Factors Driving the Spatiotemporal Variation of Dissolved Organic Carbon Flux from Croplands in the Midwestern USA

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Research Article

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Posted Date: January 14th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1223810/v1>

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2 Midwestern USA

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11

12

13 Abstract:

14 Improving understanding of dissolved organic carbon (DOC) cycling from farmlands to rivers is a
15 challenge due to the complex influence of farming practices, the hydrology of predominantly flat
16 lowlands, and seasonal snowpack effects. Monthly field DOC concentrations were measured throughout
17 the year at sub-basin scale across the Chippewa River Watershed, which falls within the Corn Belt of the
18 Midwestern United States. The observations from croplands were benchmarked against the data sampled
19 from hilly forested areas in the Connecticut River Watershed. The Soil Water Assessment Tool
20 (SWAT) was used to simulate daily soil water properties. This method tests for a framework for using
21 the combination of new field data, hydrological modelling, and knowledge-based reclassification of
22 Land Use/Land Cover (LULC) to analyze the predictors of both the spatial and temporal changes of
23 DOC over farmlands. Our results show: 1) DOC concentrations from cropland baseflow were
24 substantially high throughout the year, especially for spring runoff/snowmelt scenarios, 2) gradient
25 analysis with spatial factors only was able to explain ~82% of observed annual mean DOC
26 concentrations, and 3) with both spatial and temporal factors: [Evapotranspiration, Soil Water, and
27 Ground Water], the analysis explained ~81% of seasonal and ~54% of daily variations in observed DOC
28 concentrations.

29

30 **Keywords:** dissolved organic carbon, inland water, anthropogenic activity, crop residue management,
31 baseflow, agricultural landscape, hydrological modelling

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33

34 INTRODUCTION

35 Terrestrial organic carbon in the dissolved form (DOC) is easily transported to inland or coastal
36 waters via hydrological processes (Dusek et al. 2017; Heppell et al. 2017). Excessive riverine carbon has
37 a pronounced impact on aquatic ecosystems via processes such as amplifying microbial activity,
38 diminishing the quantity and quality of light penetrating the water column, and controlling toxic metal
39 availability (Butman and Raymond 2011; Spencer et al. 2013; Stedmon et al. 2006). As a major use of
40 land (Ellis et al. 2010), agricultural landscapes are a significant source of DOC in freshwater
41 ecosystems (Tranvik 2014). Recent studies raised a public health concern that rivers receiving runoff
42 from croplands have elevated DOC concentrations at regional and worldwide scales (Bhattacharya and
43 Osburn 2020; Qiao et al. 2017). DOC originating from croplands are enriched in aromatic structures and
44 exhibit high labile properties, thereby significantly affecting freshwater nutrient pathways (Bhattacharya
45 and Osburn 2020; Holgerson and Raymond 2016; Kellerman et al. 2020; Tranvik 2014).

46 In recent decades, there has been an increased interest in studying terrestrial carbon-source dynamics
47 and their impact on freshwater interactive processes (Heppell et al. 2017). As such, studies have made
48 significant progress towards gaining a better understanding of the impacts of climate change and
49 extreme storm events on variations of riverine DOC concentrations originating from terrestrial
50 environments (Kellerman et al. 2020). However, these studies are often limited in scope because they
51 were set at entire river basin scales without considering the heterogeneity and do not include sub-basin
52 land-surface characteristics and hydrological processes. In addition, these studies have largely focused
53 on semi-natural habitats involving little or no agriculture such as estuarine wetland, scrub-shrub, and
54 forested areas (Raymond and Saiers 2010; Rudolph et al. 2020; Tian et al. 2012). Studies focused on
55 forested landscapes are typically dominated by sloped landscapes that generate DOC fluxes
56 predominantly through surface runoff (Raymond and Saiers 2010; Singh et al. 2015). A representative

DOC model for studying hilly forested regions is the Integrated Catchments model for Carbon (INCA-C) (Futter et al. 2011). By using the INCA-C model, a study revealed that variations in DOC concentrations was primarily driven by soil temperature and surface runoff over forested, mountainous watersheds in Sweden (Clark et al. 2007; Fu et al. 2019; Pers et al. 2016). However, several other studies further clarified that event-based fluxes do not necessarily occur without baseflow during rainfall events; rather, event-based flows usually account for both surface runoff and baseflow during, and a few days after, a rainfall event (Ågren et al. 2008; Olsson et al. 2009). Therefore, DOC models that are based on measurements sampled from semi-natural habitats are not readily adaptable to agricultural landscapes in which carbon sources are typically more heavily influenced by complex anthropogenic factors, have a higher degree of heterogeneity of land cover types, and exhibit the major role of baseflow in lowland/flatland hydrological processes.

The DOC dynamics in streamflow generated from agricultural landscapes are significantly different than those reported for semi-natural habitats. This is especially true for the Corn Belt region of the Midwestern USA, where flatland hydrology dictates temporal variations in DOC concentrations via baseflow rather than overland surface runoff (Qiao et al. 2017). This is in sharp contrast to hilly forested areas where the majority of annual DOC fluctuations are dictated predominantly by surface runoff during rainfall events. Even over forested lands, it has been reported that low-flow conditions are ideal in order to best understand the transport processes of nutrients (e.g., N and P) from the soil profile and land surface (Lindström et al. 2010; Pers et al. 2016).

