dissolved organic matter, thereby significantly affecting freshwater nutrient pathways (Bhattacharya and Osburn, 2020; Holgerson and Raymond, 2016; Kellerman et al., 2020). However, little is known about what factors regulate carbon export in agriculturally influenced streams (Royer and David, 2005).

In recent decades, there has been an increased interest in studying terrestrial carbon-source dynamics and their impact on freshwater interactive processes (Heppell et al., 2017). As such, studies have made significant progress towards gaining a better understanding of the impacts of climate change and extreme storm events on variations of riverine DOC concentrations originating from terrestrial environments (Kellerman et al., 2020). These studies have mostly focused on sloped forested watersheds that generate DOC fluxes predominantly through surface runoff during storm events (Lindström et al., 2010; Pers et al., 2016; Singh et al., 2015). For example, the DOC contributions of event flows were found as high as 86 % for forested catchments (Raymond and Saiers, 2010). A representative model, the Integrated Catchments model for Carbon (INCA-C) was specifically developed for hilly forested regions (Futter et al., 2011). The INCA-C model was indeed helpful in revealing that variations in DOC concentrations were primarily driven by soil temperature and surface runoff for forested, mountainous watersheds in Sweden (Clark et al., 2007; Fu et al., 2019; Pers et al., 2016).

The DOC dynamics in streamflow generated from agricultural landscapes are significantly different from those reported for forested habitats. Studies have demonstrated that stream water inputs from baseflow drive the temporal dynamics of DOC concentrations in agricultural watersheds (Bhattacharya and Osburn, 2020; Humbert et al., 2020). Although instantaneous baseflow DOC concentrations less than that in storm event flows, the annual baseflow DOC flux is much higher than that of annual event flows in cropland watersheds (Qiao et al., 2017). Furthermore, an improved understanding of DOC dynamics in baseflow is essential to study both seasonal effects and influences of anthropogenic activities. Such an understanding provides a quantifiable baseline for potentially modeling spatial and temporal DOC variations when adding additional information associated with storm effects. This is especially important for the Corn Belt region of the Midwestern USA, where flatland hydrology dictates temporal variations in DOC concentrations via both baseflow (i.e., groundwater) and surface runoff during storm events (Buffam et al., 2001; Qiao et al., 2017). In addition to having different hydrological processes, cropland soils typically contain enriched organic carbon (Ågren et al., 2008; Olsson et al., 2009). Lack of quantitative analyses remains a significant barrier when modeling the variation of cropland DOC concentrations in streams (Qiao et al., 2017).

The goal of this study is to explore the potential of quantifying temporal (monthly or daily) and spatial variations of DOC concentrations originating from crop-dominant lowlands. This study aims to identify a range of predictive variables that are useful in modeling the spatial disparities and trends of DOC variations instead of using soil C:N ratio as a surrogate (Aitkenhead-Peterson et al., 2003). Our research niche includes the incorporation of primary field observations, hydrologic variables, and high spatial-resolution land surface characteristics. This study focuses on identifying a workable spatiotemporal scale for both field observations and quantitative analysis of DOC source dynamics, fate, and transport processes. This research is both novel and urgent because DOC export from agricultural landscapes occurs largely at the expense of the water quality of adjacent freshwater systems and, to a lesser extent, land sustainability. Detrimental cropland management policies and practices can inherently lead to degraded water quality through both physical and biochemical processes (Jones et al., 2004; Jones and Knowlton, 2005; Monaghan et al., 2007; Valentin et al., 2008). Clearly, DOC is part of a delicately balanced synergistic system, and thus, the concentration of DOC in lakes and rivers can be a useful indicator of land-water ecology (Gómez-Gener et al., 2021). The Soil Water Assessment Tool (SWAT) has the advantage over other models in that it incorporates of plant-based biological processes. Which is why it was utilized to provide the required hydrological properties for each tributary area.

2. Materials and methods

2.1. Study basins

Two contrasting study basins were referenced in this investigation to allow direct comparison of DOC dynamics over croplands versus sloped forestlands. The primary study basin consisted of the Chippewa River watershed that includes the Pine River as a major tributary (Fig. 1). The Chippewa River is one of the three tributaries draining the western portion of the larger Saginaw River watershed. The Saginaw River ultimately empties into Saginaw Bay, Lake Huron, which is one of the most bioproductive coastal regions in the entire Great Lakes Ecosystem (Millie et al., 2006). The Chippewa watershed cuts across the Lower Peninsula of Michigan and meanders nearly 147.7 km to Midland, Michigan, flowing generally eastward and ultimately merging with the Tittabawassee River. The croplands in the primary study basin were dominated by row crops of corn, soy, wheat, and sugar beets, that were situated adjacent to mixed woodlands and wetlands, with a small proportion of lands dedicated to hay production and areas of development. The topography (mean slope = 1.3°) in the primary study basin were typical of the flat lowlands of the agricultural midwestern United States.

The secondary study basin included five forested sub-basins associated with the Deerfield and Millers River, in Massachusetts. These two rivers are tributaries to the greater Connecticut River Watershed, which is the longest river in the northeastern United States, draining approximately 28,490 km^2. Two of the five sub-basins (~952 km^2) located along the Deerfield River were heavily forested, with approximately 86 % of their landmass designated as forest. The remaining three sub-basins (~770 km^2) located along the Millers River were less forested, with approximately 71 % of their landmass forested. The mean slope for the entire secondary study basin was ~7.7°. Field observations collected across multiple seasons and multiple years were paramount to better understand the significant DOC contributions from croplands in comparison to forested hill lands.

2.2. Field sample protocols

In total, 278 water samples were collected from 26 sampling locations via 43 field visits spread between the Michigan and Massachusetts study basins, to measure baseflow DOC concentrations between rainfall events. Sample collection between rainfall events was earmarked to reflect seasonal variations and to reduce the influence of any single event. Within the primary study basin (Chippewa River Watershed), 21 sampling locations were visited, with 11 targeting crop dominated sub-basins (orange polygons) and 10 targeting mixed land cover (green polygons) as displayed in Fig. 1. The sub-basins were defined as crop dominated if they had >50 % crop coverage or crop coverage exceeded double that of the second highest land cover category. The percentage of each land cover type for each sub-basin is shown in Table 1 (in Supplementary Materials). For example, the sub-basin associated with sampling location 13 was crop dominated since it had 46 % crop coverage, which was more than double that of wetland,

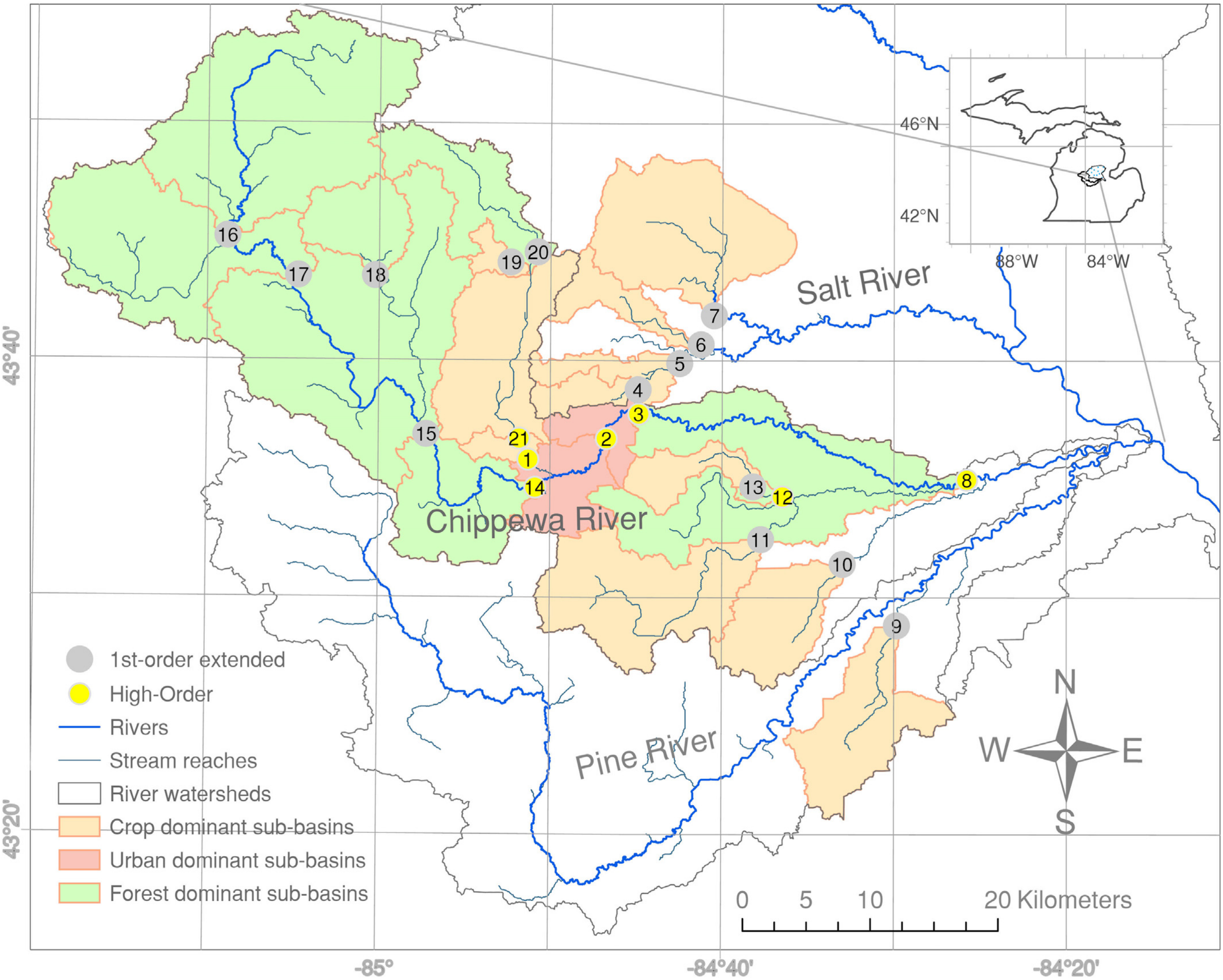


Fig. 1. The primary study site (Chippewa River and Pine River Watersheds) and associated sub-basins. Shown are 21 sampling locations; grey points are associated with 1st-order extended streams, yellow points associated with high order streams.

the 2nd highest land cover type. If a sub-basin was not categorized as crop dominated, it was classified as mixed.

