Agricultural land use changes stream dissolved organic matter via altering soil inputs to streams

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HIGHLIGHTS

- We assessed the effects of agricultural land on DOM quantity and quality in streams.
- PLS-PM models allowed disentangling the effects of agriculture vs. natural drivers.
- Agricultural land use increased the export of soil-derived DOC and DOM.
- Shallow flow path led to tne enrichment of soil-derived DOM in agricultural streams.
- PLS-PM allowed resolving allochthonous vs. autochthonous pathway by which agriculture alters streams

GRAPHICAL ABSTRACT
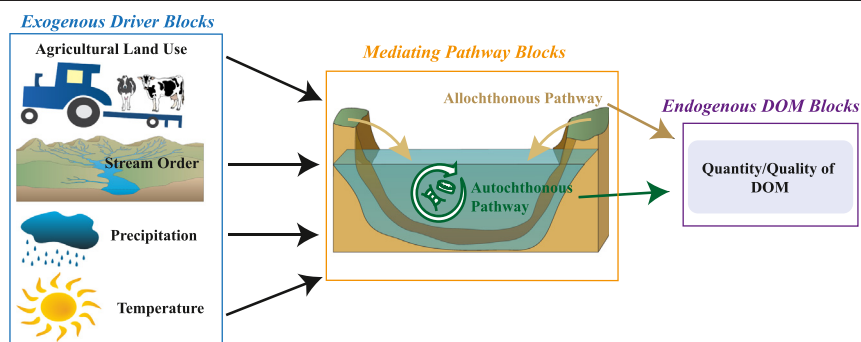
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ABSTRACT

Agricultural land use leads to significant changes in both the quality (e.g., sources and compositions) and quantity of dissolved organic matter (DOM) exported from terrestrial to aquatic ecosystems. However, the effect of agricultural activities often interacts with those of hydroclimatic drivers, making it difficult to delineate agriculture-induced changes and identify associated mechanisms. Using partial least square path modeling (PLS-PM), we examined the relative importance of agricultural land use, stream order, precipitation, and temperature in mediating allochthonous versus autochthonous sources and pathways that influenced stream DOM quality and quantity. We analyzed stream water DOM from 15 small streams draining watersheds across a gradient of agricultural land use in Southeast USA for about one year. For DOM quantity, agricultural land use increased the export of DOC and various DOM pools (terrestrial humic, microbial humic, and protein-like DOM) from land to streams, and for DOM quality, agricultural streams showed greater proportions of microbial humic compounds than forested streams. The PLS-PM model for DOM quantity accounted for 75.5% of total variance and identified that agricultural land use increased stream water DOM quantity primarily through increasing allochthonous inputs, which can be attributed to shallower flow paths in agricultural watersheds that enabled the export of organic materials from the upper, organic-rich soil horizon. PLS-PM models for DOM quality only explained ~13% of the total variance, highlighting the complex dynamics between environmental drivers and

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stream water DOM. Relative to commonly used multivariate statistic modeling (e.g., redundancy analysis (RDA)), PLS-PM models offer the advantages of identifying the primary pathway by which agricultural lands alter freshwater DOM and quantifying the relative importance of interactive effects of agriculture and hydroclimatic drivers. Therefore, structural equation modeling is a powerful tool that should be more widely adopted to distinguish among multiple drivers and mechanisms regulating freshwater biogeochemistry.

1. Introduction

The source and type of DOM in inland waters play an essential role in mediating water quality and ecosystem structure and function (Cole et al., 2007; Kaushal et al., 2018; Williams et al., 2010; Wilson and Xenopoulos, 2008). Freshwater DOM is a complex mixture of compounds with varied sources, compositions and reactivities, but it can be broadly classified into allochthonous DOM and autochthonous DOM. Allochthonous DOM comprises abundant aromatic, high-molecular-weight (HMW), humic substances derived from soil and plant decay, while autochthonous DOM produced by instream sources is relatively less complex in structure and more enriched in nitrogenous molecules (Fellman et al., 2011; Kowalczuk et al., 2009; Yamashita et al., 2008; Lu et al., 2015a). Due to its compositional features, allochthonous DOM is usually more photoreactive but less biologically labile than autochthonous DOM (Hansen et al., 2016; Lu et al., 2013). Understanding allochthonous versus autochthonous DOM contributions in aquatic environments and the underlying environmental drivers offer insights into substrate and energy transferred across the terrestrial-aquatic boundary and biogeochemical fate of carbon of different origins.

Agricultural land use covers 40% of the Earth's land surface (Foley et al., 2005). There is growing evidence that agricultural land use leads to widespread changes in hydrological and biochemical processes that shift the quantity and quality of DOM in freshwater environments (Lu et al., 2013, 2014; Sankar et al., 2019; Shang et al., 2018; Wilson and Xenopoulos, 2008). In addition, it has been shown that land use can exert a significantly larger control on DOM composition, compared to the more traditionally accepted paradigm of the River Continuum Concept (RCC) that suggests DOM composition is primarily driven by stream order (Roebuck et al., 2020). However, the reported effects of agricultural land use on DOM in streams and rivers are spatiotemporally variable. Some studies found increases in bioreactive, low-molecular-weight (LMW) DOM in streams due to agricultural activities (Lu et al., 2014; Pisani et al., 2020; Williams et al., 2010; Wilson and Xenopoulos, 2009), whereas others observed increases in HMW, structurally complex, humic-like DOM (Graeber et al., 2012; Shang et al., 2018). Those previous findings are seemingly contradictory but reveal that agricultural activities can alter stream water DOM through different pathways that vary with local or regional environmental factors. On the one hand, agriculture alters autochthonous DOM by enhancing nutrient export and stimulating aquatic production and degradation of organic materials (Lu et al., 2014; Williams et al., 2012). On the other hand, agricultural practices can substantially change allochthonous DOM by altering properties of soil organic matter (Zhu et al., 2020), aggravating soil erosion (Lamba et al., 2015; McEachran et al., 2020; Pimentel and Kounang, 1998), and changing soil organics mobilized and exported to waterways (Graeber et al., 2012; Shang et al., 2018). These two pathways usually operate simultaneously, and their relative importance varies in time and space, depending on a series of natural hydroclimatic and watershed drivers (e.g., temperature, precipitation, and the network position). Resolving the allochthonous versus autochthonous pathways and their entangled effects with natural drivers (e.g., synergetic, antagonistic) will aid in clarifying the primary mechanism whereby agriculture shapes aquatic DOM. However, such efforts remain rare and challenging to date.

The partial least squares path modeling (PLS-PM) may provide an effective means to disentangle multiple drivers mediating the quantity and quality (i.e., source-compositional characters) of DOM in streams. PLS-PM is a statistical method using the partial least square approach to structural equation modeling. The model consists of two parts, an outer model, which relates manifest variables to a latent variable, and an inner model, which relates endogenous latent variables to exogenous or other endogenous latent variables (Tenenhaus et al., 2005). Relative to more commonly used multivariate statistical models (e.g., linear regression, redundancy analysis), PLS-PM can reveal the underlying causal relationships by testing causality-based hypotheses and evaluate the relative importance of environmental drivers and associated interactive effects during hypothesis testing (Dabi et al., 2016; Jalali and Abadi, 2018; Liu et al., 2021). For instance, Du et al. (2021) used PLS-PM to disentangle the direct and indirect effects of human activities on lacustrine DOM in the floodplains of the Yangtze River, China. They found that the direct input of anthropogenic organics was responsible for changes in fluorescent DOM in lakes whereas autochthonous productivity led to changes in DOC and chromophoric DOM.

Here, we attempted to distinguish and estimate the relative importance of allochthonous versus autochthonous pathways through which agricultural lands alter the quantity and quality (source-compositional characteristics) of stream water DOM. To this end, we combined monitoring data from 15 subtropical streams across agricultural gradients with structural equation modeling. We hypothesized that partial least square path modeling (PLS-PM) can: (i) identify the primary pathway by which agricultural land use changes stream water DOM quantity and quality; and (ii) evaluate the relative importance of the allochthonous pathway versus autochthonous pathway. Through the allochthonous pathway, agricultural land use can change soil-stream connectivity and hence lateral inputs of soil DOM to streams; through the autochthonous pathway, agricultural land use can stimulate instream production and degradation of DOM. Here we reported on the relative importance of each pathway on DOM quantity and quality and assessed how agricultural land use shifted these two above-mentioned pathways in interaction with three natural drivers, including precipitation, temperature, and stream order. We demonstrated that structural equation modeling is a powerful tool that should be more widely adopted to distinguish among multiple drivers and mechanisms regulating freshwater biogeochemistry.

