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Role of edaphic, hydrologic, and land cover variables in determining dissolved organic carbon in Missouri (USA) reservoirs and streams

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ABSTRACT

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In Missouri, distinct geophysical gradients influence statewide patterns in water quality. Here, we quantify the spatiotemporal variability of dissolved organic carbon (DOC) in reservoirs and streams and the edaphic, hydrologic, and land cover variables that account for cross-system variation. Datasets included statewide inventories collected over decades and studies with greater temporal resolution ($n = >6350$ DOC measurements). Among reservoirs, the smallest DOC concentration was measured in a spring-fed system within a forested watershed, and the largest was where agricultural biosolids were applied to the land (range 1.0–15.9 mg/L, overall mean 5.8 mg/L). Reservoir values increased from the southern forested Highlands (mean 4.7 mg/L) to the northern agricultural Plains (mean 7.0 mg/L). Stream DOC was similar to reservoir values (overall mean in streams 6.3 mg/L; Highlands mean 4.0 mg/L; Plains mean 6.6 mg/L), despite differences in study design and collection period. Reservoir DOC increased in spring, indicative of allochthonous loading, with small autochthonous additions during a broad summer peak. Temporal variability in DOC was low relative to macronutrients and chlorophyll in both reservoirs and streams, indicating DOC may be a sensitive and readily detected indicator of temporal change in these systems. In regression analyses, watershed features accounted for more than 60% of overall cross-system variability in DOC in both reservoirs and streams. Driver-response relations, however, differed between regions. This analysis extends our understanding of environmental influences on surface water chemistry in Missouri and indicates DOC is nearly as predictable as macronutrients using landscape-level features.

KEYWORDS

Dissolved organic carbon; reservoirs; streams; trophic state


Dissolved organic carbon (DOC) directly influences the global carbon cycle (Tranvik et al. 2009, Toming et al. 2020, Xenopoulos et al. 2021), and plays a key role in regulating the cycling of carbon and energy in freshwater ecosystems (Sobek et al. 2007, Battin et al. 2009).

As a mobile part of the freshwater carbon pool, DOC is determined by both allochthonous inputs, as regulated by features of the drainage basin, flowpaths, and hydrology (Findlay et al. 2001, Mulholland 2003, Lapierre, Seekell, and del Giorgio 2015, Tian et al. 2022), and autotrophic activity (Hanson et al. 2011, Evans et al. 2017, Zhou et al. 2018, Bhattacharya et al. 2022).

Global and regional assessments show that DOC pools are largely determined by climate and

topography within a given region, while catchment and other properties regulate values in individual systems (Mulholland 2003, Sobek et al. 2007, Seekell et al. 2014). Human activities, both agricultural and urban, also alter the amount and composition of this material in freshwaters (Stanley et al. 2012, Seekell et al. 2014, Williams et al. 2016, Xenopoulos et al. 2021). Collectively, these studies document temporal and among-system variation in DOC within geographic regions.

Missouri, located in the midcontinent section of the United States, straddles the temperate ecotone between western Great Plains and eastern forests and between northern glaciated and southern unglaciated regions (Figure 1; Nigh and