There were 153 water samples collected monthly at 21 outlets of select sub-basins across the Chippewa River watershed for directly measuring DOC concentrations in the laboratory. The sampling period spanned 14 months beginning in October 2012 and ending in January 2014. Field sampling activities were primarily conducted during the spring and fall when soil biochemical processes and nutrient fluxes are more prevalent (Sela et al., 2019; Sharratt et al., 1998). A reduced number of field samples were collected in both summer and winter months for the purpose of analyzing the seasonal transition of DOC concentrations.

The sampling locations were selected to examine what sub-basin scales were appropriate for modeling DOC concentrations. Fourteen sampling locations were identified that met one of the following three criteria to be considered a 1st-order extended sub-basin: 1) area was <26 km^2, 2) the streams feeding into a sampling site were a 1st, 2nd or 3rd order stream, and 3) all their upper-tributary sub-basins had the same dominant land uses. For example, there were 11 sub-basins drained via a 1st-order stream: sampling sites 4, 6, 7, 9, 10, 11, 13, 16, 18, 19, and 20 (Fig. 1). Three sub-basins were associated with 2nd and 3rd order streams: sampling sites 5, 15 and 17. However, the dominant land cover type within these three sub-basins was the same as their upper tributary sub-basins. Therefore, these three sub-basins were also designated as the 1st-order extended sub-basins. Therefore, all 14 1st-order extended sub-basins in the primary study basin were numbered 4, 5, 6, 7, 9, 10, 11, 13, 15, 16, 17, 18, 19, and 20 (grey sampling locations in Fig. 1). The remaining 7 yellow sample locations (1, 2, 3, 8, 12, 14, and 21) in Fig. 1 are associated with non-extended sub-basins. These non-extended sub-basins were used to benchmark DOC performance against that of 1st-order extended subbasins.

For the second study basin in Connecticut River, 125 water samples were collected monthly from the five sub-basins from 2011 to 2016 (Li et al., 2018). Deciduous and mixed forest were the dominant land covers in the Deerfield River watershed. The dominant forest types across the remaining three sub-basins were evergreen and mixed.

2.3. Laboratory measurement of DOC concentration

Field samples were obtained from stream water using clean 500 ml bottles (acid washed). Bottles were fully immersed and tilted while capping to ensure that no air remained. The samples were immediately stored on ice until arrival and transported to the laboratory for immediate filtering. Water samples were filtered through pre-combusted glass-fiber filters (nominal 0.7 μm pore size) to remove any non-dissolved organic matter, and the filtrate was then stored (i.e., acidified and refrigerated) until analyzed for DOC content. All laboratory processes were completed within 12 h of sample collection times. The DOC concentration of each water sample was measured using a Shimadzu TOC-V analyzer with high temperature combustion (Vlahos et al., 2002). For each, 50 μl injections of sample water was combusted at 800 °C, from which the DOC concentration was calculated from the resultant CO_2 yield and measured with a non-dispersive infrared detector.

2.4. Land cover composition

National Land Cover Data (NLCD) from 2011 were used because it was chronologically closest to our sampling dates (2012–2014). The 2011 baseline NLCD data referenced 13 land cover categories. These baseline land cover data were reclassified into three more broadly defined classes. The three landcover classes are Mixed (dominated by forest and wetland), Crop (dominated by corn), and Other (Fig. 2). The reclassification was based on both measured and derived DOC transformation rates of the major land covers: forested (including shrubs) and crop land rates were measured directly in our previous mesocosm experiments (Li et al., 2018). The mixed land scenario rates were derived from clustering the results of a principal components analysis (PCA) of the trophic states in streams for the Chippewa River Watershed (Carrick et al., 2022). The percent-areal composition of these three aggregated classes extracted from the NLCD data were calculated for each drainage sub-basins of Chippewa River Watershed (i.e., Cells in Table 1). These data were used to analyze DOC dynamics at the sub-basin level. It is important to note that land cover data was calculated for the entire area draining to an individual sampling location and not just the sub-basin in which the sampling location resided. For instance, sampling point 15 receives runoff not only from its immediate sub-basin, but also from upstream sub-basins that contained points 16, 17 and 18.

2.5. Hydrological modeling

The SWAT model was used to generate daily hydrologic properties for all sub-basins of the primary study basin. The hydrological properties were statistically analyzed to identify which variables, if any, were significant estimators of seasonal variation in DOC concentrations from croplands. The SWAT model is recognized worldwide as one of the most effective tools for estimating hydrological processes from agricultural lands (Arnold and Fohrer, 2005; Olaoye et al., 2021; Tian et al., 2012). For this study, the SWAT was calibrated using 38 consecutive years of daily hydrologic input data spanning from 1981 to 2018. In addition, spatially explicit, high resolution (4 km^2 grid) daily weather forcing data (precipitation, maximum temperature, and minimum temperature) were downloaded from the PRISM website (https://prism.oregonstate.edu/recent/) and were used as SWAT inputs. Daily discharge flow of the Chippewa River was obtained from the USGS 04154000-gauge station and used to calibrate the SWAT model. Three aggregate LULC types were extracted from NCLD 2011 as described above and used as model inputs. Soil input parameters were extracted from SWAT's built-in STATSGO data. Finally, elevation data were extracted from a 30 m Digital Elevation Model (DEM) of Isabella County, Michigan. Based on all these input data, the SWAT model delineated our primary study basin into 126 sub-basins.

Next, the observed hydrographs were partitioned into three components by assuming a watershed's hydrologic behavior varied between rainfall events, transition period, and periods without rain, similar to previous studies (Boyle et al., 2001; Confesor and Whittaker, 2007). Thus, the Chippewa River daily flow data were categorized into high (rainfall driven, top 10 percentile), medium (transition flows, 10th–50th percentile), and low (non-rainfall driven flows, lowest 50th–100th percentile) flows. The SWAT model was then calibrated through a multi-objective and automatic calibration for these three flow regimes to minimize the simulation error and bias for the period from 2011 to 2018 using the method developed by (Confesor and Whittaker, 2007). The overall daily Nash–Sutcliffe model efficiency coefficient (NSE) was 0.67 and the corresponding R^2 was 0.89 (Fig. 3). The SWAT model captured the high soil water content associated with winter snowpack and subsequent spring melting. The disparity between simulated and gauged snow effects for February indicate that the SWAT underestimated the stream flow from snowy seasons in February for the Chippewa study basin. The SWAT's performance was satisfactory for March and beyond, which corresponded well with our sampling period. The simulated hydrologic properties were used as independent variables for quantitative analysis of daily DOC observations.

2.6. Exploratory statistical analysis

Multiple linear regression analyses were used to explore which independent variables were most significant in explaining variation in DOC concentrations at various spatial and temporal scales. In essence, these linear regressions aimed to fit observed/sampled DOC data to a linear equation with $m + n$ independent variables, where m is the number of spatial variables associated with the characteristics of each drainage sub-basin and n

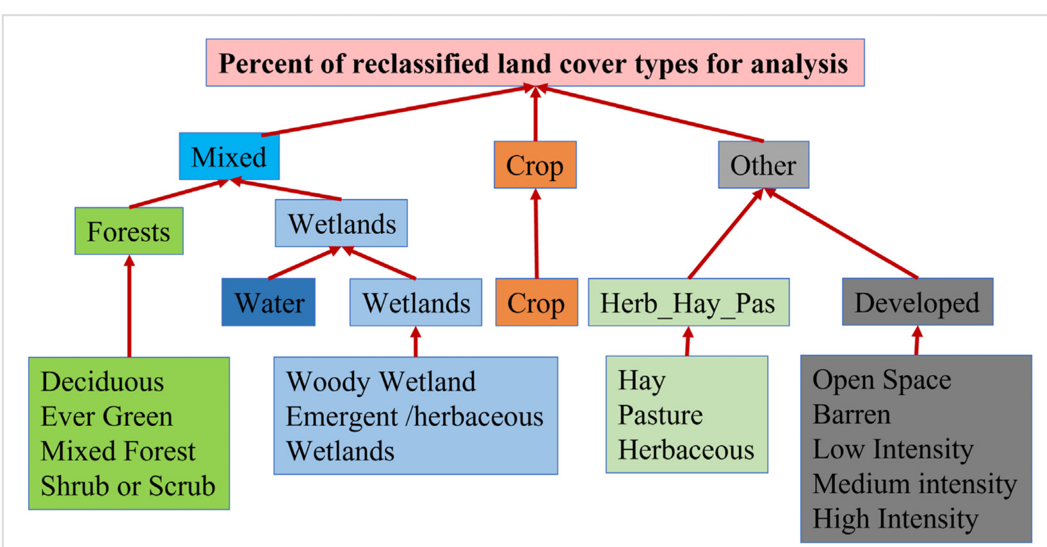


Fig. 2. Reclassification scheme of the original National Land Cover Data (NLCD) into three landcover classes suitable for modeling: mixed (dominated by forest and wetland), crop (dominated by corn), and other.