In general, the factors driving spatiotemporal variation of DOC concentrations in streams of croplands between rainfall events are not well understood. These temporal DOC variations are assumably controlled by soil properties such as organic matter content, level of saturation, and temperature. The spatial variations are likely associated with heterogeneity of the landscape, such as the

80 typical patchwork of small water bodies, wetlands, forest, and a broad range of crop density. More
81 variation or heterogeneity is introduced when considering the varied crop residue management policies
82 implemented by land managers. It remains largely unproven if both the spatial and temporal variations
83 of DOC fluxes from croplands to receiving waters can be reliably quantified, and what the appropriate
84 sub-basin scales are for quantifying these spatiotemporal variations

85 The goal of this study is to analyze how DOC concentrations originating from crop-dominant
86 lowlands vary by season and spatial distribution. We aim to identify a range of potential drivers that are
87 useful to modelling the spatial disparities and trends of DOC variations instead of using soil C:N ratio as
88 a surrogate (Aitkenhead-Peterson et al. 2003). The research niche includes the incorporation of detailed
89 hydrologic variables, the adaptation of high spatial-resolution land surface features, and the collection
90 and utilization of primary field observations. This study is focused on identifying a workable
91 spatiotemporal scale of both field observations and quantitative analysis of DOC source dynamics, fate,
92 and transport processes. This research focus is both novel and urgent because DOC export from
93 agricultural landscapes occurs at the expense of the water quality of adjacent freshwater systems and to a
94 lesser extent the land sustainability. Detrimental agricultural land management policies and practices can
95 inherently lead to degraded water quality through both physical and biochemical processes (Jones et al.
96 2004; Jones and Knowlton 2005; Monaghan et al. 2007; Valentin et al. 2008). Clearly, DOC is part of a
97 delicately balanced synergistic system and thus, modelling the concentration of DOC in lakes and rivers
98 can provide a useful index of land-water ecology (Gómez-Gener et al. 2021).

99 MATERIALS AND METHODS

100

101 *Study site:*

102 Two contrasting study sites (cropland versus sloped forestland) were referenced in this study to
103 allow direct comparison of DOC dynamics from croplands to a more homogeneous, forested landscape.
104 The primary study site consisted of the Chippewa River watershed, which is one of the three tributaries
105 draining the western portion of the larger Saginaw River watershed. The Saginaw River ultimately
106 empties into Saginaw Bay, Lake Huron, which is one of the most bio-productive coastal regions in the
107 entire Great Lakes Ecosystem (Millie et al. 2006). The Chippewa watershed cuts across the Lower
108 Peninsula of Michigan and extends nearly 92 miles to Midland, Michigan, flowing predominantly
109 eastward and ultimately merging with the Tittabawassee River. The croplands in our primary study site
110 were dominated by row crops of corn, soy, wheat, and sugar beets, that were situated adjacent to mixed
111 woodlots and wetlands, with a small proportion of lands dedicated to hay production and areas of
112 development. The topography (mean slope $< 0.3^\circ$), and climate in the primary study site were typical to
113 the flat lowlands of the midwestern United States. In-situ DOC samples (153) were collected monthly at
114 key locations across the Chippewa River watershed from 2012 to 2014.

115 The secondary study site for this study included five largely forested sub-basins within the greater
116 Connecticut River Watershed, which is the longest river in the northeastern United States. DOC samples
117 extracted from these forested sub-basins provided direct comparisons to those collected in the primary
118 study site. The Connecticut River Watershed is one of the larger watersheds in the Northeast, draining
119 approximately 11,000 square miles. In-situ DOC samples (125 samples) were collected monthly from
120 2011 to 2016 across these five forested sub-basins within the Connecticut River Watershed (Li et al.
121 2018). Two of the five sub-basins had landcover types dominated by northeastern deciduous forests.
122 Northeastern conifer forests were the dominant vegetation in two of the sub-basins. The fifth sub-basin's
123 land cover was classified as a northeastern conifer/deciduous mixed forest. These 125 forested, in-situ

124 field observations collected across multiple years and seasons were paramount to better quantify the
125 significant DOC contributions from croplands in comparison to forested landscapes.