2. Materials and methods

2.1. Study sites and sample collection

Our study sites included a group of 15 first- to fourth-order (Strahler order) streams within the Bear Creek Watershed (BCW), northern Alabama, Southeast USA (Fig. 1). BCW was situated at the boundary of the East Gulf Coast Plain and Highland Rim. The bedrock of this area mainly consisted of limestone and sandstone underlying loamy and clayey alluvium or sandy marine deposits. The climate was humid subtropical with hot summers and mild winters. The mean annual precipitation (MAP) of 2016, 2017 and 2018 was 942 ± 55 mm, 1401 ± 80 mm and 1656 ± 72 mm, respectively, and the mean annual temperature (MAT) was 17.31 ± 8.08 °C, 16.72 ± 6.60 °C and 17.13 ± 8.43 °C, respectively. Relative to the long-term meteorological data (2008–2018: MAP = 1217 ± 66 mm, MAT = 16.22 ± 8.50 °C), the weather was relatively dry in 2016 and it was back to the average during 2017–2018.
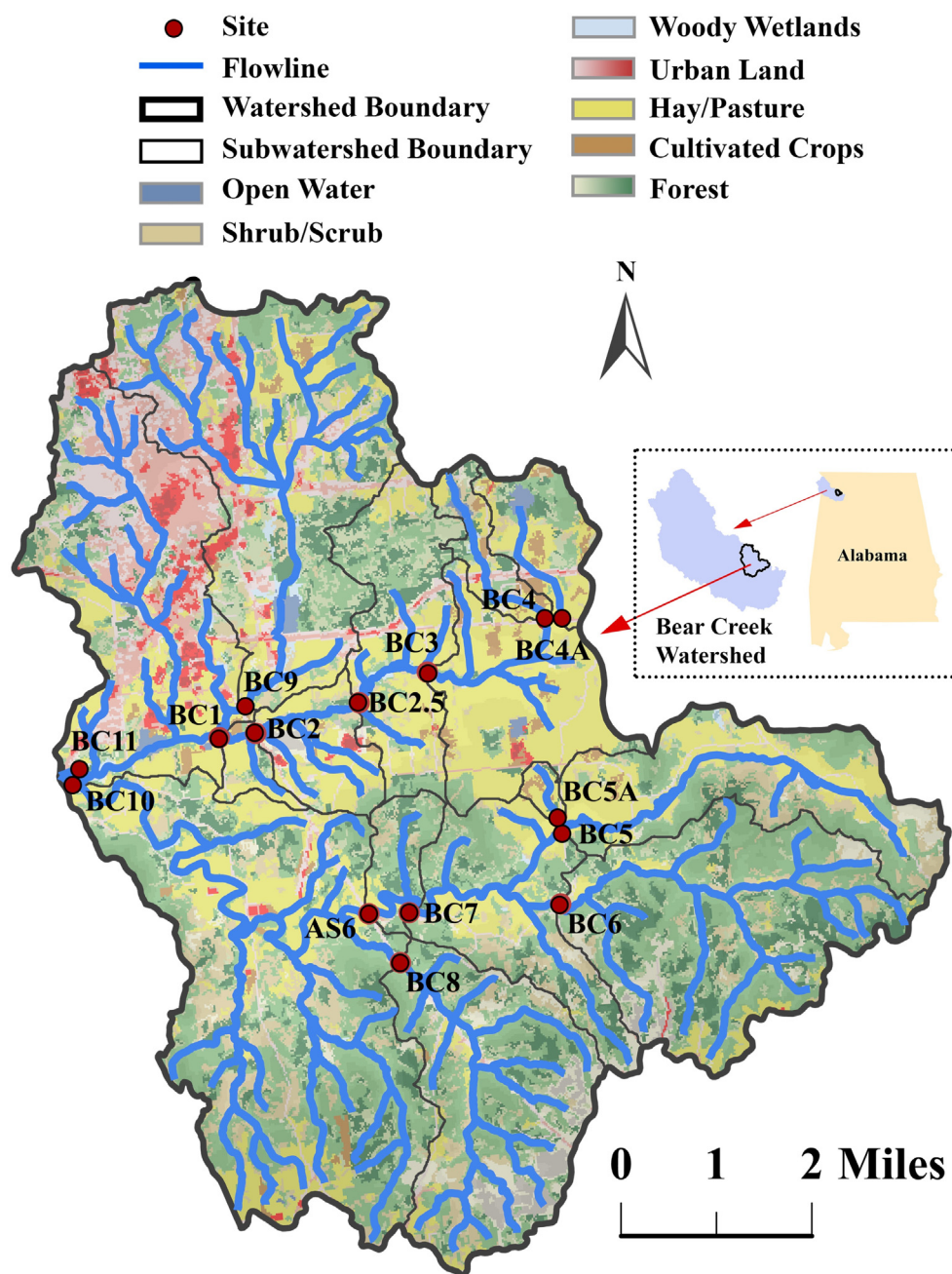
Fig. 1. Map of sampling locations and land use types in the Bear Creek Watershed, SE USA.

The 15 study streams were selected because they drain watersheds spanning across a gradient of agricultural land use ranging from 13% to 87%. The watershed boundary of each sampling stream was delineated using the National Hydrography Dataset (NHDPlus), and the land use of the watershed of each study stream was determined according to the National Land Cover Database 2011 (NLCD2011; https://www.mrlc.gov/nlcd11_data.php). The watershed area, slope, and soil drainage characters of the study streams are listed in Table 1. Based on the dominant land use type, the study streams were broadly classified into forested streams (n = 5, 59 to 75% of forest), agricultural streams (n = 5, 53 to 87% of agricultural land), and mixed-land streams (n = 5, the ratio of forested to agricultural land is approximately 1:1). The forests consisted of a mixture of upland hardwoods, white oak, red oak, hickory and loblolly pine. Agricultural lands in BCW were dominated by pasturelands growing Bermuda and Fescue grasses for cattle grazing (Shang et al., 2018). Agricultural practices were relatively simple, without the application of large-scale irrigation or tillage to pastures, except for a few surface water-fed, central pivot irrigation systems. Chicken litter from the local poultry industry was the primary fertilizer used in BCW, and they were usually applied twice a year (in March/April and August/September).

Stream water samples were collected from 15 sites monthly to bimonthly from February 2016 through April 2017 (eight sampling campaigns), and one additional sampling campaign was conducted in April 2018. A suite of in situ water quality parameters (i.e., water temperature, dissolved oxygen concentration, conductivity) was measured along with sample collection. To assess the hydrological variation, we calculated accumulative two-day precipitation before the sampling date as antecedent precipitation, using daily precipitation data from the National Oceanic and Atmospheric Administration (NOAA, https://w2.weather.gov/climate/).

Table 1
Watershed characteristics of fifteen study streams in the Bear Creek Watershed, SE USA.

Site	GPS coordinates (°)	Agricultural land (%)[a]	Forest (%)[a]	Urban land (%)[a]	Dominant land use[a]	Watershed area (km²)[b]	Stream order[b]	Slope (%)[c]	Natural soil drainage class[c]
AS6	34.44131N 87.70207W	24	61	2	Forest	37.71	3	2–3	Well drained
BC1	34.46902N 87.72404W	54	28	8	Agricultural land	25.68	3	0–2	Somewhat poorly drained
BC2	34.46918N 87.71723W	54	28	8	Agricultural land	23.26	3	2–6	Well drained
BC2.5	34.47244N 87.69766W	53	30	8	Agricultural land	20.96	3	2–15	Well drained
BC3	34.47615N 87.68460W	63	20	7	Agricultural land	13.23	3	0–2	Poorly drained
BC4A	34.48257N 87.65996W	45	35	7	Mixed land	3.07	1	0–2	Poorly drained
BC4	34.48252N 87.66173W	40	30	14	Mixed land	2.07	1	0–2	Somewhat poorly drained
BC5A	34.45169N 87.66250W	87	8	6	Agricultural land	0.17	1	0–2	Somewhat poorly drained
BC5	34.45065N 87.66251W	42	38	3	Mixed land	11.04	2	2–6	Well drained
BC6	34.43954N 87.66383W	13	75	1	Forest	16.27	3	0–2	Well drained
BC7	34.44022N 87.69183W	25	60	2	Forest	35.50	3	2–10	Well drained
BC8	34.43279N 87.69425W	18	60	4	Forest	13.03	3	2–15	Well drained
BC9	34.47303N 87.71942W	24	37	28	Mixed land	20.79	4	0–2	Poorly drained
BC10	34.46502N 87.75324W	23	59	3	Forest	79.02	4	1–2	Well drained
BC11	34.46517N 87.75300W	35	28	27	Mixed land	63.64	4	0–2	Well drained

[a] Land use was determined based on the National Land Cover Database 2011.
[b] Stream order and watershed area were determined based on the National Hydrography Database.
[c] Landform, watershed slope, and natural drainage class were determined based on the datasets of National Resources Conservation Service Soils.

At each site, stream water discharge (Q) was measured and calculated following the velocity-area method (Buchanan and Somers, 1969).

Surface water samples were collected into pre-combusted amber glass bottles and stored in a cooler with ice before filtration through 0.2 μm filters (VWR syringe polyethersulfone filter) in the laboratory within 24 h. The filtrates were divided into four fractions into acid-washed HDPE bottles for the analysis of DOC, DOM, dissolved nutrients, and cations. The filtrates for DOC and nutrient analysis were stored frozen at −20 °C in the dark, and the filtrates for DOM optical measurement were stored at 4 °C in the dark and analyzed within two weeks. Samples for cation analysis were acidified with ultrapure concentrated HNO_3 (2% by volume) and stored at 4 °C in the dark. Samples for δD and $\delta^{18}O$ analysis were collected in the field by gently submerging acid-washed HDPE bottles and sealing them below the water surface to eliminate headspace and air bubbles. These samples were stored at 4 °C in the dark prior to the analysis. *Escherichia coli* (*E. coli*) samples were collected into autoclaved polypropylene bottles (121 °C for 20 min) in the field. All samples were analyzed in duplicate.