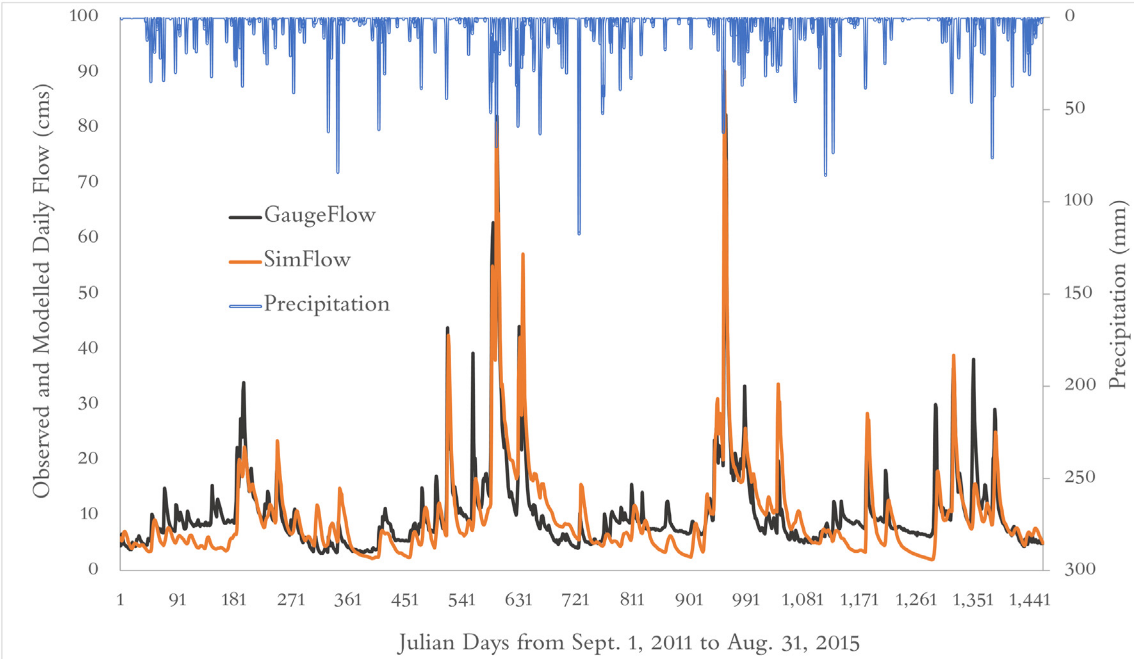


Fig. 3. SWAT simulated flows versus observed daily flows (Nash Sutcliffe = 0.67 and R^2 = 0.89). Top sensitive parameters calibrated are CN (+20%), Alpha_BF (0.9), Sol_AWC (+10%), ESCO (0.2), SMFMN (1.8), and SMFMX (5.5).

is the number of temporal/seasonal variables. The specification of the linear model was as follows:

$$y(i,t) = c + \sum_{j=1}^{m} \alpha_j x_j(i) + \sum_{k=1}^{n} \beta_k S_k(i,t) \tag{1}$$

Let $X(i) = [x_1(i)\ x_2(i) \ldots x_m(i)]$ be the *m* exploratory spatial variables for the sub-basin associated with sampling location *i* for $i \in [1, L]$. *L* is the number of sampling locations. Similarly, let $S(i, t) = [s_1(i,t), s_2(i,t), \ldots s_n(i,t)]$ be the *n* exploratory seasonal (temporal) variables for the sub-basin *i* and Julian day *t*, for $t \in [1, Q]$. Q is the last Julian day of field sampling visits. Each variable set X(*i*) were in three categories: land cover (e.g., percent cropped area, percent forested), soil properties (e.g., percent silt, percent organic matter), and geomorphology (e.g., sub-basin area, average slope). The spatial variables were derived from each drainage area. The seasonal variables *S*(*i, t*) were used as input data in according to two categories: hydrologic characteristics (e.g., *SW*: soil water content, *PET*: potential evapotranspiration, *GW*: ground water volume) and weather inputs (e.g., point specific precipitation and air temperatures). The observed DOC, *y* (*i, t*) corresponded with all sampling locations *i*, and the Julian days *t* of field visits. The observed values *y* (*i, t*) for all *i*s and *t*s were fitted to Eq. (1) to estimate the coefficients c, a_1, a_2, …, a_m, b_1, b_2, …, b_n.

Statistical metrics used to evaluate relative importance and/or inclusion of variables into the models were *p*-value, coefficient of determination (R^2), and F values reflecting the overall significance of each regression model. An alpha of 0.05 was used as the threshold to determine if any one variable was statistically meaningful. The analysis included all exploratory variables (in varying combinations) within each category (temporal, spatial, physical, and biological). Our objective was to identify which variables were significant at three temporal scales (i.e., daily, monthly, or annually). Accordingly, all associated data had to be averaged when moving to a more course temporal scale. For example, ~30 daily hydrologic variables were averaged to yield a single monthly value. Similarly, ~365 daily hydrologic variables were averaged to yield an annual average. Ultimately, a variety of variables were fit to both raw and averaged (monthly and yearly) DOC observations to obtain the desired coefficients of the multiple variate linear regression model.

One of our research objectives was to evaluate the appropriate spatial scale (i.e., contributing hydrologic areal extent) for quantifying the inherent relationship between a variety of independent variables and the variation of observed DOC concentrations from cropland areas. Here, stream segment *i* and sub-basin *i* were designated as the immediate stream segment and sub-basin in which the sampling location *i* resides. With this designation, this study tested two spatial scale scenarios: 1st-order extended sub-basins and non-extended drainage areas as defined in a previous section.

3. Results and discussion

Our overarching research objective was to establish a theoretical understanding of the relationship of the observed DOC concentrations to a variety of independent and spatiotemporal variables in cropland areas. This study presents pertinent results and related discussion within four distinct sections: 1) Spatial disparity of mean annual DOC concentrations; 2) Seasonal patterns of the DOC observations; and 3) Variables useful to estimate spatial and temporal distributions of daily DOC concentrations in streamflow throughout the year. These estimated daily DOC concentrations were then aggregated to evaluate the final section: 4) an analysis of the observed monthly DOC trends.

3.1. Spatial disparity of mean annual DOC

The observed DOC concentrations were averaged to yield an annual mean for each of the 14 sampling locations within the 1st-order extended subbasins in the primary study area. Aggregated annual mean DOC values ranged from 5.5 to 10.5 mg/L, which effectively eliminated temporal influences and focused on the influences of the spatial characteristics across all the 1st-order extended sub-basins. Through statistical analysis, four significant variables were identified to the spatial variability of mean annual DOC concentrations, $\bar{y}(i)$, observed in sampling site *i* which was associated with each 1st-order extended sub-basins. The resultant linear regression model is below (Eq. (2)).

$$f(X) = 0.52crp + 1.19frt + 0.52wetl + 18.74dum - 63.07 \tag{2}$$

where the first three variables (i.e., *crp*, *frt*, *wetl*) were percent of crops, forest, and wetland. The *dum* was the binary dummy variable useful for separating crops and mixed land covers (crop = 1, mixed = 0). All slopes and y-intercept from the resulting models were significant with respect to the observed mean annual DOC concentrations (0.0006 ≪ p-values ≪ 0.0034). The overall model explained >82 % (R^2_{adj} = 0.74) of the variation in the observations (F = 10.22, p-value = 0.0021) as displayed in Fig. 4a. The dummy variable specified above in Eq. (2) played a role as a constraining condition. The dummy variable expanded the capability of the linear regression for more complex scenarios exhibiting highly heterogeneous land cover composition.

The linear regression in Eq. (2) resulted in positive coefficients for the three vegetative cover related variables as well as the one dummy variable. The positive coefficients indicate that higher plant density increases the DOC concentrations as reported in previous studies (Schaefer et al., 2020; Tian et al., 2013). A geomorphological variable, the natural log of the contributing watershed area, ln(A) was eliminated from Eq. (2) because its *p-value* was 0.06 (>0.05). Several studies reported that the increasing size of sub-basin area degrades DOC concentrations before entering the stream (Rana et al., 2008; Van de Griend et al., 2002). Consistently, our observed mean annual DOC concentrations also exhibited an explicit inverse relationship to $ln(A)$ for crop dominant sub-basins as displayed in Fig. 4b. Ours together with early studies suggests that it is appropriate to include the variable $ln(A)$ in the regression model by lessening the significance level from 0.05 to 0.10.

With a lessened significance level of 0.10, the variable, $ln(A)$ became statistically significant in the linear regression analysis (p-values ≤ 0.1). Inclusion of the variable $ln(A)$ demonstrates the utility and viability of our spatially explicit modeling approach in Eq. (3).

$$f(X) = 0.43crp + 1.03frt + 0.41wetl + 16.01dum - 0.45\ \ln(A) - 46.09 \quad (3)$$

The addition of the spatial variable $ln(A)$ improved the estimation of the DOC observations (R^2 = 88 %, R^2_{adj} = 0.82, p = 0.0010) compared to the model that excluded this variable (Eq. (2)). The *p-values* for all variables ranged from 0.0011 to 0.0630. The negative coefficient of $Ln(A)$ reflects the hydrologic processes occurring within the relatively larger and flatter sub-basins, and the inherent DOC degradation. Given the same land cover conditions, the hydrologic processes over a large land area result in the reduction of DOC concentrations because of both longer transport and residence times that allow for greater soil carbon adsorption, infiltration and degradation (Chalise et al., 2019). Therefore, larger sub-basins act to inherently dilute soil-profile DOC concentrations (Schilling et al., 2016).