126

127 *Field Sample Protocols*

128 There were 278 water samples collected in total, from 26 sampling locations via 43 field visits
129 spread between the two study sites. Within the primary study site, a range of locations were selected and
130 organized into two sampling groups (crop dominated and mixed croplands) as displayed in Figure 1. The
131 13 sampling locations (IDs 1-13) associated with the first group focused on crop-dominated drainage
132 sub-basins. The 8 sampling locations (IDs 14-21) associated with the second group was added to include
133 drainage sub-basins dominated by the croplands mixed with a large proportion of forests and wetlands.
134 Monthly field visits were arranged between rainfall events to best reflect seasonal variations and to
135 reduce the influence of any single event. The entire cropland field campaign ran for 14 months
136 beginning in October 2012 and ending in January 2014. Field sampling activities were primarily
137 conducted during the spring and fall when soil biochemical processes and nutrient fluxes are more
138 prevalent(Sela et al. 2019; Sharratt et al. 1998). DOC concentrations are generally elevated in the
139 springtime months due to snowpack dependent biochemical processes, soil moisture conditions, and
140 runoff from snowmelt (Qiao et al. 2017). DOC concentrations are also elevated in the autumn months
141 when crop biomass is at its peak and when such biomass is actively manipulated due to harvest, residue
142 management practices, and fall tillage(Kelly et al. 2015; Vetsch and Randall 2002). A reduced number
143 of field samples were collected for the purpose of analyzing the transition of DOC concentrations
144 between seasons. In total,153 water samples were collected to satisfactorily quantify seasonal patterns in
145 DOC variation within receiving waters.

146

147 *Laboratory Protocols to Estimate DOC concentration*

148 Field samples were obtained from all sampling locations using clean 500 mL bottles (acid washed)
149 to collect stream water for DOC analysis. Bottles were fully immersed while capping to ensure that no
150 air remained. The samples were immediately stored on ice until arrival at the lab for immediate
151 filtering. Water samples were filtered through pre-combusted glass-fiber filters (nominal 0.7 μm pore
152 size) to remove any non-dissolved organic matter, and the filtrate was then stored (acidified and
153 refrigerated) until analysis for DOC content. All Laboratory processes were completed within 12 hours
154 of sample collection. The DOC concentration of each water sample was measured using a Shimadzu
155 TOC-V analyzer with high temperature combustion (Vlahos et al. 2002). For each, 50 μl injections of
156 sample water was combusted at 800 $^{\circ}\text{C}$, from which the DOC concentration was calculated from the
157 resultant CO_2 yield and measured with a non-dispersive infrared detector.

158

159 *Land Cover Composition*

160 National Land Cover Data (NLCD) data from 2011 was used because this date was closest to our
161 sampling dates (2012-2014). The original baseline NLCD data referenced 13 land cover categories. We
162 reclassified these baseline land cover data into three more broadly defined classes according to their
163 general DOC transforming rates based on preliminary modelling runs (Figure 2). The percent-area
164 composition of the three new classes extracted from the NLCD data were calculated for each drainage
165 sub-basin in the primary study site and are shown in Table 1. These data were used to analyze DOC
166 dynamics at the sub-basin level. It is important to note that land cover data was needed for the entire
167 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 home (immediate) sub-basin, but also from upstream sub-basins that contained points 16, 17 and 18.

Hydrological Modeling

The Soil Water Assessment Tool (SWAT) was used to generate daily hydrologic characteristics for all sub-basins of the primary study site. We examined the simulated outputs 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, we implemented SWAT using 38 years of daily hydrologic input data spanning from 1981 to 2018. In addition, spatially explicit, high resolution (4 km² grid) daily weather forcing data (precipitation, maximum temperature, and minimum temperature) were downloaded from the PRISM website (<https://prism.oregonstate.edu/recent/>) and also 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. LULC types were extracted from NCLD 2011 as described above and used as inputs. Soil input parameters were extracted from SWAT's built-in STATSGO data. Elevation data were extracted from a 30m Digital Elevation Model (DEM) of Isabella County, Michigan. As a result, the SWAT model delineated our primary study site into 126 sub-basins.

Next, Chippewa River daily flow data were categorized into high (top 10 percentile), medium (10th-50th percentile), and low (lowest 50th – 100th percentile) flows. The SWAT model was then calibrated through a multi-objective auto-calibration for these three flow regimes for the period from 2011 to 2018 using the method developed by (Confesor Jr and Whittaker 2007). The overall daily Nash–

191 Sutcliffe model efficiency coefficient (NSE) was 0.67 and the corresponding R^2 was 0.886. The
 192 simulated hydrologic properties for each of the 126 SWAT modeled sub-basins were used as
 193 independent variables for quantitative analysis of daily DOC observations.

194

195 *Exploratory Statistical Analysis*

196 Multiple linear regression analysis was used to explore which independent variables were most
 197 relevant in explaining variation in DOC concentrations at various spatial and temporal scales. In
 198 essence, these linear regressions aimed to fit observed/sampled DOC data to a linear equation with $m + n$
 199 independent variables, where m is the number of variables associated with the characteristics of each
 200 drainage sub-basin and n is the number of temporal/seasonal variables. The specification of the linear
 201 model was as follows:

$$202 \quad y(i, t) = c + \sum_{j=1}^m \alpha_j x_j(i) + \sum_{k=1}^n \beta_k S_k(i, t) \quad (1)$$