2.2. DOC and DOM optical properties

DOC concentrations were analyzed on a Shimadzu TOC-V total organic carbon analyzer, following the method described by Shang et al. (2018). Two to three samples were randomly selected for duplicate measurements in each batch, yielding the relative standard deviation (RSD) between 0.06% and 3.07%.

The DOM quality was determined using optical properties commonly applied in the literature (Fellman et al., 2010; Jaffé et al., 2014). The measurement of DOM optical properties followed the methods described previously by Chen et al. (2019). Briefly, samples were warmed to room temperature and then decanted to a 1-cm quartz cuvette. Absorption reading was collected on a UV-1800 Shimadzu

spectrophotometer, at the scanning wavelength from 190 to 670 nm across 1-cm intervals. DOM fluorescence reading was collected using a Horiba Jobin-Yvon Fluoromax-3 spectrofluorometer. Fluorescence intensity was measured at the excitation wavelength of 240–500 nm at 5 nm intervals and the emission wavelength of 280–538 nm at 3 nm intervals, generating a three-dimensional fluorescence excitation-emission matrix (EEM). Fluorescence spectra were corrected for the inner filter effect, blanks (carbon-free ultrapure water measured daily), and manufacture correction factors, before they were normalized to the area under the water Raman peak (Cory and McKnight, 2005; McKnight et al., 2001; Stedmon et al., 2003). The fluorescence components were identified using the parallel factor analysis (PARAFAC) conducted in MATLAB with the DrEEM toolbox (Murphy et al., 2013; Stedmon et al., 2003). The final EEM-PARAFAC model was validated via the split-half analysis via both random initialization and $S_4C_4T_3$ (Split -4, Combination -4, Test -3) methods (Murphy et al., 2013).

A suite of optical indices was calculated to assess the source-composition characteristics of DOM, inducing specific ultraviolet absorbance at 254 nm ($SUVA_{254}$; L mg C^{-1} m^{-1}), spectral slope ratio (S_R), freshness index (β/α), humification index (HIX), and fluorescence index (FI). Their calculation and interpretations can be found in numerous previous studies (Cory and McKnight, 2005; De Haan and De Boer, 1987; Hansen et al., 2016; Helms et al., 2008; Jaffé et al., 2008; Lu et al., 2013, 2014, 2015b; Ohno, 2002; Weishaar et al., 2003; Wilson and Xenopoulos, 2008), and they are summarized in Supplemental materials (Supplemental Table 1).

2.3. Ancillary biogeochemical and hydrological parameters (nutrient, E. coli, major cation, δD/δ¹⁸O)

The concentration of dissolved inorganic nutrients, including nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+) and soluble reactive

phosphorus (SRP), were measured on a San^{++} Automated Wet Chemistry Analyzer, following the EPA methods 353.2, 350.1, and 365.1, respectively. The RSD of duplicate measurements for nutrients varied from 0.42% to 6.56%. The number of *E. coli* in the water samples was determined following the IDEXX Quanti-Tray/2000 method (USEPA, 2003).

The concentrations of seven major cations were measured on a Perkin Elmer Optima 4300DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), including dissolved calcium (Ca^{2+}), iron (Fe^{2+}/Fe^{3+}), magnesium (Mg^{2+}), manganese (Mn^{3+}), potassium (K^+), silicon (Si), and sodium (Na^+). RSDs of duplicate measurements were 0.09%–2.98% for Ca^{2+}, 0.82%–6.26% for Fe^{2+}/Fe^{3+}, 0.18%–2.01% for Mg^{2+}, 0.29%–3.94% for Mn^{3+}, 0.52%–3.12% for K^+, 0.18%–0.70% for dissolved Si, and 0.14–3.28%for Na^+. The stable isotopes (δD and $\delta^{18}O$) of stream water were analyzed on a Continuous Flow-Isotope Ratio Mass Spectrometers (CF-IRMS, Thermo Finnigan DeltaPLUS XP and Delta V Advantage) at Environment and Natural Resources Institute in the University of Alaska Anchorage. The RSDs of δD and $\delta^{18}O$ ranged from −0.45% to −6.50% and −0.12 to −0.85, respectively.

2.4. Two-dimensional electrical resistive tomography (2D ERT) measurements

We utilized resistivity differences between saturated local lithologies at the hyporheic zone to identify and compare subsurface groundwater-stream water exchange flow paths. A single-time "snapshot" of electrical resistivity tomography (ERT) measurements were employed at two sites, BC1 representing agricultural streams and BC6 representing forested streams. The measurements of the two sites were completed on the same day to allow comparison under the same hydrological regime. An 84 m cable (56 electrodes with 1.5 m spacing) connected to SuperSting®R8 eight channel system was deployed perpendicular to each stream in dipole-dipole configuration. This allowed a penetration depth of 21 m below the stream bed. Data from ERT were processed and interpreted using the commercially available software EarthImager 2D (AGI Inc.). The root mean square error (RMS) and L2-norm (sum of the squared weighted data errors) were used for data quality control. Detailed data processing procedures can be found in Dimova et al. (2012). Various lithological units and saturated lithologies were identified by comparing the resistivity values of in-situ resistivity measurements to values available in literature (Benabdelouahab et al., 2019; Rhodes et al., 2017; Saad et al., 2012). In addition, previously collected sediment cores from the sites and field observations were used to ground truth and verify the ERT interpretations (National Resources Conservation Service Soils; https://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx).

2.5. Statistical analysis

All statistical tests were performed in R Core Team (2020). Two-sample Wilcoxon tests were conducted to evaluate the significant difference of DOM quantity and quality parameters between land use types ("stats" package in R). Kendall's rank correlation coefficients (τ) were calculated to evaluate the strength and direction of correlation, and the level of significance was set at 0.05.

Further, redundancy analysis (RDA; "vegan" package in R) was used to assess the effects of watershed and environmental variables on the variability of DOM in streams, following the steps described in Oksanen et al. (2020). Separate RDA models were built for DOM quantity and DOM quality. For the DOM quantity model, dependent variables were DOC and the intensities of the PARAFAC fluorescent components (C_i); for the DOM quality model, the dependent variables were the relative contributions of fluorescent components (%C_i), β/α, SUVA$_{254}$, FI, HIX and S_R. For predicators, all measured watershed and environmental variables were considered, but some were removed based on the variance inflation factor (VIF < 8) to avoid multicollinearity (e.g., $\delta^{18}O$

was excluded due to the strong correlation with δD). The predictors that were retained for RDA included percent agricultural lands in the watershed, stream water temperature, stream order, stream water discharge, soil drainage (based on NRCSS soil drainage class), 2-day accumulative antecedent precipitation (2-day AAP), δD, NH_4^+, NO_2^-, NO_3^-, SRP, *E. coli*, and two cations (Ca^+ and Na^+). Prior to running RDA, all predictors and dependent variables were normalized. The detrended correspondence analysis (DCA) with the first length of gradient less than 3 was used to evaluate the suitability of RDA for the dataset. Monte-Carlo permutation test (999 permutations without restriction) was performed to test the significance of the first and second canonical axes for RDA ($P < 0.01$).

2.6. Structure equation modeling: PLS-PM

The PLS-PM is applicable to non-normally distributed and small-sized data, providing a flexible tool to delineate a multi-block structure of latent variables for the manifest data (Tenenhaus et al., 2005; Tenenhaus, 2008). The approach uses simple algorithm and includes two steps, computing multivariate relationships between manifest and latent variables by PLS algorithm and estimating the direction and strength of linear correlations (measured by path coefficients, β) between latent variables through PLS regression (Sanchez, 2013; Tenenhaus, 2008).

We built the PLS-PM models using the R package "plspm" (Sanchez, 2013). Using the PLS-PM models, we evaluated if agricultural land use changed stream water DOM via the allochthonous pathway (i.e., soil-stream connectivity and the lateral inputs of soil DOM to streams) or the autochthonous pathway (i.e., instream production and degradation of DOM). To this end, we built three levels of latent blocks: (i) Endogenous DOM Blocks describing DOM quantity or quality; (ii) Mediating Pathway Blocks describing the two pathways directly influencing DOM, allochthonous and autochthonous; and (iii) Exogenous Driver Blocks describing agricultural land use and other relevant environmental drivers (temperature, precipitation, and stream order) that can influence DOM through the Mediating Pathway Blocks. Three sets of Endogenous DOM Blocks were modeled separately, yielding one model for DOM quantity (manifest variables: DOC concentration, the fluorescence intensities of PARAFAC fluorescence components) and two models for DOM quality, including one predicting "%Humic, allochthonous DOM" (manifest variables: %terrestrial, humic-like fluorescence and HIX), and another predicting "%Fresh, autochthonous DOM" (%autochthonous, protein-like DOM and S_R). The Mediating Pathway Blocks included "Allochthonous pathway" (manifest variables: Na^+, SPR and δD) and "Autochthonous pathway" (NO_3^-, NO_2^-, NH_4^+ as manifest variables). The Exogenous Driver Blocks included "Agricultural land use", "Stream order", "Temperature", and "Precipitation". The selection of manifest variables for each block was based on the physical meaning of each variable (further discussion in Section 4.2) as well as model fitting, i.e., only manifest variables with loadings greater than 0.7 were included in the corresponding block. The model was validated via non-parametric bootstrapping (resampling number = 1000, Supplemental Table 2). The inter-block relationships, from Exogenous Driver to Mediating Pathway Blocks and from the Mediating Pathway to Endogenous DOM Blocks, were described by path coefficients (β), which was considered significant when $P < 0.05$. β describing the influence of Exogenous Driver Blocks on Endogenous DOM Blocks was calculated as the product of β from Exogenous to Mediating Blocks and β from Mediating to Endogenous Blocks.