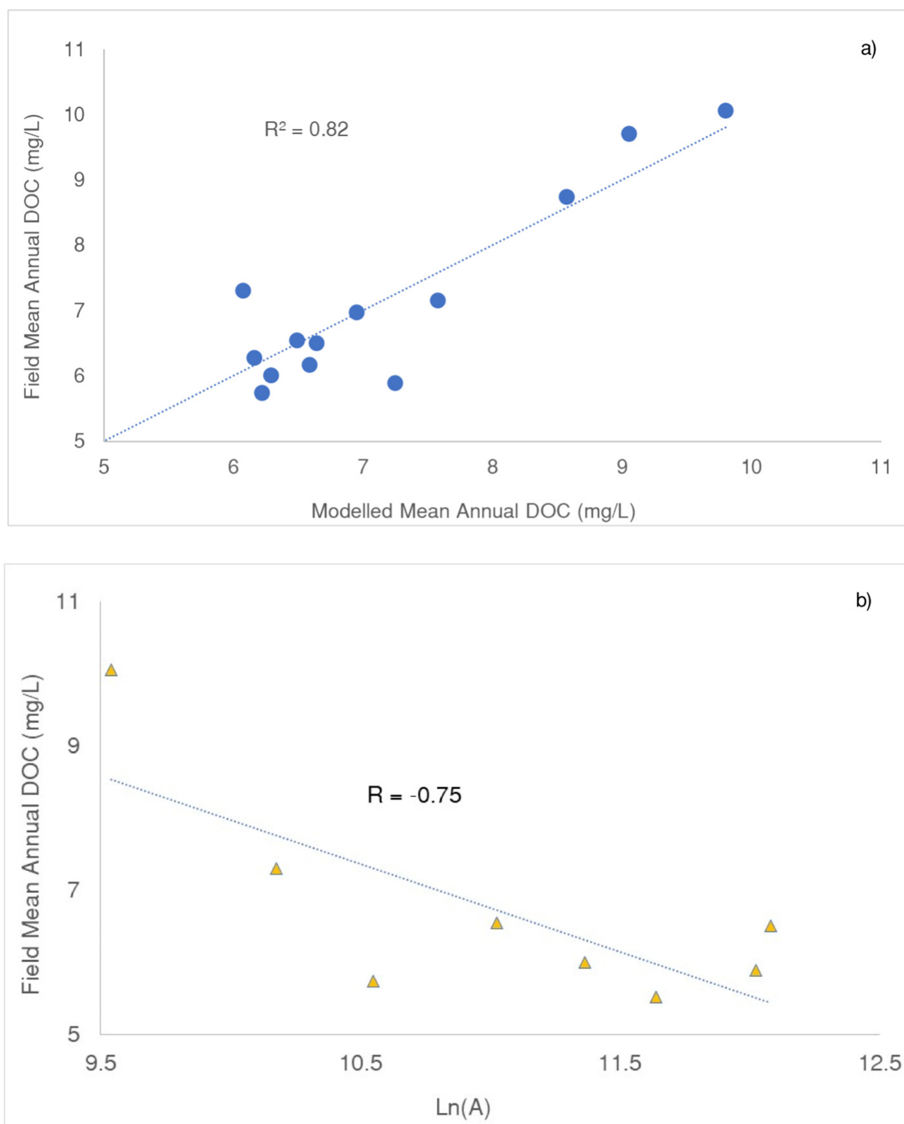


Fig. 4. a) Linear regression of modelled DOC concentrations (mg/L) versus observed mean annual DOC concentrations from 1st-order Extended sub-basins. and b) Inverse relationship of the natural log (Ln) of areas (cells) draining into the sampling locations, $ln(A)$ versus observed mean annual DOC concentrations from cropland dominant sub-basins.

The predictive power of our regression results (i.e., Eqs. (2) and (3)) highlight the viability of modeling the spatial variations of mean annual DOC concentrations across a cropland dominated river basin. However, predictive variables identified for croplands were very different compared to previous studies on semi-natural habitats (Kaushal et al., 2018; Monteith et al., 2015; Vidon et al., 2014). Many of these previous research efforts were based on sloped hill land with very different hydrology regimes from that of flat croplands dominated by baseflow (Jantze et al., 2015; Terajima and Moriizumi, 2013). Our large sample size distributed across scales made it possible to identify those predictive variables based on a reliable level of realism (Lambert et al., 2015; Lapierre et al., 2015). Note that all the required variables in Eqs. (2) and (3) are easily downloadable and derivable from the NLCD database. Thus, our presented empirical analyses are potentially adaptable to study broad scenarios of DOC cycling processes of freshwater habitats across the United States.

3.2. Observed seasonal (monthly) DOC trends from crop and forest lands

The DOC observations were aggregated monthly mean and then were averaged for all sampling locations that were in the 1st-order extended sub-basins over the primary study basin in Fig. 5a. The data aggregation is to focus on seasonal variations. Strong seasonal patterns in DOC concentrations were very evident across our analyses. These fluctuations of DOC concentrations were largely associated with baseflows because the sampling days were purposefully selected between large storm runoff events. Accordingly, the fluctuations were attributed to baseline seasonal phenomenon with little influence from any one single episodic precipitation event.

During the late winter season, snowpack often elevates soil water content. It has been reported that such high soil moisture content enhances certain saturation-dependent metabolic processes and biogeochemical reactions (Leakey et al., 2006) as well as increased accumulation of DOC in the topsoil (Ågren et al., 2010). In early spring (i.e., middle of March),

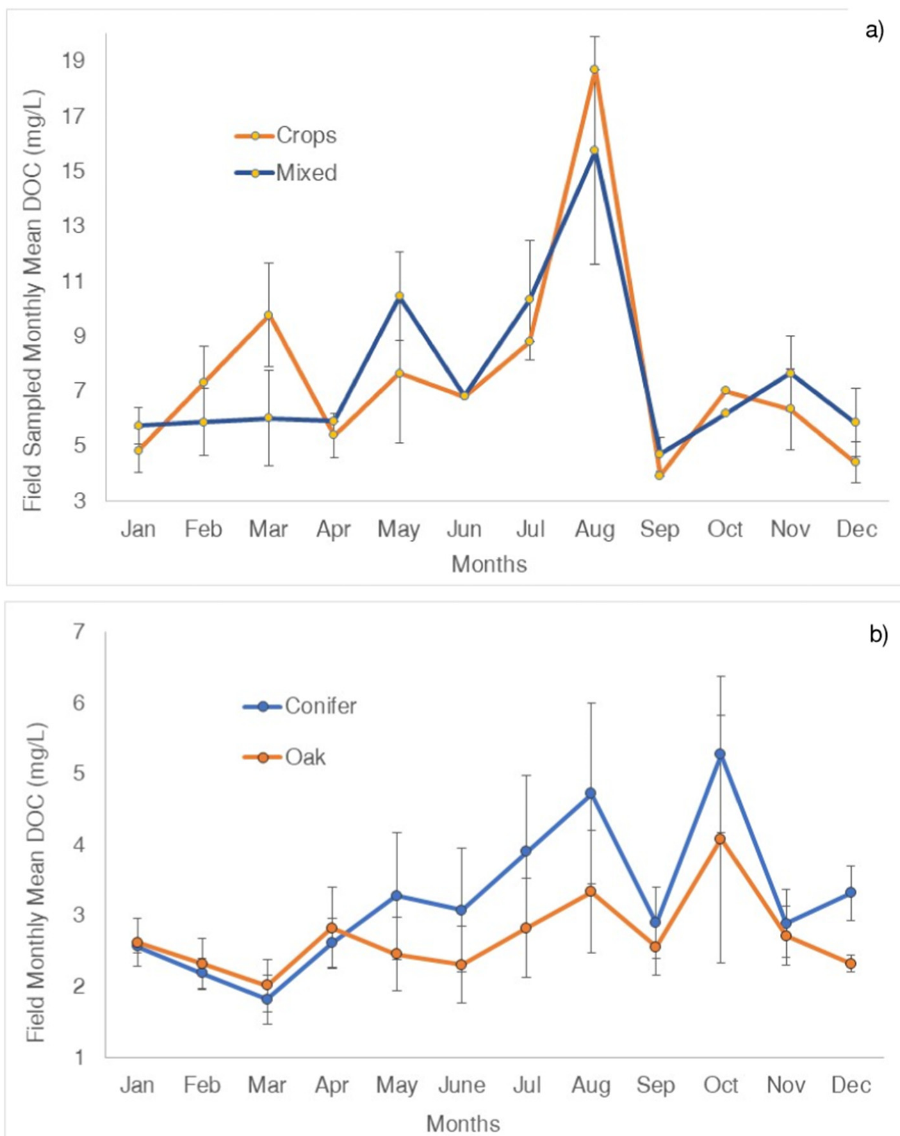


Fig. 5. a): Monthly observed mean DOC concentrations (mg/L) for Crop and Mixed landcovers for each of the 1st-order extend sub-basins. Note: February DOC concentrations were interpolated by using the average value of adjacent months. Error bars are standard deviations of the observations. b): Monthly mean DOC concentrations (mg/L) observed across multiple years for each of the five sub-basins in the Connecticut River Watershed. Note: February and July data were interpolated by averaging data from the adjacent months.

rapidly increased baseflow transports soil DOC via groundwater baseflow to streams. The peak of DOC concentrations observed in March from crop dominant subbasins corresponds well with baseflow resulting from snowmelt, which acts to flush DOC stored in the topsoil created by these saturation-dependent metabolic processes and biogeochemical reactions (Fig. 5a, orange curve). The phenomena suggests that the effect of metabolic and biogeochemical reaction processes on corn residues is more significant compared with the effect of dilution by way of spring snow melt.

The observed monthly mean DOC concentrations (i.e., March) from the mixed drainage sub-basins (Fig. 5a, blue curve) had a slight spike in spring. Generally, mixed sub-basins were dominated by forest interspersed with wetlands and contained 30 %–45 % croplands. Inspection of Fig. 5a (blue curve) does show a slight DOC spike associated with the infiltration of snowmelt and elevated soil water content. For both cropland and mixed drainage sub-basins, rich crop residue biomass is indeed the main anthropogenic source of geochemically active and transformable DOC. Gaining a better understanding of these spikes in DOC concentrations in the spring is important, since spring is a critical time of the year with respect to benthic and shallow water habitats in relation to biological communities, aquacultural production, and water quality to public health (Lehosmaa et al., 2018; Puczko et al., 2018).