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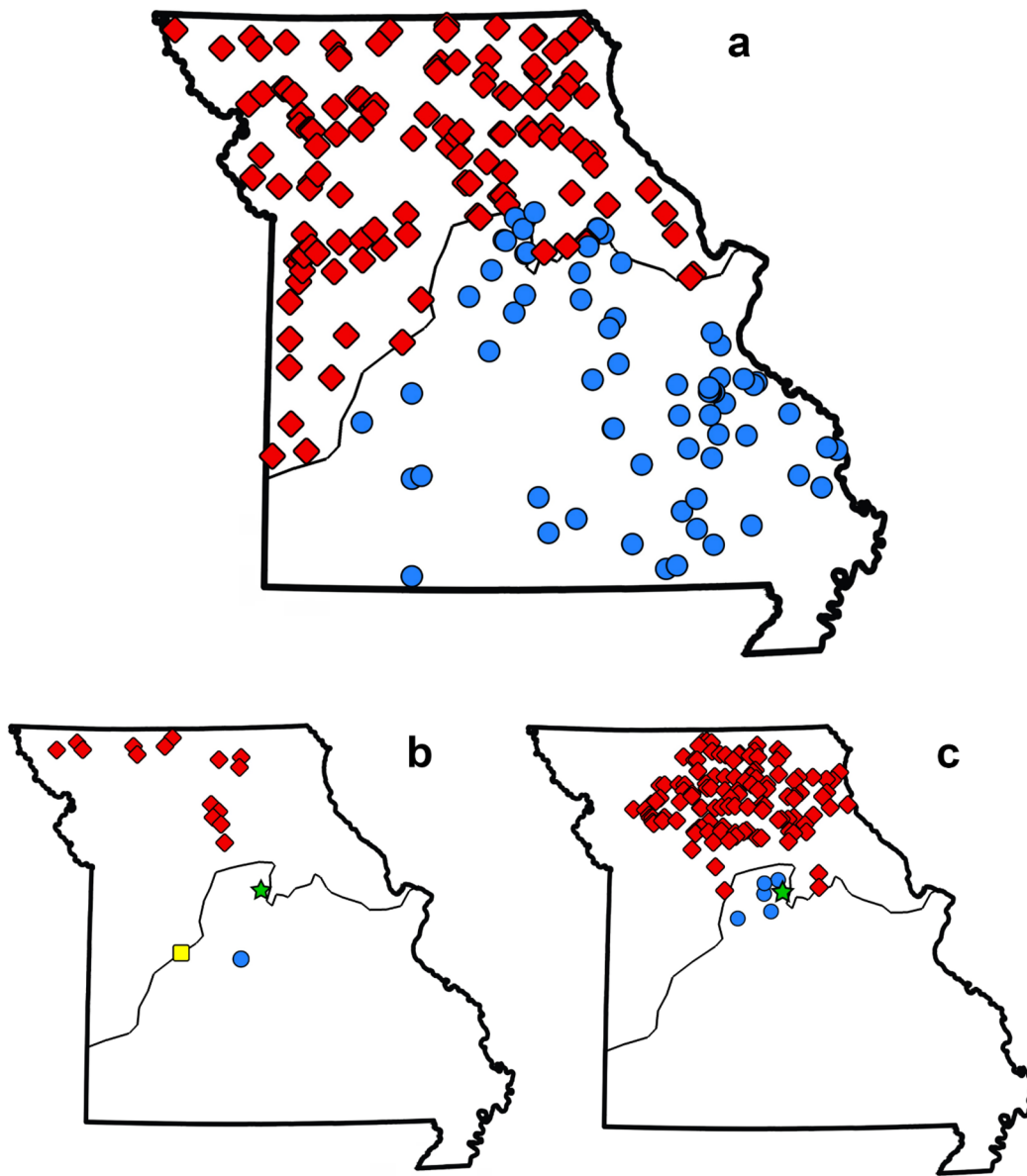


Figure 1. Maps of the locations of the (a) reservoirs included in the statewide assessment, with red diamonds indicating those located in the Plains region and blue circles indicating those located in the Highlands region; (b) 15 Plains reservoirs (red diamonds), Lake Woodrail (green star), Lake of the Ozarks (blue circle), and Truman Lake (yellow square); and (c) streams included in the statewide assessment, with red diamonds indicating Plains streams and blue circles indicating Highlands streams; Hinkson Creek is indicated with a green star.

Schroeder 2002). As such, soil properties differ considerably between the 2 major physiographic regions (Plains and Highlands; Figure 1). Prairies that originally dominated the Plains were converted to intensive agriculture well over a century ago. In contrast, the southern Highlands region is characterized by thin, permeable soils, greater relief, and a landscape dominated by forests and grasslands (Jones et al. 2004, 2008b, 2009). This midcontinent area is within the humid zone where lentic systems are mostly reservoirs (many

comparatively small with rapid flushing rates), elevation differences are modest, and wetlands typically account for <0.5% of watersheds in the dissected terrain (Jones, Thorpe, and Obrecht 2020b).