3. Results

3.1. DOM quality: source-composition metrics

Optical measurement provides information about the source and composition of DOM in natural waters (Fellman et al., 2010; Jaffé

Table 2

Results of two-sample Wilcoxon tests to assess variation in environmental parameters and solutes (mean ± standard deviation[a]) among different land covers. Non-overlapping superscripted letters within a column (A or B) indicate that significant differences between different land covers were detected at the 95% confidence level.

DOC quantity								
Land use	DOC (mg L^{-1})	C1 (R.U.)	C2 (R.U.)	C3 (R.U.)	DOC flux (Gg yr^{-1} km^{-2})	C1 flux (R.U. m yr^{-1})	C2 flux (R.U. m yr^{-1})	C3 flux (R.U. m yr^{-1})
Forest	2.61 ± 2.60^A	1.79 ± 2.20^A	1.14 ± 1.33^A	1.88 ± 1.87^A	1.04 ± 1.28^A	0.60 ± 0.78^A	0.42 ± 0.57^A	0.68 ± 0.82^A
Mixed land	3.09 ± 1.83^B	2.36 ± 1.73^B	1.34 ± 0.99^B	2.66 ± 1.80^{A,B}	1.30 ± 1.72^{A,B}	0.88 ± 1.11^{A,B}	0.53 ± 0.75^{A,B}	1.08 ± 1.37^A
Agricultural land	3.72 ± 2.20^B	3.16 ± 2.23^B	1.93 ± 1.26^B	2.66 ± 1.82^B	2.19 ± 2.81^B	1.62 ± 2.18^B	1.03 ± 1.34^B	1.51 ± 2.51^A

DOM quality (source-compositional indices)								
Land use	%C1	%C2	%C3	FI	HIX	β/α	SUVA$_{254}$ (L mg-C^{-1} m^{-1})	S$_R$
Forest	35.61 ± 4.56^A	24.27 ± 4.90^A	40.12 ± 8.68^A	1.86 ± 0.08^A	0.62 ± 0.08^A	1.30 ± 0.14^A	2.76 ± 0.52^A	1.44 ± 0.77^A
Mixed land	37.15 ± 4.84^A	22.63 ± 5.94^A	40.21 ± 9.83^A	1.85 ± 0.05^A	0.61 ± 0.10^{A,B}	1.26 ± 0.09^A	2.68 ± 0.55^A	1.31 ± 0.65^{A,B}
Agricultural land	40.44 ± 5.18^B	25.56 ± 3.85^A	34.00 ± 8.80^B	1.88 ± 0.09^A	0.68 ± 0.07^B	1.30 ± 0.15^A	2.93 ± 0.73^A	1.01 ± 0.41^B

[a] Standard deviation was calculated from samples collected for each site from nine sampling campaigns, with eight of the campaigns from February 2016 to April 2017 and one additional campaign conducted in April 2018.

et al., 2014). For absorbance-based indices, SUVA$_{254}$ of BCW streams ranged from 1.44 to 4.60 L mg C^{-1} m^{-1} and averaged 2.73 ± 0.56 L mg C^{-1} m^{-1} (mean ± standard deviation), and S$_R$ varied from 0.24 to 3.67 and averaged 1.24 ± 0.61. For the fluorescence-based indices, HIX varied from 0.46 to 0.83 (mean: 0.64 ± 0.10), FI ranged from 1.73 to 2.33 (1.87 ± 0.09), and β/α was from 1.06 to 5.35 (1.24 ± 0.61). Among these optical indices, FI, SUVA$_{254}$ and β/α did not vary due to land use types (Table 2). In contrast, S$_R$ was significantly lower in the agricultural streams than in the mixed-land and forested streams, and HIX

was significantly higher in the agricultural streams (Table 2). As the proportion of agricultural land use increased, S$_R$ declined ($\tau = -0.172$, $P = 0.011$) and HIX increased ($\tau = 0.193$, $P = 0.005$; Fig. 2).

The PARAFAC model identified three fluorescence components in DOM of BCW streams, microbial humic-like DOM (C1), terrestrial humic-like DOM (C2) and protein-like DOM (C3) (Fig. 3, Table 3). The dominant compositions were C1 (37.91 ± 5.21%) and C3 (37.50 ± 9.41%), and C2 was less abundant (24.60 ± 5.01%). Percent C1 (%C1) was significantly higher in agricultural streams than that in forested
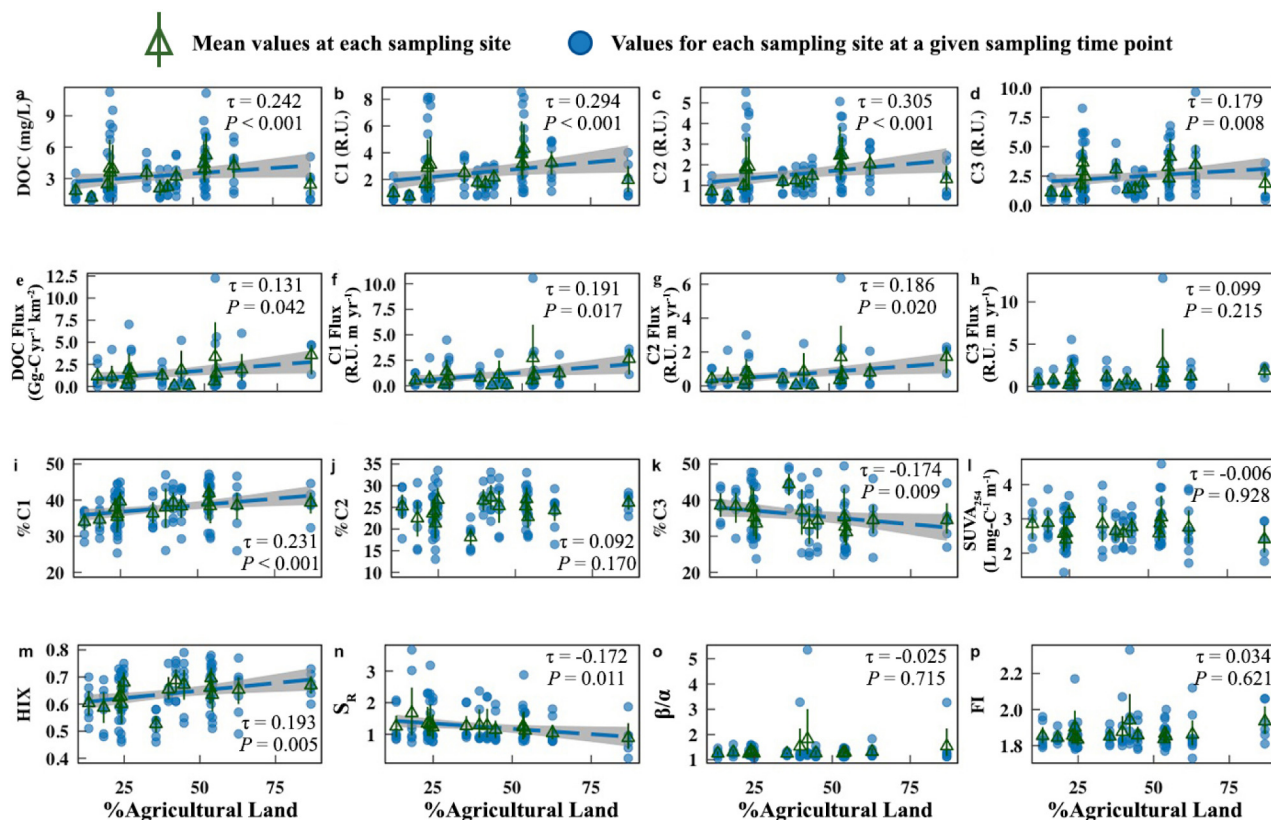