In contrast, an early spring DOC peak was not observed (Fig. 5b) from the steeper forested watersheds of the second study basin despite similar weather conditions. Traditionally, farming practices for both sweet corn and dent corn leave most plant residues in the field, which greatly increases soil organic matter (Guo et al., 2018; Motavalli et al., 1992; Oberle and Keeney, 1990). These accumulated residues enrich soil organic biomass more so than the leaf-liter from forest canopies in autumn (Du et al., 2019). In addition, the increased slopes associated with these non-cropped, forested hills encouraged direct surface runoff with limited water infiltration through the soil profile. Less infiltration results in less DOC transport which corresponds to the lack of a DOC peak in early spring for these forested locations (Fig. 5b).

Other DOC peaks from May to December matched well between the two study basins: crop versus forest (correlation > 0.65). The good match of the peaks across this period at both study basins highlights that these DOC concentration curves are reflecting broad seasonal effects rather than the influence of any one individual storm event since the curves were derived from a large set of multi-year, independent field measurements (i.e., ~50 field visits). High precipitation and high ground water levels were exhibited from late April to early May as simulated via SWAT (i.e., black curve in Fig. 6). DOC concentrations were raised in this period for all scenarios: cropland, mixed land use sub-basins, and forested hill lands, suggesting that high precipitation is the key driving factor for these seasonal DOC spikes.

The magnitudes of DOC spikes from croplands in May were more than double those of the forested hill lands. The high DOC concentrations from croplands were likely triggered by many factors, such as elevated ground water volumes, manure/nutrient application, tillage for seeding, and increased soil temperatures (Fig. 5a). All these factors together help explain the trend of DOC concentrations observed between rainfall events in the late spring season. The case is different for surface runoff during storms when the manure/nutrient management strongly impact DOC observations (Singh et al., 2014; Vidon et al., 2008). The higher DOC levels for croplands compared to forested hill lands was partially due to other crop farming practices, such as tillage in preparation for spring seeding. The optimum corn planting period for much of Michigan is from the beginning to middle of May, and the amount of soil manipulation would inherently rise as fields are prepped for planting.

The highest peak of DOC concentrations was observed in the late summer (August) for both croplands and forested hill lands (Fig. 5a & b). High soil temperatures drove the increased DOC concentrations in August for both primary and secondary study basins due to the higher rates of microbial activities and faster turnover of DOC in organic soils (Bowering et al., 2020; Haaland and Mulder, 2010). Furthermore, elevated crop root mass in summer and autumn months expedite soil-based DOC productivity. These two peaks in August and October corresponded well to the supplemental irrigation in June and July supporting corn plant size increases (Apland et al., 1980) and to the end season irrigation in early September depending on weather conditions (Ward, 2022). All these factors are reasons

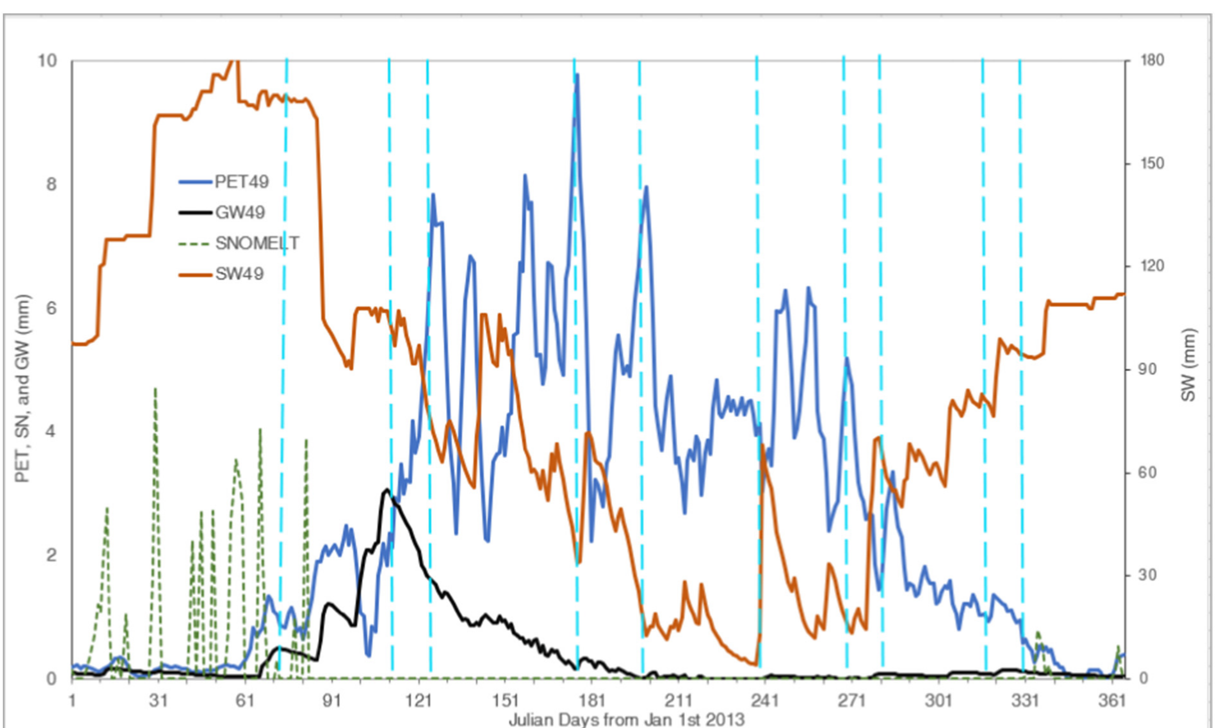


Fig. 6. SWAT modelled daily PET, GW, SM and SW of sub-basin 49 for year 2013. Sub-basin 49 is where the USGS gage station resides. The dashed light blue vertical lines indicate the sampling date. PET: Potential Evapo-Transpiration, GW: Ground Water, Snowmelt: Snow Liquid Equivalent, and SW: Soil Water content.

for the higher magnitudes of DOC concentrations from the primary versus the secondary site (forested hill lands) for August and October peaks (Kelly et al., 2015; Vetsch and Randall, 2002).

The mean monthly DOC concentrations for croplands were >2-fold greater (Fig. 5a) compared with those for forested hill lands (Fig. 5b) throughout the year. However, our mesocosm experiments revealed that DOC transformation (i.e., foliar to dissolved) rates were often 2.5 times faster for forest foliage compared with sweet corn foliage (Li et al., 2018). Given the same biomass, corn plant foliage generates a lower DOC concentration compared with forest leaf-liter (per unit mass). This suggests that the higher DOC concentrations from croplands were likely regulated by cropland management practices that physically breakdown corn plants, where they are allowed to further degrade in the field after harvesting. The high DOC concentrations from croplands are the effects of crop residue accumulation across multiple years and related break-down as well as manure application (Du et al., 2019). Intuitively, the amount of organic biomass of croplands must therefore be 5–6 times higher than that of forested lands to result in the 2-fold greater DOC concentrations. Furthermore, the monthly precipitation and temperature patterns between the two study basins were very comparable. Clearly it is the farming practices in the Corn Belt as opposed to climate or temperature variations driving DOC dynamics. With the same hydrological processes, the enriched organic biomass in soils generated higher DOC concentrations in stream flow.

3.3. Variables attributable to spatial variation of daily DOC concentrations

Seven variables were tested and proved to be statistically significant as strong predictors of the spatial variations of daily DOC concentrations (Eq. (4)). Three out of these seven variables vary with time (daily) and are inherently related to potential baseflow: soil water content (*sw* in mm), ground water volumes (*gw* in mm), and potential evapotranspiration (*pet* in mm). The remaining four variables (i.e., *crp*, *frt*, *wetl* and *dum*) represent the landcover characteristics of any given sub-basin. Note that these spatial variables are the same as those utilized (Eqs. (2) and (3)) in analyzing mean annual DOC variations across the Chippewa River watershed. If let S represent those three variables that represent temporal characteristics and let X represent the 4 variables that account for spatial characteristics, then S and X for a specific sub-basin draining to a sampling location *i*, and at a particular Julian day, *t*, are:

$$\mathrm{X}(i) = [crp(i), frt(i), wetl(i) \text{and } dum(i)],$$
$$\text{for every } i \in [\text{sampled 1st} - \text{order extended sub} - \text{basins}]$$

$$\mathrm{S}(i,t) = [sw(i,t), gw(i,t) pet(i,t)],$$
$$\text{for all } t: \text{the Julian day when field samples were taken}$$

The three temporal variables for *S*(*j*, *t*), where *j* is for gauge station (sub-basin #49) and all *t*. The modelled daily variation of *S*(*j*, *t*) throughout year from the SWAT simulation are displayed in Fig. 6. Sub-basin *j* contained the USGS gauge station. *S*(*j*, *t*) was different from *S*(*i*, *t*) for all *i* in magnitude depending on the size of the sub-basins, but they were highly correlated (Correlations ≥ 0.8). For the purpose of exploring predictive variables effective in estimating DOC concentrations (not DOC flux), only *S*(*j*, *t*) was used as the temporal data for this preliminary analysis. Linear regression statistics were applied to daily *S*(*j*, *t*) for all *t* and X(*i*) for all *i*. The resulting linear regression analysis equation (Eq. (4)) explained approximately 54 % of *y*(*i*, *t*), daily DOC concentrations for all samples from 1st-order extended sub-basins (crop and non-crop, $R^2_{adj} = 0.503$, $N = 100$) as displayed in Fig. 7 (hollow points). In the cases of analyzing only crop dominant sub-basins, the model explained approximately 50.44 % ($R^2_{adj} = 0.46$, $N = 63$, yellow triangle points).