203 Let $X(i) = [x_1(i) \ x_2(i) \dots x_m(i)]$ be the m exploratory spatial variables for the sub-basin associated
 204 with sampling location i for $i = 1 \dots L$. L is the number of sampling locations. Similarly, let $S(i, t) =$
 205 $[s_1(i, t), s_2(i, t), \dots s_n(i, t)]$ be the n exploratory seasonal (temporal) variables for the sub-basin i and Julian
 206 day t , for $t = 1, 2 \dots Q$. Q is the last Julian day of field sampling visits. Each variable set $X(i)$ were split in
 207 three categories: land cover (e.g., percent cropped area, percent forested), soil properties (e.g., percent
 208 silt, percent organic matter), and geomorphology (e.g., sub-basin area, average slope). The spatial
 209 variables were derived from each drainage area. The seasonal variables $S(i, t)$ were split into two
 210 categories: hydrologic characteristics (e.g., SW : soil water content, PET : potential evapotranspiration,
 211 GW : ground water volume) and weather inputs (e.g., point specific precipitation and temperatures). The
 212 observed DOC, $y(i, t)$ corresponded with all sampling locations i , and the Julian days t of field visits.

213 The observed values $y(i, t)$ for all i s and t s were fitted to eq. 1 for estimating the parameters

214 $c, \alpha_1, \alpha_2, \dots, \alpha_m, \beta_1, \beta_2, \dots, \beta_n$.

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

226

227 One of our research objectives was to evaluate the appropriate spatial scale (i.e., contributing
228 hydrologic areal extent) for quantifying the inherent relationship between a variety of independent
229 variables and the variation of observed DOC concentrations from cropland areas. Here, we designated
230 stream segment i and sub-basin i as the immediate stream segment and sub-basin in which the sampling
231 location i resides. With this designation, this study tested two spatial scale scenarios: 1st-order
232 extended sub-basins and non-extended drainage areas. All 1st-order extended sub-basins met one of the
233 following two criteria: (1) all sub-basins associated with sampling sites within a 1st-order stream, such
234 as sampling locations 4, 6, 7, 9, 10, 11, 13, 16, 18, 19, and 20, or (2) all sub-basins associated with
235 sampling sites within a 2nd or 3rd order stream if they had the same dominant land cover as all their

upper-tributary sub-basins. Sampling locations 5, 15, and 17 met this second criterion and were designated as extended drainage sub-basins. For example, sub-basin 5 resides in a 2nd-order stream and its dominant land cover is identical to that of its upper tributary sub-basin, which in this case was sub-basin 4 (1st-order). Thus, the modelled drainage area associated with sampling location 5 included both the areal extent of the upstream 1st-order sub-basin 4 and its immediate 2nd order sub-basin 5. Therefore, the extended sub-basins in this project consisted of 14 sub-basins: 4, 6, 7, 9, 10, 11, 13, 16, 18, 19, 20, 5, 15, and 17. The remaining 7 sample locations (1, 2, 3, 8, 12, 14, and 21) are associated to the non-extended drainage areas.

244

RESULTS AND DISCUSSION

Our overarching research objective was to establish a theoretical understanding of the relationship and significance between a variety of independent, spatiotemporal variables and observed DOC concentrations in cropland areas. We present pertinent results and related discussion within four distinct sections: 1) Spatial disparity of mean annual DOC, 2) Seasonal/temporal patterns from the observations for both croplands and forested lands, 3) Variables useful to estimate spatial and temporal distributions of DOC concentrations in streamflow throughout the year, and 4) A quantitative analysis of mean monthly DOC trends.

253

1. Spatial disparity of mean annual DOC

DOC concentrations ranged from 5.5 to 10.5 mg/L, and these values varied greatly across the drainage sub-basins of the primary study area. Our results revealed that the DOC observations averaged over the entire year for each sampling location were largely controlled by four spatial variables for the 1st-order extended areas. Specifically, a resultant linear regression model (eq. 2) explained more than

259 82% ($R^2_{\text{adj}} = 0.74$) of mean annual DOC, $\bar{y}(i)$, the concentrations observed across 14 sampling locations:
260 4, 5, 6, 7, 9, 10, 11, 13, 15, 16, 17, 18, 19, and 20 (Figure 3A).

$$261 \quad f(X) = 0.52crp + 1.19frt + 0.52wetl + 18.74dum - 63.07 \quad (2)$$

262 Where the first three variables (i.e., *crp*, *frt*, *wetl*) were percent of crops, forest, and wetland, and *dum*
263 was the binary dummy variable useful for separating crops and mixed land covers (*crop* = 1, *mixed* = 0).
264 All coefficients for each of the four variables and the y-intercept were significant with respect to the
265 observed DOC data (p-values $\ll 0.05$). The overall model explained a significant portion of variation in
266 DOC values ($F = 10.22$, $p\text{-value} = 0.0021$). The dummy variable used in this modeling effort played a
267 role as a constraining condition. The dummy variable expanded the capability of the linear regression for
268 these complex scenarios of mixed land cover composition.

269

270 The positive coefficient for the variable *crp* shown above indicates a positive correlation between
271 DOC concentrations and crop density (*crp*), as one might expect given that crop density and the
272 resulting residues usually increase DOC loadings (Tian *et al.*, 2013). However, inspection of the 3-D
273 graph in Figure 3B clearly contradicts such a positive relationship, for the highest DOC values were
274 clearly associated with the low *crp* values. This negative correlation seemed to be regulated by a
275 geomorphological feature, $\ln(A)$ which is the logarithm of the drainage areas.