Fig. 2. DOC and DOM optical proxies across a gradient of agricultural land use in the Bear Creek Watershed, SE USA. (a) DOC concentration (n = 108), (b – d) DOM intensities of three components (n = 108), (e – h) fluxes of DOC and DOM fluorescence (n = 79), (i – k) the proportion of three DOM components (n = 108), and (l – p) DOM optical indices (n = 108). Blue dots denote values of each sampling site at a given sampling time point; green triangles indicate the mean value at each sampling site and the associated error bars (green lines) represent standard deviation due to temporal variations. The τ and P values are calculated from Kendall's non-parametric correlation. Linear fitting lines of all data points (blue dashed lines) with 95% confidence intervals (grey shades) are plotted when $P < 0.05$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
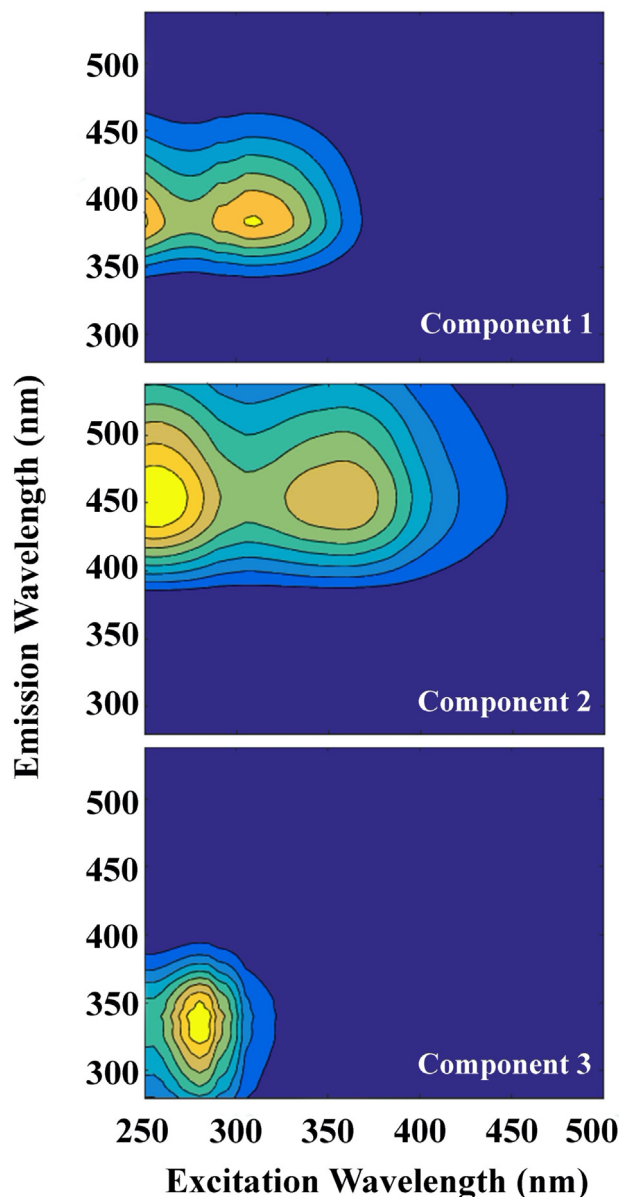
Fig. 3. Excitation-emission fluorescence matrices of the three components (C1 – C3) identified by the PARAFAC analysis of DOM samples from the Bear Creek Watershed, SE USA.

streams, whereas percent C3 (%C3) was significantly lower in agricultural streams (Table 2). Percent agricultural land use correlated positively with %C1 ($\tau = 0.231$, $P < 0.001$) but negatively with %C3 ($\tau =$ -0.174, $P = 0.009$; Fig. 2). Percent C2 (%C2) did not vary due to land use types ($P = 0.170$; Fig. 2).

3.2. DOM quantity: concentration and flux

DOC concentrations in BCW streams ranged from 0.90 to 11.26 mg L^{-1} and averaged 3.25 ± 2.28 mg L^{-1}. DOC concentrations were significantly higher in agricultural and mixed-land streams than in forested streams (Table 2), and DOC showed a positive correlation with percent agricultural land in the watershed ($\tau = 0.242$, $P < 0.001$; Fig. 2). As for the watershed export of DOC, the watershed area-specific flux of DOC (concentration $*$ discharge/watershed area) ranged from 0.01 to 12.25 Gg-C yr^{-1} km^{-2} (mean $= 1.49 \pm 2.05$ Gg-C yr^{-1} km^{-2}) and it also varied due to land use (Fig. 2; Table 2). The flux from the agricultural watersheds (2.19 ± 2.81 Gg-C yr^{-1} km^{-2}) was approximately two-fold higher than that from forested watersheds (1.04 ± 1.28 Gg-C yr^{-1} km^{-2}), and the flux of mixed-land streams fell in between (1.30 ± 1.72 Gg-C yr^{-1} km^{-2}). Consistently, the area-specific DOC flux increased with percent agricultural land use ($\tau = 0.297$, $P = 0.042$, Fig. 2).

The fluorescence intensities of three DOM components ranged from 0.42 to 8.53 R.U. (C1), 0.26 to 5.52 R.U. (C2) and 0.42 to 9.62 R. U. (C3), respectively. All three components varied across the land use types, and they were significantly higher in agricultural streams than in forested streams (Table 2) and increased along the agricultural gradient (C1: $\tau = 0.294$, $P < 0.001$; C2: $\tau = 0.305$, $P < 0.001$; C3: $\tau = 0.179$, $P = 0.008$, Fig. 2). The area-specific fluxes of C1, C2 and C3 (fluorescence intensity $*$ discharge/watershed area) were from 0.01–10.55×10^9 R.U. m yr^{-1}, 0.01–6.36×10^9 R.U. m yr^{-1}, 0.01–12.80×10^9 R.U. m yr^{-1}, respectively. C1 and C2 fluxes were significantly higher in agricultural streams than in forested streams (Table 2) and they increased with increasing percentages of agricultural land use (C1 flux: $\tau = 0.191$, $P = 0.017$; C2 flux: $\tau = 0.186$, $P = 0.020$, Fig. 2).

3.3. Subsurface lithology and flow paths identification based on ERT in-situ measurements

Three unique lithological layers were identified at the agricultural site BC1 with a clear distinction between surface, unconsolidated sediments and deep, consolidated rocks (Fig. 4). From top to bottom, the sediment layers are: loamy farmland soils extending to 2.6 m in depth with resistivity values between 100 and 200 Ohm-m, followed by a consolidated sandstone layer from 2.6 to 5 m depth with resistivity values around 350 Ohm-m, and lastly a limestone rock deposit extending from 5 m depth through the remainder of the image up to 20 m (Saad et al., 2012). Resistivity values between 20 and 60 Ohm-m were attributed to fully saturated with unconsolidated sands/soils.

The vertical dimension of subsurface saturated areas at BC1 was on average 2 m, extending from 0.5 to 2.5 m in depth within the loamy soil, with slight spatial variation across the imaged area, i.e. across the stream (Saad et al., 2012). The hyporheic zones where surface and subsurface water mix were identified on the either bank of the stream,

Table 3
Spectral characteristics and source assignment of three PARAFAC-identified fluorophores (C1 to C3) identified in the Bear Creek Watershed, SE USA.

| Component	Maximum excitation wavelength λ_{ex} (nm)	Maximum emission wavelength λ_{em} (nm)	This study	Similar fluorophores compared in OpenFluor database (similarity score of excitation/emission ≥ 0.95, Murphy et al., 2014)
C1	310	382	Microbial humic-like DOM (Humic fluorophore group)	C3 (Lambert et al., 2016) G2 (Murphy et al., 2011) C2 (Osburn et al., 2016)
C2	255 (360)	454	Terrestrial humic-like DOM (Fulvic acid fluorophore group)	G1 (Murphy et al., 2011) C3 (Osburn et al., 2016) C360/456 (Stedmon et al., 2011)
C3	280	340	Protein-like DOM (Tryptophan-like fluorescence)	C5 (Lambert et al., 2016) C4 (Osburn et al., 2016) C275/340 (Stedmon et al., 2011)
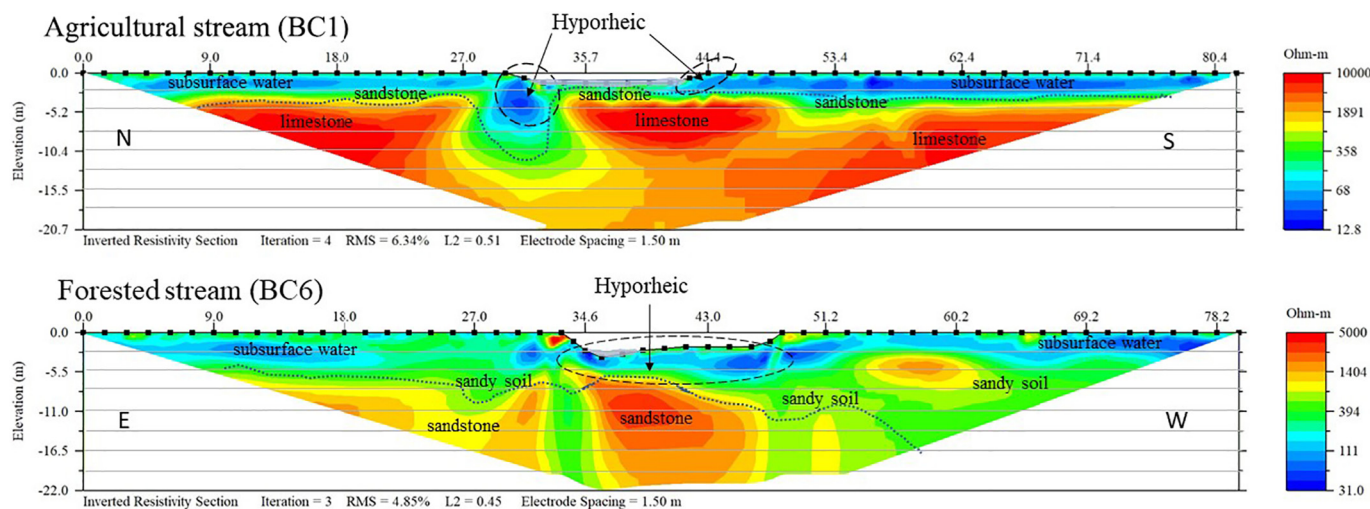
Fig. 4. Two-dimensional electrical resistivity tomography models of an agricultural stream (BC1) and a forested stream (BC6) form the Bear Creek Watershed, SE USA.

while exposed consolidated rock prevented the formation of permeable hyporheic zones beneath the stream bed. Sediment cores collected previously from the study site, and visual field observations of exposed consolidated rock were used to ground truth the resistivity measurements.