$$f(X,S) = 0.46crp + 0.95frt + 0.51wetl + 15.1dum + 1.25pet + 0.046sw - 1.68gw - 59.96 \quad (4)$$

The variables used predict daily DOC concentrations (in Eq. (4)) all explained statistically significant portions of variation in the dataset (0.000 ≪ p-value ≪ 0.005). The associated coefficients likely indicate several natural responsive processes. The coefficients of the four spatial variables (*crp*, *frt*, and *wet* and *dum*) in Eq. (4) had similar value ranges to those

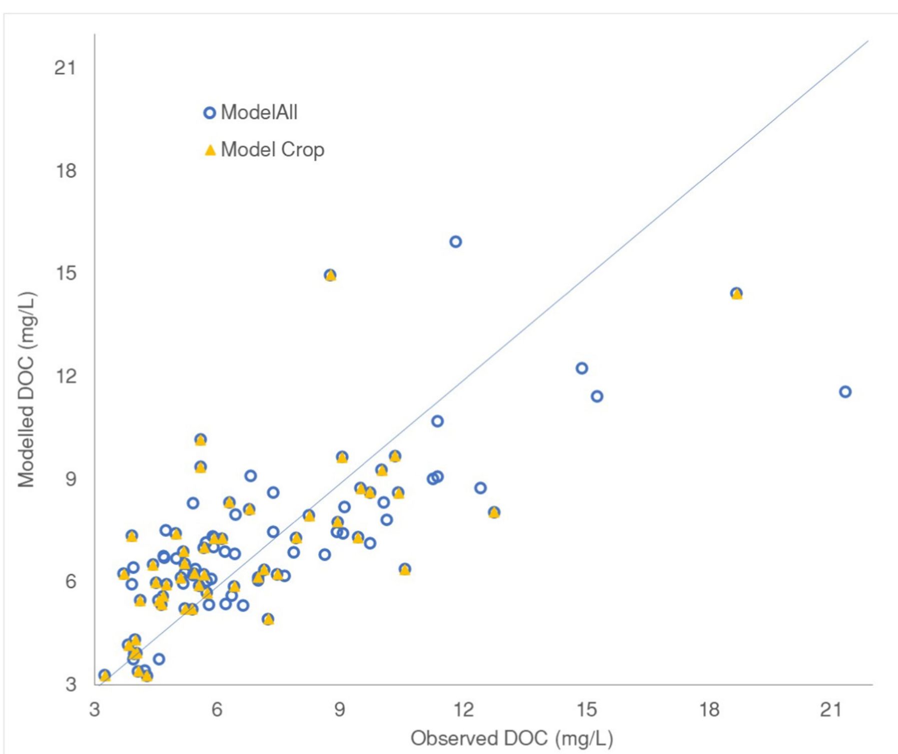


Fig. 7. Modelled (Y axis) versus observed (X axis) DOC concentrations (mg/L) of 1st-order extended sub-basins. Hollow points (N = 100) represent both crop dominant and mixed landcover sub-basins. Yellow triangles (N = 63) represent crop dominant sub-basins.

found in Eqs. (2) and (3), albeit with the exclusion of the ln(*A*) variable. The *ln*(*A*) variable of Eq. (3) was functionally replaced by the ground water variable (*gw*) in this finer spaciotemporal-scale statistical analysis (Eq. (4)). The negative coefficient of *gw* indicates an inverse relationship to daily DOC concentrations. Logically, groundwater yield is in part positively correlated to the size of the sub-basin area (Rana et al., 2008). The high soil-water content (i.e., soil moisture) for the primary study basin in late winter and early spring were predicted quite well with the SWAT hydrologic model (Fig. 6). These four spatial variables help to inform what, where, and how land surface characteristics impact the variation of riverine DOC concentrations. The resultant coefficients and listed significant variables seem to reflect underlying hydrologic scientific rationales rather than pure empirical analyses.

The three temporal variables (*pet*, *sw*, *gw*) were strong predictors of the daily variation of DOC concentrations in stream baseflow across time. This predictive power verifies that DOC concentrations in streams between storm events are indeed inherently related to the groundwater properties of said stream and its drainage area. The coefficients associated with these three variables are very similar, indicating that each variable is of nearly equal importance in this model. The results of this regression-based analysis demonstrated that SWAT simulated hydrological properties are indeed appropriate temporal variables for estimating DOC concentrations daily or monthly across both study areas. The light blue vertical lines in Fig. 6 mark the SWAT simulated hydrological properties corresponding to the Julian days when the DOC samples were collected. The SWAT model performed well in characterizing the lag of groundwater runoff in response to snowmelt in the early months of the year. In contrast, increased soil water content (*sw*) did not display such a lag and was found to be concurrent to snowmelt processes. The elevated snowmelt and associated lagged groundwater runoff peaks effectively explained the high DOC concentrations sampled throughout the spring months of the year (Fig. 5a).

The results highlighted in Fig. 7 provide persuasive evidence that the identified variables are indeed promising predictors to the spatial and temporal variations of DOC concentrations in baseflow. Most importantly, the study isolated the key factors that seem to control the seasonal trends of carbon cycling processes over midwestern croplands. If comparing these promising results to similar studies that inherently focused on DOC variations in storm event surface runoff, our results appear more suitable for analyzing long-term anthropogenic and climatic effects on freshwater ecosystems (Qiao et al., 2017; Wallin et al., 2015). Our analysis of DOC concentrations in streamflow between rainfall events is complementary to previous efforts analyzing surface runoff during storm events (Terajima and Moriizumi, 2013).

Herein, our research offers insights into the mechanisms that regulate the dynamics of daily DOC concentration as they vary from land to river, as mediated by land use (i.e., croplands). For example, the observed the minimum and maximum baseflow DOC concentrations at the gauge station of the Chippewa River were 5.12 and 10.35 (mg/L) respectively. The lowest and highest mean daily flow rates recorded for the years from 2011 to 2015 at the location were ~3.17 and ~82.4 cubic meters per second, which corresponds to 273,888 and 7,119,360 m^3 per day. Therefore, the daily DOC fluxes linked to baseflow at the location of the gauge station ranged from ~1403 to ~73,685 kgC·day^{-1}. The daily DOC fluxes attributed to episodic event flows are only ~1/3 of those attributed to baseflow (Qiao et al., 2017).

3.4. A quantitative analysis of mean monthly DOC concentrations

Fig. 8 shows how well the estimated monthly mean DOC concentration (red line) matched to that observed (bars). The estimated monthly mean DOC concentrations were aggregated from the daily linear model outputs (Eq. (4)). The observed DOC concentrations were averaged for each month from the 11 sampling locations designated as crop dominated 1st-order extended sub-basins. The estimated DOC concentrations explained ~81 % (R^2 = 0.81) of the observation data set 1 (Ob1 in Fig. 8) for six months (i.e., Jan., Mar., Apr., May, Nov., and Dec.). These six months corresponded to those months conducted more frequent field visits. The observation data set 2 (Ob2) was collected during summer months (i.e. Jun, Jul., Aug., and Sep.), for which conducted less frequent sampling field visits. As might be expected, the reduced field samples related to the Ob2 data resulted in the regression model (Eq. (4)) having less predictive power, explaining ~49 % (R^2 = 0.49) of the observed DOC. In combination (Ob1 and Ob2), the estimation accuracy of the modelled values to the observed monthly mean DOC concentrations was approximately 56 % (R^2 = 0.56).

Estimations of DOC status in streamflow at monthly intervals are ideal to both hindcast or forecast long-term impacts of climate change and human activity on carbon-cycling processes and freshwater ecosystem functions. Our analysis suggests that monthly mean DOC concentrations are indeed quantifiable and can provide a useful baseline for developing next-generation analytical models of DOC concentrations in stream baseflow. The baseline model can provide an ideal platform for including event-based DOC fluctuations (Qiao et al., 2017). Such next-generation models can then be expanded to incorporate both the spatial and temporal variables influencing DOC dynamics at sub-basin scales. Ultimately, such models can integrate both biological and physical processes to help identify

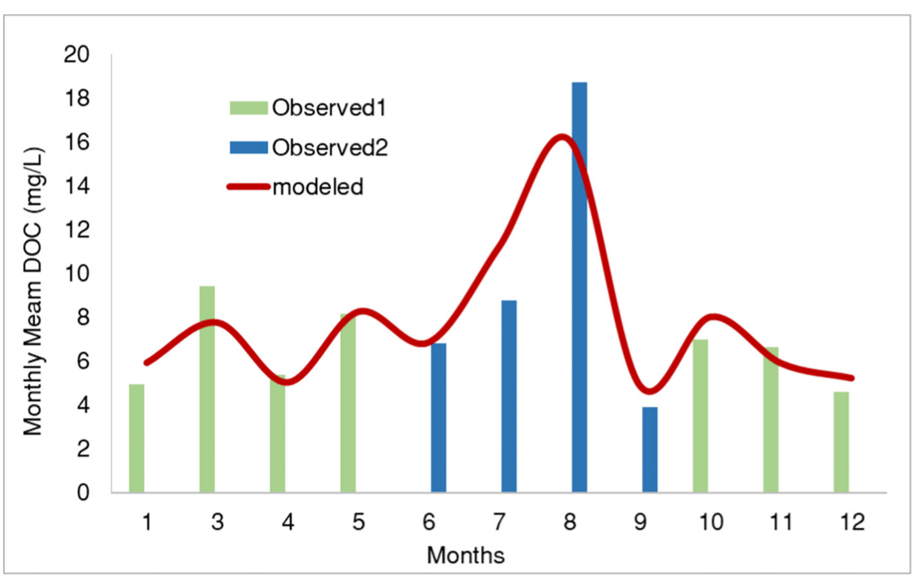


Fig. 8. Modeled (red curve) versus observed (bars) monthly mean DOC concentrations (mg/L) for crop dominant, 1st-order extended sub-basins. Observation data set 1 (Observed 1) represents Jan, Mar, Apr, May, Oct, Nov, and Dec; R^2 = 0.81. Observation data set 2 (Observed 2) represents Jun, Jul, Aug, and Sep; R^2 = 0.49.

where, when, and how DOC source and transport mechanisms respond to climatic and anthropogenic processes.