276

277 The percent of crop land cover (*crp*) is indeed positively correlated to $\ln(A)$, which was not included
278 in eq. 2 for crop dominant areas because the p -value was slightly larger than the 0.05 threshold ($p =$
279 0.0638). Moreover, further inspection of the 3-D graph in Figure 3B also revealed that both *crp* and
280 $\ln(A)$ have an inverse relationship to mean annual DOC. This result demonstrated the relative
281 importance of accounting for geomorphological parameters (A) that appear to act at the scale of

individual sampling locations. Interestingly, $\ln(A)$ was included in a linear model (eq. 3), once the p -value threshold was relaxed to 90 percent (p -values < 0.1).

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

Inclusion of the variable $\ln(A)$ demonstrates the viability of our spatially explicit modelling approach in eq. 3. This spatial variable was helpful in estimating mean annual DOC concentrations in runoff from croplands with varying levels of crop percentages across a larger region. It is logical to assume that its negative coefficient reflects the hydrologic processes occurring on and within the relatively larger and flatter (i.e., equated to higher percentage of crops) sub-basin. The alteration of hydrologic processes would result in the reduction of DOC concentrations because of the longer transport and residence time, allowing for greater soil carbon adsorption and infiltration. The second model (eq. 3) explained DOC observations better (88%, $R^2_{adj} = 0.69$, $p=0.001$) than the model (eq. 2) which did not directly reference this geomorphologic variable, drainage area.

The predictive power of our regression results (i.e., eq. 2 and eq. 3) highlight the viability of modelling mean annual DOC concentrations at the individual sub-basin level. Verification of model performance at the individual sub-basin level is indeed a necessary step before coupling multiple sub-basins into a more integrative model for use at a larger or regional scale. In other words, integrative modelling can indeed estimate DOC concentrations within high order stream segments by cumulatively aggregating or mixing DOC loadings from modelled upstream sub-basins (Tian et al. 2002). This integrative and hydrologically cumulative approach appears to better approximate the reality of how the many interconnected watershed components exchange materials from 1st-order to higher-order downstream receiving waters.

306

307 Both our statistical analyses and encouraging modelling outputs of DOC dynamics at the annual
308 scale advances the scientific communities understanding of how anthropogenic agricultural land use
309 changes and related management practices can help to explain spatial disparities of DOC concentrations
310 originating from croplands. Our results also highlight the need for comprehensive in-situ sampling
311 campaigns across different ecoregions and climatic zones to help fine tune regional and global models.
312 The variables identified in eqs. 2 and 3 are extractable from satellite images, which helps bridge the gap
313 from more localized modelling efforts to more regional and global spatial scales that take advantage of
314 remote sensing technologies. Thus, this investigation verified the feasibility of using easily-obtainable
315 satellite image data to detect DOC dynamics and to study the impacts of human activities and
316 management policies on both land sustainability and the ecology of freshwater habitats.

317

318 2. *Seasonal DOC trends from crop and forest lands*

319 Strong seasonal patterns in DOC concentrations were inherent in our data, and the associated driving
320 factors became readily apparent from the analysis of daily and monthly DOC export rates. The patterns
321 in Figure 4A describe the DOC observations averaged in each month from all sampling locations that
322 were in the 1st-order extended sub-basin scenario. Sampled peak DOC concentrations were not
323 associated with runoff events, because we purposefully established our sampling periods to occur
324 between rainfall and storm runoff events. Accordingly, modeled DOC concentration peaks were the
325 result of seasonal phenomenon and not just a single episodic event. Generally, snowpack elevates soil
326 water content during late winter and early spring (i.e., middle of March). It has been reported that high
327 soil moisture content enhances certain saturation-dependent metabolic processes and biogeochemical
328 reactions (Leakey et al. 2006) as well as increased accumulation of DOC in the topsoil (Ågren et al.

2010). The seasonal peak observed in March 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. The high soil-water content (i.e., soil moisture) for the primary study site in late winter and early spring were predicted quite well by the simulation results of the SWAT hydrologic model (Figure 5). The SWAT model also accurately predicted the high soil water content associated with winter snowpack and its subsequent spring melting. The seasonal accuracy of the SWAT model stands to reason, given the promising calibration performance ($NSE = 0.66$, $R^2 = 0.88$) when referencing daily flow records for 38 years. As such, a slight spike in DOC concentrations (i.e., March) originating from these organic-rich croplands appeared to be triggered by the infiltration of snowmelt and elevated soil water content, coupled with the with flat topographic characteristics of the mixed drainage sub-basins (blue curve in figure 4A). The mixed drainage sub-basins have relatively less area for crop residue accumulation across multiple years, due to their relatively large percentage of forest and wetland land covers. Rich crop residue biomass is indeed the dominant anthropogenic source of geochemically active and transformable DOC. Spring is a critical time of the year with respect to benthic and shallow water habitat in relation to biological communities, aquacultural production, and water quality to public health(Lehosmaa et al. 2018; Puczko et al. 2018), which corresponds to spikes in DOC concentrations.