At the forested site BC6, the shallow lithology is unconsolidated sandy soil with resistivity values around 400 Ohm-m extending to 11 m depth on the east side of the stream and throughout the entire depth of the imaged area on the west side. Below the sandy soil on the east side was fractured sandstone. Resistivity values between 31 and 60 Ohm-m identified subsurface water (Saad et al., 2012). The subsurface flow path at BC6 was around 3.5 m in vertical thickness and extended from 1 to 4.5 m depth on the east side and 0.5 to 4 m depth on the west side of the stream. Hyporheic zones were identifiable below the stream bed at BC6, compared to the hyporheic zones identified at the sides of the stream bed at BC1. Observed surface sediment and sediment cores collected from the area were used to verify the resistivity measurements.

3.4. RDA models: environmental predictors versus the quantity and quality of DOM

For the DOM quantity model with dependent variables as DOC, and fluorescence intensities of three fluorescence components (C1, C2, and C3), two axes (RDA1 and RDA2) together explained 83.78% of the total variance (Fig. 5a). RDA1 accounted for the majority (80.23%) of the variance, and RDA2 explained only 3.40%. DOC and humic fluorescence (C1 and C2) were aligned better with RDA1, and they were positively predicted by %agricultural land use, water temperature, δD, Na^+, Ca^{2+}, SRP, 2-day AAP, and *E. coli*, but negatively by stream discharge. Protein fluorescence (C3) was better aligned with RDA2 and it was positively predicted by stream order, inorganic nitrogen nutrients (nitrite, nitrate and ammonium) but negatively by the degree of soil drainage.

By comparison, the RDA model explaining the DOM quality did not perform as well as that for DOM quantity. The two axes explained only 20.80% of the total variance (Fig. 5b). RDA1 and RDA2 accounted for 13.91% and 6.89% of the variance, respectively. HIX, percentage contributions of the three fluorescence components (%C1 – %C3) and S_R were better aligned with RDA1. S_R (high value indicting low molecular weight; Helms et al., 2008) and percent protein-like DOM (%C3) were positively predicted by stream order, *E. coli*, and inorganic nitrogen nutrients, but negatively predicted by %agricultural land use, Ca^{2+}, Na^+ and δD. In contrast, contributions of humic-like DOM (HIX, %C1 and %C2) were negatively predicted by stream order, *E. coli*, and nitrogen nutrients and positively by %agricultural land use, Ca^{2+}, Na^+ and δD. Three indices,

$SUVA_{254}$, β/α and FI, were better aligned with RDA2. The aromaticity of DOM ($SUVA_{254}$) was positively influenced by water temperature and SRP, yet the proportion of recently produced, microbially-derived DOM (indicated by β/α and FI) was positively predicted by precipitation, the degree of soil drainage, and stream water discharge.

3.5. PLS-PM models

The PLS-PM model explained 75.5% of the total variance of "DOM quantity" (Fig. 6a). One of the Mediating Pathway latent blocks, "Allochthonous pathway", was significant in positively predicting DOM quantity ($\beta = 0.911$, $P < 0.001$), and the four Exogenous Driver blocks associated with this mediating pathway all showed significant positive effects, with the path coefficient β as "Precipitation" (0.377) > "Agricultural land use" (0.360) > "Stream order" (0.280) > "Temperature" (0.232). In contrast, the effect of the other Mediating Pathway Block "Autochthonous pathway" was not significant in predicting DOM quantity ($\beta = 0.003$, $P = 0.952$). As such, none of the Exogenous Blocks were significant in predicting DOM quantity via this pathway.

Similar to the RDA models, the PLS-PLS models for DOM quality can explain only a small fraction of the variance. The model for "%Humic, allochthonous DOM" explained 13.0% of the total variance, and the model for "%Fresh, autochthonous DOM" explained 13.4% of the total variance. Unlike the DOM quantity model, both Mediating Pathway blocks, "Allochthonous pathway" and "Autochthonous pathway", had significant effects on Endogenous DOM blocks (Fig. 6b and c). Specifically, "Allochthonous pathway" had a positive effect on "%Humic, allochthonous DOM" ($\beta = 0.309$, $P < 0.001$) but a negative effect on "%Fresh, autochthonous DOM" ($\beta = -0.378$, $P < 0.001$). On the contrary, "Autochthonous pathway" had a positive effect on "%Fresh, autochthonous DOM" ($\beta = 0.310$, $P < 0.001$) but a negative effect on "%Humic, allochthonous DOM" ($\beta = -0.314$, $P < 0.001$).

As expected, the effects of the Exogenous Driver blocks on "%Humic, allochthonous DOM" and "%Fresh, autochthonous DOM" were opposite. Through the "Allochthonous pathway", all four exogenous drivers significantly and positively predicted "%Humic, allochthonous DOM", with the associated path coefficients as 0.119 ('Precipitation') > 0.108 ('Agricultural land use') > 0.078 ('Stream order') > 0.073 ('Temperature'), but they negatively predicted "%Fresh, autochthonous DOM", and the associated effects were |−0.145| for "Precipitation" > |−0.130| for "Agricultural land use" > |−0.094| for "Stream order" > |−0.091| for "Temperature". Through the "Autochthonous pathway", "Agricultural land use" and "Stream order" negatively predicted "%Humic, allochthonous DOM", with the associated effect of "Agricultural
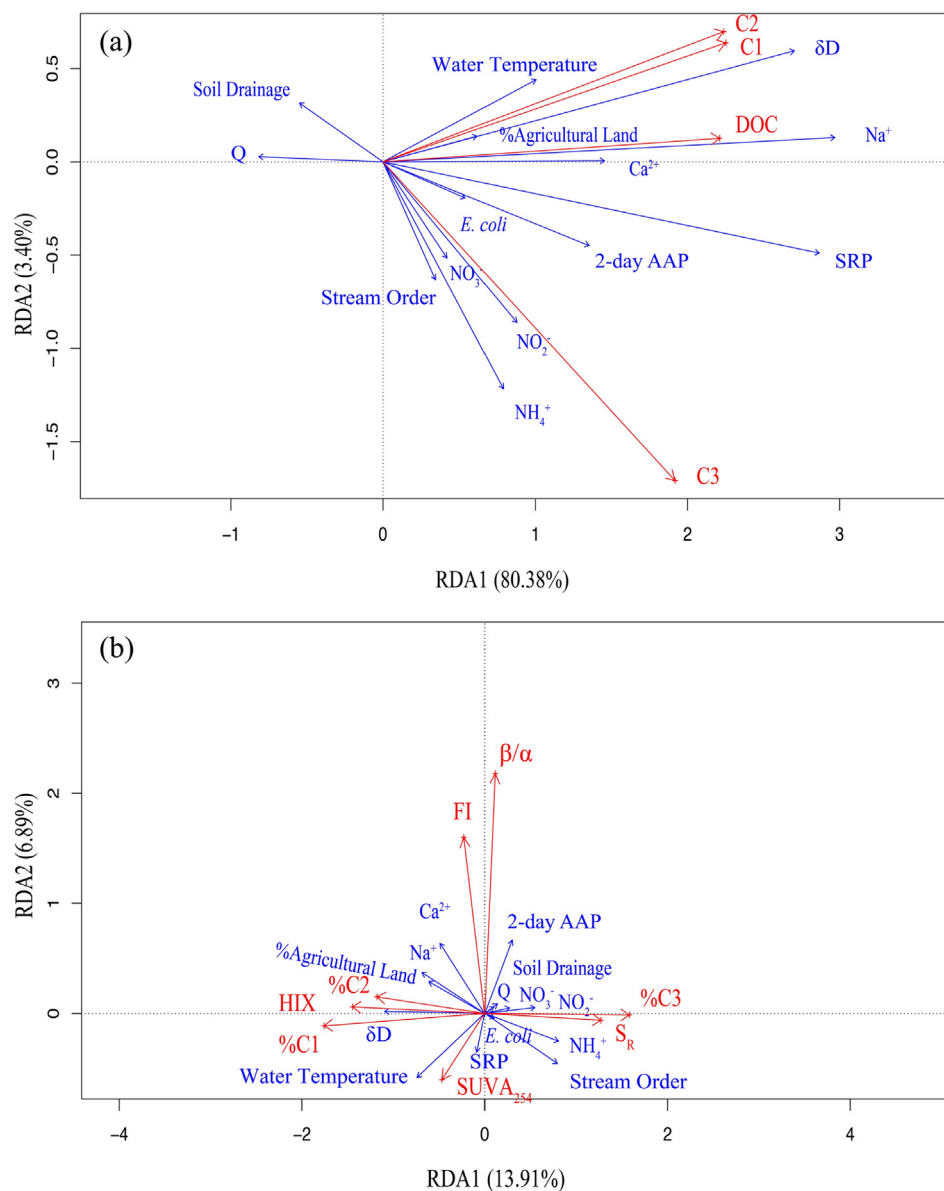
Fig. 5. Redundancy analysis (RDA) of watershed and hydroclimatic variables (blue arrows) as predictors for (a) DOM quantity, and (b) DOM quality in the Bear Creek Watershed streams, SE USA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

land use" (|−0.177|) greater than that of "Stream order" (|−0.132|), but positively predicted "%Fresh, autochthonous DOM" (0.176 for "Agricultural land use" > 0.131 for "Stream order").