4. Conclusions

The spatiotemporal distributions of DOC concentrations in streamflow were observed from a cropland representative of the Midwestern United States. The main contributions of our research efforts are summarized below.

- The elevated DOC concentrations in early spring were in response to snowpack and snowmelt processes over croplands with plant residue accumulation.
- Baseflow plays an important role in driving seasonal changes of DOC concentrations across spatial scales.
- The 1st-order extended drainage sub-basins are indeed an appropriate spatial scale for quantifying the inherent relationship between a variety of independent variables and DOC concentrations in cropland areas.
- Integrating an appropriate LULC reclassification, hydrological processes, and systematic analysis of geospatial and temporal features is indeed a viable approach for understanding DOC dynamics of agricultural landscapes with lowland hydrology.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.160744.

CRediT authorship contribution statement

Here we describe individual contributions in following five categories:

1. ***Research concept, design, and question***
   All authors
2. ***Funding***
   Yong Tian, Qian Yu, Hunter Carrick
3. ***Material preparation, and data collection***
   Yong Tian, Qian Yu, Hunter Carrick, Brain Becker, and Remegio Confesor
4. ***Data analyses***
   Yong Tian, Qian Yu, and Anderson, C. Olivia
5. ***Manuscript preparation and Final Manuscript Approval***
   All authors

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study is supported by a collaborative National Science Foundation, United State Grant (1025547, PI, Q. Yu; 1025546, PI: Y.Q. Tian). Authors would like to thank Ashley Blunden (Lowran) for completing the bulk of the field sampling as part of her graduate work at CMU and Donald Uzarski for making his laboratory services available to process our DOC samples. This paper is contribution number xxx, Institute for Great Lakes Research at Central Michigan University. All supporting data have been listed in a pdf file that can be downloaded at: http://people.se.cmich.edu/tian2y/onlinedata.pdf.

References

Ågren, A., Haei, M., Köhler, S., Bishop, K., Laudon, H., 2010. Regulation of stream water dissolved organic carbon (DOC) concentrations during snowmelt; the role of discharge, winter climate and memory effects. Biogeosciences 7, 2901–2913.

Ågren, A., Jansson, M., Ivarsson, H., Bishop, K., Seibert, J., 2008. Seasonal and runoff-related changes in total organic carbon concentrations in the River Öre, Northern Sweden. Aquat. Sci. 70, 21–29.

Aitkenhead-Peterson, J.A., McDowell, W.H., Neff, J.C., 2003. Sources, production, and regulation of allochthonous dissolved organic matter inputs to surface waters. Aquatic Ecosystems. Elsevier, pp. 25–70.

Apland, J., McCarl, B.A., Miller, W.L., 1980. Risk and the demand for supplemental irrigation - CASE-study in the CORN belt. Am. J. Agric. Econ. 62, 142–145.

Arnold, J.G., Fohrer, N., 2005. SWAT2000: current capabilities and research opportunities in applied watershed modelling. Hydrol. Process. 19, 563–572.

Bhattacharya, R., Osburn, C.L., 2020. Spatial patterns in dissolved organic matter composition controlled by watershed characteristics in a coastal river network: the Neuse River basin, USA. Water Res. 169, 115248.

Bowering, K.L., Edwards, K.A., Prestegaard, K., Zhu, X., Ziegler, S.E., 2020. Dissolved organic carbon mobilized from organic horizons of mature and harvested black spruce plots in a Mesic boreal region. Biogeosciences 17, 581–595.

Boyle, D.P., Gupta, H.V., Sorooshian, S., Koren, V., Zhang, Z.Y., Smith, M., 2001. Toward improved streamflow forecasts: value of semidistributed modeling. Water Resour. Res. 37, 2749–2759.

Buffam, I., Galloway, J.N., Blum, L.K., McGlathery, K.J., 2001. A stormflow/baseflow comparison of dissolved organic matter concentrations and bioavailability in an Appalachian stream. Biogeochemistry 53, 269–306.

Butman, D., Raymond, P.A., 2011. Significant efflux of carbon dioxide from streams and rivers in the United States. Nature Geoscience 839–842.

Carrick, H.J., Marble, C., Tian, Y.Q., 2022. Differential responses for stream algal assemblages exposed to factorial N and P enrichment along an in situ DOC gradient. Front. Environ. Sci. Manuscript ID: 1066586.

Chalise, K.S., Singh, S., Wegner, B.R., Kumar, S., Perez-Gutierrez, J.D., Osborne, S.L., Nleya, T., Guzman, J., Rohila, J.S., 2019. Cover crops and returning residue impact on soil organic carbon, bulk density, penetration resistance, water retention, infiltration, and soybean yield. Agron. J. 111, 99–108.

Clark, J.M., Lane, S.N., Chapman, P.J., Adamson, J.K., 2007. Export of dissolved organic carbon from an upland peatland during storm events: implications for flux estimates. J. Hydrol. 347, 438–447.

Confesor Jr., R.B., Whittaker, G.W., 2007. Automatic calibration of hydrologic models with multi-objective evolutionary algorithm and Pareto optimization 1. J. Am. Water Resour. Assoc. 43, 981–989.

D'Amario, S.C., Xenopoulos, M.A., 2015. Linking dissolved carbon dioxide to dissolved organic matter quality in streams. Biogeochemistry 126, 99–114.

Du, X., Zhang, X., Mukundan, R., Hoang, L., Owens, E.M., 2019. Integrating terrestrial and aquatic processes toward watershed scale modeling of dissolved organic carbon fluxes. Environ. Pollut. 249, 125–135.

Dusek, J., Vogel, T., Dohnal, M., Barth, J.A., Sanda, M., Marx, A., Jankovec, J., 2017. Dynamics of dissolved organic carbon in hillslope discharge: modeling and challenges. J. Hydrol. 546, 309–325.

Ellis, E.C., Klein Goldewijk, K., Siebert, S., Lightman, D., Ramankutty, N., 2010. Anthropogenic transformation of the biomes, 1700 to 2000. Glob. Ecol. Biogeogr. 19, 589–606.

Fu, B., Merritt, W.S., Croke, B.F., Weber, T.R., Jakeman, A.J., 2019. A review of catchment-scale water quality and erosion models and a synthesis of future prospects. Environ. Model Softw. 114, 75–97.

Futter, M., Löfgren, S., Köhler, S., Lundin, L., Moldan, F., Bringmark, L., 2011. Simulating dissolved organic carbon dynamics at the Swedish integrated monitoring sites with the integrated catchments model for carbon, INCA-C. Ambio 40, 906–919.

Gómez-Gener, L., Hotchkiss, E.R., Laudon, H., Sponseller, R.A., 2021. Integrating discharge-concentration dynamics across carbon forms in a boreal landscape. Water Resour. Res. 57, e2020WR028806.

Guo, R., Qin, W., Jiang, C., Kang, L., Nendel, C., Chen, Q., 2018. Sweet corn significantly increases nitrogen retention and reduces nitrogen leaching as summer catch crop in protected vegetable production systems. Soil Tillage Res. 180, 148–153.

Haaland, S., Mulder, J., 2010. Dissolved organic carbon concentrations in runoff from shallow heathland catchments: effects of frequent excessive leaching in summer and autumn. Biogeochemistry 97, 45–53.

Heppell, C.M., Binley, A., Trimmer, M., Darch, T., Jones, A., Malone, E., Collins, A.L., Johnes, P.J., Freer, J.E., Lloyd, C.E., 2017. Hydrological controls on DOC: nitrate resource stoichiometry in a lowland, agricultural catchment, southern UK. Hydrol. Earth Syst. Sci. 21, 4785–4802.

Holgerson, M.A., Raymond, P.A., 2016. Large contribution to inland water CO2 and CH4 emissions from very small ponds. Nature Geoscience 222–226.

Humbert, G., Parr, T.B., Jeanneau, L., Dupas, R., Petitjean, P., Akkal-Corfini, N., Viaud, V., Pierson-Wickmann, A.C., Denis, M., Inamdar, S., Gruau, G., Durand, P., Jaffrezic, A., 2020. Agricultural practices and hydrologic conditions shape the temporal pattern of soil and stream water dissolved organic matter. Ecosystems 23, 1325–1343.

Jantze, E.J., Laudon, H., Dahlke, H.E., Lyon, S.W., 2015. Spatial variability of dissolved organic and inorganic carbon in subarctic headwater streams. Arct. Antarct. Alp. Res. 47, 529–546.

Jones, J., Knowlton, M., Obrecht, D., Cook, E., 2004. Importance of landscape variables and morphology on nutrients in Missouri reservoirs. Can. J. Fish. Aquat. Sci. 1503–1512.

Jones, J.R., Knowlton, M.F., 2005. Suspended solids in Missouri reservoirs in relation to catchment features and internal processes. Water Research 3629–3635.

Kaushal, S.S., Gold, A.J., Bernal, S., Johnson, T.A.N., Addy, K., Burgin, A., Burns, D.A., Coble, A.A., Hood, E., Lu, Y.H., Mayer, P., Minor, E.C., Schroth, A.W., Vidon, P., Wilson, H., Xenopoulos, M.A., Doody, T., Galella, J.G., Goodling, P., Haviland, K., Haq, S., Wessel, B., Wood, K.L., Jaworski, N., Belt, K.T., 2018. Watershed "chemical cocktails': forming novel elemental combinations in anthropocene fresh waters. Biogeochemistry 141, 281–305.