In contrast, an early spring DOC peak was not observed (Figure 4B) from the steep forested lands of the second study site 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-litter fell 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 flux movements which corresponds to the lack of such a DOC peak in early spring for these forested locations (Figure 4B).

Other DOC peaks matched well between the two study sites (crop versus forest) from May to December (correlation > 0.65). We feel confident that these parallel DOC export curves are seasonal effects rather than of individual storm events since the curves were derived from a large set of multi-year, independent field measurements (i.e., 50 field visits). DOC spikes in May were triggered by increased soil temperatures followed by elevated ground water volumes (Figure 4). It seems logical that soils at depth take a longer time to warm up than the land surface temperature. Thus, the flux of DOC stored in such soil profiles were delayed until May at-depth soil temperatures began to rise (Figure 4A). High ground water levels and low soil water content were exhibited from the late April to early May as simulated via SWAT (i.e., black curve in Figure 5). Further examination of Figure 5 revealed that higher DOC export for croplands compared to forested areas was partially due to the crop farming practices, namely tillage in preparation for spring seeding. The optimum corn planting period for much of Michigan is from the beginning to middle of May, and soil manipulations would inherently rise as fields are prepped for planting. Soil temperature combined with the elevated soil moistures associated with summer rains may affect the DOC peaks in August for both study sites. Higher temperatures are associated with higher rates of microbial activities and faster turnover of DOC in the Carbon cycle of organic soils (Bowering et al. 2020; Haaland and Mulder 2010).

374 The mean monthly DOC concentration for croplands were more than 3-fold greater (Figure 4A)
375 compared with those for forestlands (Figure 4B) throughout the year. The monthly precipitation and
376 temperature patterns between the two study sites were very comparable. Therefore, the excessive soil
377 DOC production rates from croplands were caused by anthropogenic effects in terms of crop residue
378 accumulation and related break-down. Our previous study's preliminary mesocosm experiments
379 revealed that corn plants have a slower metabolic process for transforming foliar organic matter into the
380 dissolved form when compared to deciduous (D) and evergreen (E) foliage (Li et al. 2018). Figure 6
381 illustrates how DOC production rate changed for the same applied biomass (260-g dry biomass), the
382 same number of incubation days, and two different temperatures (L:20 °C or H:25°C) for these three
383 vegetation types. Figure 6 illustrates that DOC transformation (i.e., foliar to dissolved) rates were often
384 2.5 times faster for forest foliage as compared to sweet corn foliage. Intuitively, the amount of organic
385 biomass of croplands must therefore be 5-6 times higher than that of forested lands to result in the 3-fold
386 greater DOC concentrations. Clearly both farming and crop residue practices cause increased DOC
387 concentrations originating from croplands as opposed to climate or temperature variations.

388

389 3. *Variables attribute to spatial and temporal DOC variations in croplands*

390 Seven variables were identified as being statistically significant in driving DOC variation (eq. 5) in
391 reference to finer spatial and temporal scales. Three out of these seven variables were related to seasonal
392 effects that acted to quantify combined hydrologic and climatic properties: soil water content (*sw* in
393 mm), ground water volumes (*gw* in mm), and potential evapotranspiration (*pet* in mm). The remaining
394 four variables were related to the spatial characteristics of any given sub-basin (i.e., *crp*, *frt*, *wetl* and
395 *dum*). Note that these spatial variables are the same as those found to be significant when analyzing

mean annual DOC dynamics. Specifically, for an area draining to sampling location i , and at a particular Julian day, t , seasonal variable set S and spatial variable set X are:

$X(i) = [crp(i), frt(i), wetl(i), \text{ and } dum(i)]$ for all $i = 4, 5, 6, 7, 9, 10, 11, 13, 15, 16, 17, 18, 19, 20$

$S(i, t) = [sw(i, t), gw(i, t), pet(i, t)]$ for all $t = \text{Julian day when had a field sampling}$

For the purpose of statistical data exploration, the linear regression was based on daily data $X(i)$ for all i and $S(i, t)$ for $i=\text{gauge}$ and all t (Figure 5). The seasonal data is specified for the sub-basin that contained the USGS gauge station, since all $S(i, t)$ are highly correlated (Correlations ≥ 0.8). Given these circumstances, $S(\text{gauge}, t)$ changes with Julian days and does not change spatially for each sampling location. This linear regression analysis (eq. 4) explained approximately 54% of $y(i, t)$, DOC concentrations for all samples (crop and non-crop, $R^2_{\text{adj}} = 0.503$, $N=100$) as displayed in Figure 7 (both yellow and blue points). For crop dominant drainage sub-basins, the model explained approximately 50.44% ($R^2_{\text{adj}} = 0.46$, $N=63$, yellow triangle points).