4. Discussion

4.1. The construction of PLS-PM models

Theoretically, agricultural land use can influence freshwater DOM through two primary pathways, allochthonous and autochthonous. Allochthonously, agricultural land use influences DOM export via altering the properties and mobilization of soils as well as shifting hydrological paths that connect terrestrial OM to streams (Findlay et al., 2001; Graeber et al., 2012; Shang et al., 2018). Autochthonously, instream production and degradation of DOM tend to be more intensive in human-impacted streams due to greater nutrient and light availability (Hu et al., 2016; Li et al., 2020; Tank et al., 2010). Our PLS-PM models were constructed to integrate both pathways and the respective drivers. Na^+, SRP and δD were used to indicate the allochthonous pathway based on the following assumptions. Dissolved mineral cations and

phosphorus in fluvial systems mainly originate from terrestrial land-scapes (Trudgill, 1977) and hence can indicate soil inputs (Vidon et al., 2008). Water stable hydrogen and oxygen isotopic signatures indicate stream water sources and flow paths and measure the relative contributions of 'old', subsurface baseflow versus 'new', surface runoff (Rostron and Holmden, 2000). Inorganic N species were used as indicators of the strength of autochthonous pathway because they serve as nutrients that can increase in-stream production of autochthonous DOM via enhancing primary productivity or instream microbial processing and excretion of organics (Ensign and Doyle, 2006; Williams et al., 2010). Although phosphorus is also an essential inorganic nutrient for algal growth and bacterial metabolism, SRP was not included in the autochthonous pathway because it loaded highest in the allochthonous pathway block (Supplemental Table 3).

In addition to agricultural land use, multiple environmental drivers play a role in mediating the strength of each pathway, and they were integrated into the PLS-PM models. Three natural drivers were included to evaluate their relative importance relative to agriculture, including precipitation, temperature, and stream order. We evaluated precipitation and temperature as drivers because their effects on fluvial DOM
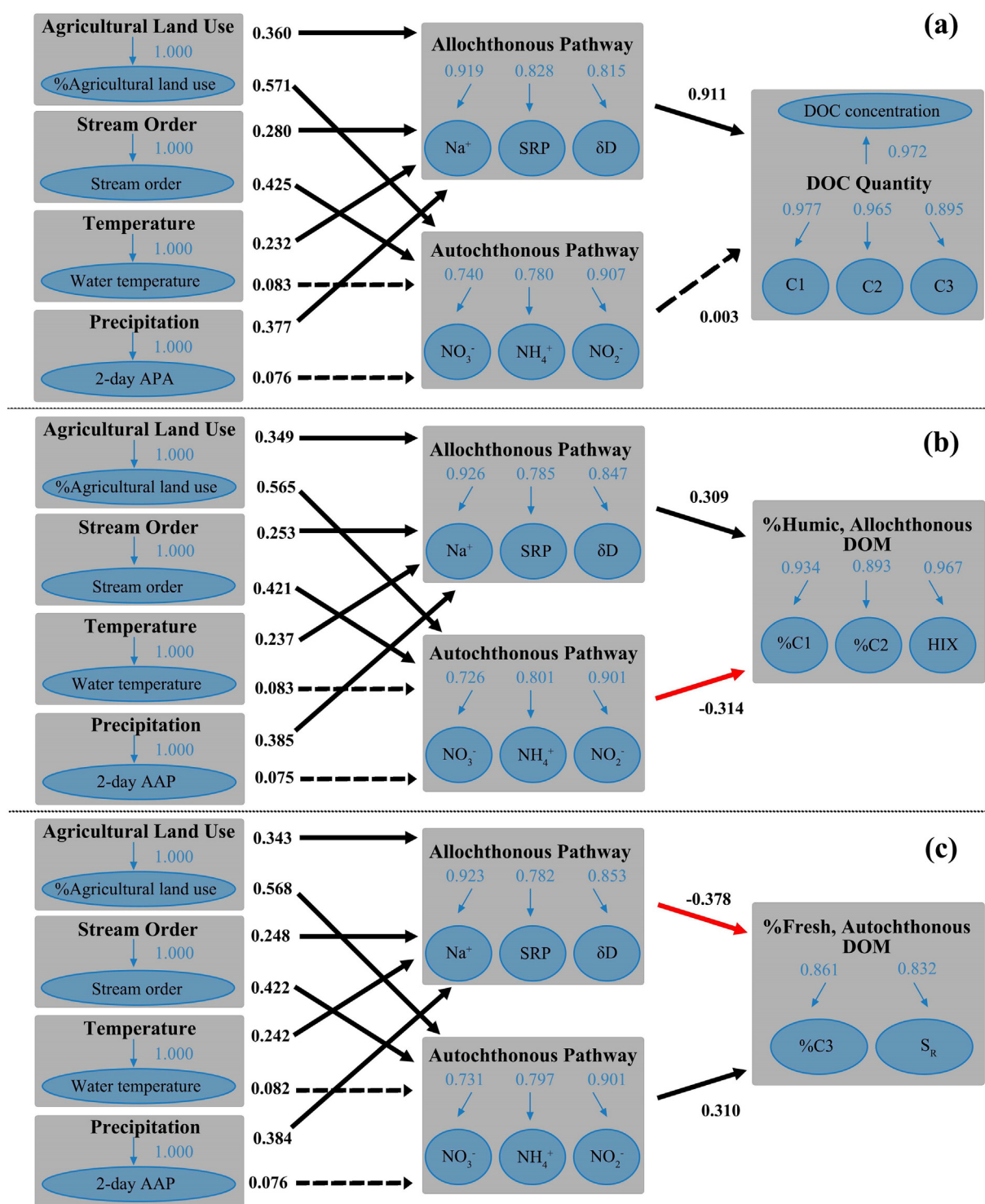
Fig. 6. The PLS-PM models of the environmental predictors influencing DOM quantity and quality in the Bear Creek Watershed, SE USA. (a) DOM quantity, (b) contributions of humic-like DOM, and (c) contributions of protein-like DOM. Rectangle and circles indicate latent and manifest variables, respectively. Outer models of each latent variable consist of paths (blue arrows) and loadings (blue numbers) of the manifest variables. Arrows connecting latent variables indicate inner model paths, and their colors represented the causal relationships that are positive (black) or negative (red). Numbers in black are the inner model path coefficients and their statistical significance is indicated by arrow types (solid arrows, $P < 0.05$; dashed arrows, $P > 0.05$). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

quantity and compositional characteristics have been widely documented (Huang and Chen, 2009; Pisani et al., 2020). Generally, temperature mediates DOM production and decomposition in soils and streams, and precipitation mobilizes soil organic detritus to streams (Duan and Kaushal, 2013; Nguyen et al., 2010; Vidon et al., 2008). High stream water DOC values (>15 mg L^{-1}) were reported from warm, humid southeastern US, and extremely low (<2 mg L^{-1}) DOC

values were from arid western US (Yang et al., 2017). We also included stream order as a driver because DOM composition varies with watershed size and network position, based on the RCC model and empirical observations. DOC concentration usually increases with watershed size, and DOM tends to shift to more autochthonous signatures during the downstream transport, due to the increasing degree of biochemical and photochemical alterations and less shaded surface water by riparian

vegetation (Casas-Ruiz et al., 2020; Creed et al., 2015; Hosen et al., 2021; Vannote et al., 1980).

4.2. Agricultural influences on the quantity of DOM in streams

Significant spatial variations in DOM quantity and quality were observed among BCW streams, and some variations can be directly linked to agricultural land use. The monitoring data showed that agricultural land use amplified the amount of DOM in streams, as evidenced by overall higher fluxes and concentrations of DOC, terrestrial humic fluorescence, and microbial humic fluorescence in agricultural streams (Fig. 2). Consistently, the RDA model indicated that percent agricultural land use positively predicted DOM quantity (Fig. 5). The PLS-PM model, however, can take a step further in determining the underlying mechanism. The model identified that agricultural land use increased DOM quantity primarily through the allochthonous pathway (Fig. 6a), i.e., enhancing terrestrial DOM export to agricultural streams. This effect can be linked to flow paths and associated pools of soil organic materials exported to streams. Soils are usually more compact in agricultural watersheds due to reduced rooting networks, livestock stomping, and heavy instrument use (Lee and Lauenroth, 1994; Reiners et al., 1994; Celik, 2005; Harden, 2006). Soil compaction reduces water infiltration and leads to short and shallow soil-to-stream flow paths. This change tends to constrain the export of organic compounds from upper soil columns, which are usually more enriched in organic materials, particularly humic, HMW compounds derived from terrestrial plant decay. As DOM percolates down through a soil profile, its abundance can dramatically decrease due to sorption to minerals (Aitkenhead-Peterson et al., 2003; Ussiri and Johnson, 2004).

The streambed ERT data support the above interpretation by demonstrating that flow path differences between agricultural and forested streams. ERT can be an effective technique to map subsurface flow paths because of its sensitivity to subsurface geoelectrical structures, especially to saturated pore spaces (Miller et al., 2008). ERT has been widely used in characterizing lithological profiles (Benabdelouahab et al., 2019), evaluating water content and infiltration process in soil and rock aquifers (Zhou et al., 2001; Martel et al., 2018). The ERT data from the two end-member streams, BC1 (agricultural stream) and BC6 (forested stream) show that the flow path of BC1 was overall shallower than BC6, substantiating our argument that shallow flow paths interacting with upper organic-rich soil horizons are responsible for increased DOM quantities in agricultural streams.