Kellerman, A.M., Arellano, A., Podgorski, D.C., Martin, E.E., Martin, J.B., Deuerling, K.M., Bianchi, T.S., Spencer, R.G., 2020. Fundamental drivers of dissolved organic matter

composition across an Arctic effective precipitation gradient. Limnol. Oceanogr. 65, 1217–1234.
Kelly, V., Stets, E.G., Crawford, C., 2015. Long-term changes in nitrate conditions over the 20th century in two midwestern corn belt streams. J. Hydrol. 525, 559–571.
Lambert, T., Darchambeau, F., Bouillon, S., Alhou, B., Mbega, J.D., Teodoru, C.R., Nyoni, F.C., Massicotte, P., Borges, A.V., 2015. Landscape control on the spatial and temporal variability of chromophoric dissolved organic matter and dissolved organic carbon in large African rivers. Ecosystems 18, 1224–1239.
Lapierre, J.F., Seekell, D.A., del Giorgio, P.A., 2015. Climate and landscape influence on indicators of lake carbon cycling through spatial patterns in dissolved organic carbon. Glob. Chang. Biol. 21, 4425–4435.
Leakey, A.D., Uribelarrea, M., Ainsworth, E.A., Naidu, S.L., Rogers, A., Ort, D.R., Long, S.P., 2006. Photosynthesis, productivity, and yield of maize are not affected by open-air elevation of CO2 concentration in the absence of drought. Plant Physiol. 140, 779–790.
Lehosmaa, K., Jyväsjärvi, J., Ilmonen, J., Rossi, P.M., Paasivirta, L., Muotka, T., 2018. Groundwater contamination and land drainage induce divergent responses in boreal spring ecosystems. Sci. Total Environ. 639, 100–109.
Li, J., Yu, Q., Tian, Y.Q., Boutt, D.F., 2018. Effects of landcover, soil property, and temperature on covariations of DOC and CDOM in inland waters. J. Geophys. Res. Biogeosci. 123, 1352–1365.
Lindström, G., Pers, C., Rosberg, J., Strömqvist, J., Arheimer, B., 2010. Development and testing of the HYPE (Hydrological predictions for the Environment) water quality model for different spatial scales. Hydrol. Res. 41, 295–319.
Millie, D.F., Weckman, G.R., Pigg, R.J., Tester, P.A., Dyble, J., Wayne Litaker, R., Carrick, H.J., Fahnenstiel, G.L., 2006. Modeling phytoplankton abundance in Saginaw bay, Lake Huron: using artificial neural networks to discern functional influence of environmental variables and relevance to a great lakes observing system 1. J. Phycol. 42, 336–349.
Monaghan, R., Wilcock, R., Smith, L., Tikkisetty, B., Thorrold, B., Costall, D., 2007. Linkages between land management activities and water quality in an intensively farmed catchment in southern New Zealand. Agric. Ecosyst. Environ. 211–222.
Monteith, D.T., Henrys, P.A., Evans, C.D., Malcolm, I., Shilland, E.M., Pereira, M.G., 2015. Spatial controls on dissolved organic carbon in upland waters inferred from a simple statistical model. Biogeochemistry 123, 363–377.
Motavalli, P., Bundy, L., Andraski, T., Peterson, A., 1992. Residual effects of long-term nitrogen fertilization on nitrogen availability to corn. J. Prod. Agric. 5, 363–368.
Oberle, S., Keeney, D., 1990. Factors influencing corn fertilizer N requirements in the northern US corn belt. J. Prod. Agric. 3, 527–534.
Olaoye, I.A., Confesor, R.B., Ortiz, J.D., 2021. Effect of projected land use and climate change on water quality of Old Woman Creek Watershed, Ohio. Hydrology 8, 62.
Olsson, M.T., Erlandsson, M., Lundin, L., Nilsson, T., Nilsson, Å., Stendahl, J., 2009. Organic carbon stocks in swedish podzol soils in relation to soil hydrology and other site characteristics. Silva Fennica 43, 209–222.
Pers, C., Temnerud, J., Lindström, G., 2016. Modelling water, nutrients, and organic carbon in forested catchments: a HYPE application. Hydrol. Process. 30, 3252–3273.
Puczko, K., Zieliński, P., Jusik, S., Kołakowska, A., Jekatierynczuk-Rudczyk, E., 2018. Vascular plant and bryophyte species richness in response to water quality in lowland spring niches with different anthropogenic impacts. Environ. Monit. Assess. 190, 1–16.
Qiao, H., Tian, Y.Q., Yu, Q., Carrick, H.J., Francek, M., Li, J., 2017. Snowpack enhanced dissolved organic carbon export during a variety of hydrologic of events in an agricultural landscape, Midwestern USA. Agric. For. Meteorol. 31–41.
Rana, T., Khan, S., Rahimi, M., 2008. Spatio-temporal optimisation of agricultural drainage using groundwater models and genetic algorithms: an example from the Murray irrigation area, Australia. Hydrogeol. J. 16, 1145–1157.
Raymond, P.A., Saiers, J.E., 2010. Event controlled DOC export from forested watersheds. Biogeochemistry 100, 197–209.
Royer, T.V., David, M.B., 2005. Export of dissolved organic carbon from agricultural streams in Illinois, USA. Aquat. Sci. 67, 465–471.
Schaefer, M.V., Bogie, N.A., Rath, D., Marklein, A.R., Garniwan, A., Haensel, T., Lin, Y., Avila, C.C., Nico, P.S., Scow, K.M., Brodie, E.L., Riley, W.J., Fogel, M.L., Berhe, A.A., Ghezzehei, T.A., Parikh, S., Keiluweit, M., Ying, S.C., 2020. Effect of cover crop on carbon distribution in size and density separated soil aggregates. Soil Systems 4.
Schilling, K.E., Streeter, M.T., Quade, D., Skopec, M., 2016. Groundwater loading of nitrate-nitrogen and phosphorus from watershed source areas to an Iowa great Lake. J. Great Lakes Res. 42, 588–598.
Sela, S., Woodbury, P., Marjerison, R., van Es, H., 2019. Towards applying N balance as a sustainability indicator for the US Corn Belt: realistic achievable targets, spatio-temporal variability and policy implications. Environ. Res. Lett. 14, 064015.
Sharratt, B., Benoit, G., Voorhees, W., 1998. Winter soil microclimate altered by corn residue management in the northern Corn Belt of the USA. Soil Tillage Res. 49, 243–248.
Singh, S., Dutta, S., Inamdar, S., 2014. Land application of poultry manure and its influence on spectrofluorometric characteristics of dissolved organic matter. Agric. Ecosyst. Environ. 193, 25–36.
Singh, S., Inamdar, S., Mitchell, M., 2015. Changes in dissolved organic matter (DOM) amount and composition along nested headwater stream locations during baseflow and stormflow. Hydrol. Process. 29, 1505–1520.
Spencer, R.G., Aiken, G.R., Dornblaser, M.M., Butler, K.D., Holmes, R.M., Fiske, G., Mann, P.J., Stubbins, A., 2013. Chromophoric dissolved organic matter export from US rivers. Geophys. Res. Lett. 40, 1575–1579.
Stedmon, C.A., Markager, S., Søndergaard, M., Vang, T., Laubel, A., Borch, N.H., Windelin, A., 2006. Dissolved organic matter (DOM) export to a temperate estuary: seasonal variations and implications of land use. Estuar. Coasts 29, 388–400.
Terajima, T., Moriizumi, M., 2013. Temporal and spatial changes in dissolved organic carbon concentration and fluorescence intensity of fulvic acid like materials in mountainous headwater catchments. J. Hydrol. 479, 1–12.
Tian, Y.Q., Wang, D., Chen, R.F., Huang, W., 2012. Using modeled runoff to study DOC dynamics in stream and river flow: a case study of an urban watershed southeast of Boston, Massachusetts. Ecol. Eng. 42, 212–222.
Tian, Y.Q., Yu, Q., Feig, A.D., Ye, C., Blunden, A., 2013. Effects of climate and land-surface processes on terrestrial dissolved organic carbon export to major US coastal rivers. Ecol. Eng. 54, 192–201.
Valentin, C., Agus, F., Alamban, R., Boosaner, A., Bricquet, J.-P., Chaplot, V., De Guzman, T., De Rouw, A., Janeau, J.-L., Orange, D., 2008. Runoff and sediment losses from 27 upland catchments in Southeast Asia: impact of rapid land use changes and conservation practices. Agric. Ecosyst. Environ. 128, 225–238.
Van de Griend, A.A., De Vries, J.J., Seyhan, E., 2002. Groundwater discharge from areas with a variable specific drainage resistance. J. Hydrol. 259, 203–220.
Vetsch, J.A., Randall, G.W., 2002. Corn production as affected by tillage system and starter fertilizer. Agron. J. 94, 532–540.
Vidon, P., Carleton, W., Mitchell, M.J., 2014. Spatial and temporal variability in stream dissolved organic carbon quantity and quality in an adirondack forested catchment. Appl. Geochem. 46, 10–18.
Vidon, P., Wagner, L.E., Soyeux, E., 2008. Changes in the character of DOC in streams during storms in two midwestern watersheds with contrasting land uses. Biogeochemistry 88, 257–270.
Vlahos, P., Chen, R.F., Repeta, D.J., 2002. Dissolved organic carbon in the mid-Atlantic bight. Deep-Sea Res. II Top. Stud. Oceanogr. 49, 4369–4385.
Wallin, M.B., Weyhenmeyer, G.A., Bastviken, D., Chmiel, H.E., Peter, S., Sobek, S., Klemedtsson, L., 2015. Temporal control on concentration, character, and export of dissolved organic carbon in two hemiboreal headwater streams draining contrasting catchments. J. Geophysi. Res.Biogeosci. 120, 832–846.
Ward, F.A., 2022. Enhancing climate resilience of irrigated agriculture: a review. J. Environ. Manag. 302.