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

All seven variables in eq. 4 tested significant ($p\text{-value} \ll 0.05$). The coefficients of eq. 4 likely indicate several responsive processes. The coefficients of the spatial variables have similar value ranges to those associated with eq. 3, albeit with the exclusion of the variable $Ln(A)$. The $Ln(A)$ variable with eq. 3 was functionally replaced by the ground water variable (gw) in this finer spatiotemporal-scale statistical analysis (eq. 4). The negative coefficient for gw indicates an inverse relationship to DOC observations. Logically, the presence of significant amounts of ground water is likely strongly correlated to the size of the drainage area. The presence of relatively high groundwater amounts within larger sub-

basins likely acts to dilute soil-profile DOC concentrations. These four spatial variables help to inform what, where, and how land surface characteristics impact the variation of riverine DOC.

The three seasonal/temporal variables indicate that the timing (when) of increased DOC concentrations is inherently related to the potential harm of the receiving aquatic ecosystem if DOC exceeds ecosystem capacities. The coefficients of the three seasonal variables are nearly of equal importance in this model. The hydrologic properties represented by these seasonal variables were simulated well by the SWAT model. The modelled data values marked with light blue vertical lines in Figure 7 are shown with their associated Julian days of DOC sample collection. The higher snowmelt modelled with SWAT is consistent with the idea that these meltwaters infiltrate the soil and increase soil water content (sw) and thus carbon transport in the early months of the year (Figure 5).

The resultant coefficients and listed significant variables reflect underlying scientific rationales rather than pure empirical analysis. The results indeed provide substantial information and knowledge about the future development of a non-linear analytical model for exploring spatial and temporal variations of DOC export. This statistical analysis of the variation of daily DOC concentrations also implicated the necessity of extending the anticipated non-linear analytical model to incorporate seasonal trends that would ultimately be helpful in analyzing the long-term anthropogenic effects on receiving water DOC concentrations. For this purpose, we expand the statistical analysis to mean monthly DOC concentrations in the following section.

4. A quantitative analysis of mean monthly DOC trend

Modelled daily DOC concentrations were averaged for each month from all 10 sampling locations in which drainage sub-basins were crop dominated, 1st-order extended sub-basins. The mean monthly

441 modelled DOC concentrations explained about 81% ($R^2 = 0.81$) for the observation data set 1 (Ob1 in
442 Figure 8) for six months (i.e., Jan., Mar., Apr., May, Nov., and Dec.). The months related to Ob1 were
443 chosen because they represented data generated with more frequent field visits. The observation data
444 set2 (Ob2) were collected during summer months (i.e. Jun, Jul., Aug., and Sep.) and were limited in
445 sample frequency. Therefore, the model explained less (49%) in correspondence analysis for the Ob2
446 months. In general, the model explained approximately 56% ($R^2 = 0.56$) of the observations (Ob1 and
447 Ob2) throughout the year.

448

449 Monthly intervals are appropriate to both hindcast or forecast long-term impacts of climate change
450 and human activity on carbon-cycling processes. Our analysis suggests that monthly DOC
451 concentrations are indeed quantifiable and can provide an ideal baseline for developing next-generation
452 analytical models. The month-based, baseline model can provide a platform for including event-based
453 DOC fluctuations (Qiao et al. 2017). Such monthly, next-generation models can then be expanded to
454 incorporate both the spatial and temporal variables influencing DOC dynamics at sub-basin scales.
455 Ultimately, such models can integrate biological and physical processes to help identify where, when,
456 and how DOC source and transport mechanisms respond to climatic and anthropogenic processes.

457

458 CONCLUSIONS

459 Our research reported several analysis results of DOC cycling processes from croplands to
460 receiving waters. The spatiotemporal distributions of DOC concentrations were observed from a
461 cropland representative of the Midwestern United States. The main contributions of our research efforts
462 are summarized below.

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

472

473 Acknowledgements

474 This study is supported by a collaborative NSF Grant (1025547, PI: Q. Yu; 1025546, PI: Y.Q. Tian).
475 We would like to thank Ashley Blunden (Lowran) for completing the bulk of the field sampling as part
476 of her graduate work at CMU and Donald Uzarski for making his laboratory services available to
477 process our DOC samples. All supporting data have been listed in a pdf file that can be downloaded at:
478 <http://people.se.cmich.edu/tian2y/onlinedata.pdf>

479

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616 **Statements & Declarations**

617 This study is supported by a collaborative NSF Grant (1025547, PI: Q. Yu; 1025546, PI: Y.Q. Tian).

618

619	Author Contributions
620	1. Research concept, design, and question
621	All authors
622	2. Funding:
623	Yong Tian, Qian Yu, Hunter Carrick
624	3. Material preparation, and data collection
625	Yong Tian, Qian Yu, Hunter Carrick, Brain Becker, and Remegio Confesor
626	4. Data analyses
627	Yong Tian, Qian Yu, and Anderson, C. Olivia
628	5. Manuscript preparation and Final Manuscript Approval
629	All authors
630	
631	

632 Figure and table captions

633 Figure 1, The primary study area and landcover. It consists of 21 sampling locations established at sub-
634 basin outlets of the drainage sub-basins. Black polygons are the drainage sub-basins. The blue
635 vector data are the streams. (Color needed)

636 Figure 2, Original national land cover classification codes (NLCD) and three newly formed classes.

637 Figure 3, A) the linear regression estimation against the DOC observations, and B) both Crop% and
638 $\ln(A)$ have inverse correlations to DOC concentrations, yet the correlation between Crop%
639 and $\ln(A)$ is positive.