Previous studies have also related stream water DOM quantity to hydrological modifications, reporting variable results likely due to varying agricultural practices and other environmental drivers. Similar to the present study, Wilson and Xenopoulos (2008) also suggested shallow flow paths occurred in poorly-drained pastures, haylands, or marginal croplands, which prolonged water resident time in surface soil horizons and increased the quantity of soil carbon transported to streams. Kelsey et al. (2020) suggested that tilling activities can mobilize shallow-soil DOC, based on that DOC fluxes were 2-fold higher from headwater streams draining tilled cornfield than from adjacent headwater streams draining forests. Some other agricultural practices, such as the addition of ditches and subsurface drainage systems, could further tighten the linkages of upper organic-enriched soils with streams and increase the overall DOM export. Intensive drainage systems widely used in Midwest USA were reported to increase the riverine DOC flux by 60% relative to conventionally farmed lands, and the drainage system was found to increase both DOC and streamflow (Dalzell et al., 2011). However, the enhanced terrestrial DOM export may be only a short-term effect of agricultural lands. The long-term export is suggested to decrease as a result of discharge reduction due to stronger evapotranspiration and reduced infiltration, subsurface water extraction for irrigation, and reservoir construction (Döll et al., 2009; Stanley et al., 2012; Sun et al., 2017). For instance, cropland-influenced streams showed DOC fluxes lower than forested streams in northeastern China, which was

attributed to the massive withdraw of surface runoff for irrigation (Sun et al., 2017). The prolonged effects can only be assessed from long-term monitoring data, which, however, are lacking in most of the agricultural watersheds, including BCW of the present study.

4.3. Agricultural influences on the quality of DOM in streams

Agricultural land use also led to changes in some of the DOM source-composition (quality) characters in BCW streams. Specifically, agricultural land use increased the humification degree and molecular weights of DOM and raised the proportion of microbial humic-like compounds but lowered the proportion of protein-like compounds (Figs. 2, 5 and 6). Previous studies have also linked agricultural land use to increased proportions of humic, structurally complex DOM in receiving waters (although see contrasting findings in Wilson and Xenopoulos, 2009 and Lu et al., 2014). For example, DOM from agricultural headwater streams contained a higher proportion of structurally complex, humic substances than DOM from nearby forested streams in the North German plains (Graeber et al., 2012). Similarly, humic-rich DOM has been observed in agriculture-impacted water bodies, including a large river in western China (Hu et al., 2016), a Danish agricultural stream (Stedmon and Markager, 2005), several agricultural streams in Australia (Petrone et al., 2011). These highly humified compounds have been commonly ascribed to terrestrial plants or microbes, and BCW streams showed elevated microbe-sourced humic substances due to agricultural lands. Microbial humic-like DOM may be allochthonous, i.e., originating from degraded soil organic materials, or autochthonous, i.e., originating from instream microbial degradation of organic detritus (Fellman et al., 2010). In our samples, microbial humic-like DOM was sourced primarily from soils because its relative abundance was positively correlated with cation concentrations and conductivity (Ca^{2+}: $\tau = 0.253$, $P < 0.001$; Na^+: $\tau = 0.298$, $P < 0.001$; Conductivity: $\tau = 0.248$, $P = 0.001$), which are two indicators of soil inputs to streams (Cerling et al., 1989; Viers et al., 2000). As such, agricultural land use altered stream water DOM quality by strengthening the export of microbially-processed soil compounds to streams. This observation partially agrees with the previous finding that agricultural lands tend to add microbial signatures (microbially-processed humic-like DOM or protein-like DOM) in fluvial systems across climatic zones (Graeber et al., 2015), yet the strengthened microbial signatures are not necessarily a result of instream processes due to nutrient enrichment but can also occur in soils as a consequence of agriculture alterations to soil OM dynamics. Various agricultural activities (e.g., livestock stomping, soil tillage, ploughing, drainage) have been reported to facilitate the microbial transformation of humic compounds in soils (Heinz et al., 2015; Graeber et al., 2012; Lee et al., 2018). Conventional tillage can increase the humification degree of humic acids extracted from agricultural soils (Bayer et al., 2002). Additionally, agricultural watersheds usually have elevated temperatures due to the removal of the riparian canopy, which can further enhance the microbial transformation and leaching of soil humic substance (Duan and Kaushal, 2013; Melillo et al., 2011). On the other hand, forested streams were relatively more enriched in protein-like DOM, which can be explained by a deeper flow path in forested watersheds, supporting our earlier argument on the importance of flow paths in mediating DOM in BCW streams. Deep flow paths mobilize organic substances from the lower soil column, which is usually more enriched in proteinous compounds but less enriched in humic substances relative to the upper soil column (Aitkenhead-Peterson et al., 2003; Guo and Chorover, 2003; Ussiri and Johnson, 2004). It has been commonly observed that the relative abundance of protein-like DOM in subsurface water increases with depth (Dalzell et al., 2011; Hu et al., 2021; Inamdar et al., 2012).

Notably, both RDA and PLS-PM models explained only a small fraction of the variance of DOM quality (~20% or less), highlighting the difficulty in predicting DOM sources and composition using environmental drivers. However, the PLS-PM models revealed more detailed

information on the mediating processes, showing that agricultural land use simultaneously altered DOM quality via two competing pathways. For %humic allochthonous DOM, agriculture had a positive influence through increasing the export of soil-derived materials (allochthonous pathway) but also a negative influence through stimulating instream processing (autochthonous pathway). For %protein allochthonous DOM, the opposite was true. In contrast, the monitoring and RDA results only reflected the net outcome of the two competing processes. Although agricultural land use increased %humic DOM via the allochthonous pathway and increased %protein DOM via the autochthonous pathway, the RDA model revealed only the effect of the more dominant allochthonous pathway and associated drivers. It is conceivable that the effects of agricultural land use can be completely masked when the effects of the counteracting pathways are of the similar magnitude, which explains why some previous studies did not observe shifts in aquatic DOM that can be systematically linked to agricultural land use (Chow et al., 2007). Incorporating structural equation modeling, therefore, is crucial in distinguishing those pathways and drivers with antagonistic effects.

5. Conclusions and implications

Combining analyzing DOM from a regional group of low-order streams across an agricultural gradient with statistical modeling, we test the hypotheses that PLS-PM models can (i) identify the primary pathway by which agricultural land use changes stream water DOM quantity and quality; and (ii) evaluate the relative importance of the allochthonous versus autochthonous pathway. Our hypotheses are confirmed as our results clearly show that agricultural land use altered BCW stream water DOM quantity primarily through the allochthonous pathway. That is, agricultural activities accelerated the watershed export of surface soil-derived DOM pool by shifting the flow paths. This finding has implications for the longitudinal transformations of DOM from low-order streams to downstream rivers. Low-order streams are the primary sites where terrestrial DOM is loaded to the aquatic environments (Vannote et al., 1980). DOC concentration and DOM diversity often peak in medium-size streams due to the confluence of tributaries, instream primary production, and decomposition of terrestrial detritus (Casas-Ruiz et al., 2020). Our results, in agreement with previous studies (Giling et al., 2013; Roebuck et al., 2020), demonstrated significant shifts in organic substrates in small- to medium-sized streams due to anthropogenic activities. These shifts can change allochthonous vs. autochthonous characters both locally and within fluvial networks, altering the role of terrestrial organics within aquatic environments and associated biogeochemical processes such as riverine metabolism and CO_2 outgassing. Our findings, therefore, reinforce the importance of monitoring and regulating DOM pools in small and medium streams and in including agricultural land use as an important driver in modeling DOM in fluvial networks (Roebuck et al., 2020).

Furthermore, we demonstrate the advantages of employing PLS-PM in elucidating the complex drivers responsible for natural DOM variability. Relative to commonly used statistical methods (RDA, PCA) to reveal the relationship between watershed/environmental predictors and DOM metrics (e.g., Roebuck et al., 2020; Shang et al., 2018; Sankar et al., 2020), PLS-PM additionally allows: (i) quantifying the relative importance of agricultural versus natural hydroclimatic and network drivers and their interactive effects, and (ii) identifying the underlying causality and determining the pathways whereby agricultural land use alters stream water DOM. Like DOM, many aquatic biogeochemical parameters vary with multiple, simultaneously-operating environmental drivers. We thus recommend a more frequent use of structural equation modeling in aquatic biogeochemistry studies.

CRediT authorship contribution statement

Shuo Chen: Conceptualization, Methodology, Data curation, Software, Formal analysis, Writing. **YingXun Du:** Methodology, Writing – review & editing. **Parnab Das:** Data curation, Writing – review & editing. **Alexander F. Lamore:** Data curation, Software, Writing – review & editing. **Natasha Dimova:** Data curation, Writing – review & editing. **Mark Elliott:** Data curation. **Eben North Broadbent:** Funding acquisition. **Jesse Alan Roebuck. Jr:** Writing – review & editing. **Rudolf Jaffé:** Writing – review & editing. **YueHan Lu:** Conceptualization, Methodology, Data curation, Writing, Supervision, Project administration, Funding acquisition.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.148968.

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