640 Figure 4, A): Mean monthly DOC concentrations for Crop and mixed land covers over the primary
641 study site. Note that February DOC concentrations were interpolated by using the average
642 value of adjacent months. B): Monthly mean DOC concentrations of five sub-basins in the
643 Connecticut River Watershed collected in years 2011-2016. Note that February and July data
644 were interpolated by averaging data from the jacent months. In general, mean monthly DOC
645 from croplands in the Chippewa River Watershed are highly correlated (0.65) to that from
646 forested area in the Connecticut River Watershed.

647 Figure 5, SWAT modelled daily PET, SW, SN, GW and SM for sub-basin 49 for year 2013. The sub-
648 basin 49 contains the USGS gage station. The dashed light blue vertical lines indicate the
649 sampling date. (PET: Potential Evapotranspiration, SW: Soil Water content, GW: ground
650 water, and Snowmelt: Snow Liquid Equivalent).

651 Figure 6, DOC production rates of three vegetation types: corn plant (AH/AL), broad leaf liters
652 (DH/DL) and conifer leaf liters (EH/EL). The L stands for low temperature (20°C) and H is
653 the high temperature (25°C)

654 Figure 7, the modelled (Y axis) versus observed (X axis) DOC concentrations for all data points
655 collected over enhanced-area landscapes (N=100), and for crop dominant drainage areas
656 (yellow triangle points, N = 63).

657 Figure 8, Modelled (mod in red) versus observed mean monthly DOC concentrations for crop dominant
658 drainage areas over 1st-order drainage sub-basins. Observation data set 1 (Ob1) is for Jan, Mar,
659 Apr, May, Oct, Nov, and Dec, $R^2=0.81$. Observation data set 2 (Ob2) is for Jun, Jul, Aug, and
660 Sep, $R^2 = 0.49$. For combined Ob1 & Ob2 in all 12 months together, $R^2 > 0.56$

661 Table 1, Land Use Composition (%) in the area (Cells) draining to each sample location (SID). Crop%:
662 percent of crop coverage, Fort%: Forest, Wetl%: wetlands, Dev%: developed, and wat%:
663 Water body.

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Figure 2, The primary study area and landcover. It consists of 21 sampling locations established at sub-basin outlets of the drainage sub-basins. Black polygons are the drainage sub-basins. The blue vector data are the streams.

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706 Figure 8, the modelled (Y axis) versus observed (X axis) DOC concentrations for all data points collected over enhanced-area
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Figure 9, Modelled (mod in red) versus observed mean monthly DOC concentrations for crop dominant drainage areas over 1st-order drainage subbasins. Observation data set 1 (Ob1) is for Jan, Mar, Apr, May, Oct, Nov, and Dec, R²=0.81. Observation data set 2 (Ob2) is for Jun, Jul, Aug, and Sep, R² = 0.49. For combined Ob1 & Ob2 in all 12 months together, R² > 0.56

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Tables

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Table 1, Land Use Composition (%) in the area (Cells) draining to each sample location (SID).

721

Crop%: percent of crop coverage, Fort%: Forest, Wetl%: wetlands, Dev%: developed, and wat%: Water body.

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ID	Samples #	DOC Mg/L	Cells	Ln(Cells)	Crop %	Forest %	Wetland %	Developed %	Hay %	Water %
1	7	6.899	259437	12.47	64	16	13	5	3	0
2	7	5.864	1402613	14.15	38	29	18	8	4	2
3	6	6.009	1435616	14.18	37	16	15	29	2	1
4	6	7.300	26314	10.18	78	3	12	7	0	0
5	6	6.548	61578	11.03	80	3	11	6	0	0
6	6	5.739	38201	10.55	81	3	8	7	0	0
7	6	6.503	176446	12.08	75	4	14	6	1	0
8	7	6.263	1915023	14.47	39	18	26	14	3	1
9	6	5.516	113370	11.64	86	2	3	8	1	0
10	7	6.006	86448	11.37	87	2	6	5	0	0
11	6	5.890	166695	12.02	75	5	13	7	0	0
12	6	6.351	46173	10.74	26	24	33	12	5	0
13	6	6.274	41969	10.64	44	12	24	17	1	1
14	10	5.508	1079820	13.89	30	36	20	6	5	3
15	10	6.166	966081	13.78	27	37	21	6	6	3
16	10	8.736	327472	12.70	16	42	26	5	8	3
17	9	7.159	550234	13.22	20	40	24	5	7	4
18	10	6.972	62698	11.05	38	34	20	5	4	0
19	4	10.057	13910	9.54	66	10	15	6	3	0
20	8	9.704	91906	11.43	26	39	24	4	7	0
21	10	8.318	244838	12.41	59	17	16	5	3	0

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