Previous studies in Missouri show that the proportion of watershed crop cover, used as a surrogate for agricultural nonpoint nutrient input, along with basin morphology and hydrology (flushing rate), accounts for some two-thirds of cross-system variation in both reservoir nitrogen

and phosphorus (N&P) concentrations over a broad trophic range (Jones, Knowlton, and Obrecht 2008a, Jones et al. 2008b, Jones et al. 2009). Likewise, stream nutrients show a similar statewide pattern, with a positive relation with crop cover (Perkins et al. 1998, Jones, Pollard, and Obrecht 2022b). In both reservoirs and streams, algal biomass (as indicated by chlorophyll, Chl) is significantly and positively correlated with N&P (Lohman and Jones 1999, Jones and Knowlton 2005a, Jones et al. 2008b). A distinct aspect of these reservoirs is that interannual variation in summer mean N&P and Chl can be extreme; a greater than 3-fold range in seasonal averages is common in individual systems (Knowlton and Jones 2006a, 2006b, Jones, Pollard, and Obrecht 2022b). Among these trophic state metrics, Chl is typically more variable than either macronutrient.

In an analysis of summer samples from 40 Missouri reservoirs, collected routinely over decades, Bhattacharya et al. (2022) found that the influence of watershed and limnological characteristics on dissolved organic matter quantity and composition varied depending on hydroclimate; allochthonous influences were larger during wet summers, and autochthonous influences were larger during dry summers. The temporal pattern in these reservoirs is nonmonotonic, which contrasts with reports of allochthonous concentrations increasing over time in other regions (Williamson et al. 2015).

Here, we draw on multiple datasets to extend the statewide assessment of factors driving trophic state metrics (N&P and Chl) in Missouri reservoirs and streams to include drivers of spatial patterns of DOC. Given the role of allochthonous inputs and autotrophic processes in determining DOC concentrations, we posited a north-south gradient that would closely match the trophic state pattern (Jones, Pollard, and Obrecht 2022b). Paralleling previous studies in Missouri, the statewide analysis also compares DOC in the northern agricultural Plains with values in the more forested southern Highlands and quantifies how edaphic, hydrologic, and land cover features influence DOC. Additionally, temporal variation in DOC is compared with measured changes in trophic state metrics (N&P and

Chl) in both reservoirs and streams. This analysis also includes specific conductance (a measure of conservative ion content), with the expectation that variation in DOC, both within and among systems, would be most similar to ionic content because temporal changes are associated with hydrology (Bhattacharya et al. 2022).

This analysis builds on DOC studies conducted elsewhere (Xenopoulos et al. 2003, Sobek et al. 2007, Lapierre, Seekell, and del Giorgio 2015) to account for cross-system and temporal variation in Missouri. In contrast with the global importance of both wetlands and elevation as predictors of DOC (Xenopoulos et al. 2003), the lentic systems in our analysis are reservoirs (not natural lakes) and wetlands, and elevation differences are modest in the study region. Annual sampling and short-interval sampling of a reservoir and a stream document both seasonal and daily variation in DOC, with comparisons to concurrent measurements of N&P and Chl. Comparisons of spatiotemporal variability in DOC with macronutrients and algal biomass are uncommon (Maranger, Jones, and Cotner 2018).

Site description and methods

Field studies included in the analyses

The DOC data, collected over decades, come from several sources: a long-term reservoir monitoring program (statewide reservoirs; Jones, Thorpe, and Obrecht 2020b), a 1 year sampling of 15 Plains reservoirs (15 Plains reservoirs; Jones et al. 2016), daily collections from a suburban reservoir (Woodrail; Jones and Knowlton 2005a), long-term sampling of a reservoir in series (Lake of the Ozarks; Jones, Obrecht, and Thorpe 2022a), various statewide stream studies (statewide streams; Jones, Pollard, and Obrecht 2022b), and a daily sampling of a central Missouri stream (Hinkson Creek; Parris 2000). Concentrations of DOC were measured with Technicon Method No. 451-76W from 1997 to 2007, and from 2009 to 2016 on a Shimadzu TOC-V_{CHP} analyzer using method APHA 5310 B (American Public Health Association [APHA] 1985). All samples were also analyzed for total nitrogen (TN), total phosphorus (TP), algal chlorophyll (Chl, uncorrected for

degradation pigments), and specific conductance as detailed in Jones et al. (2008b), Jones et al. (2020a), and Jones, Thorpe, and Obrecht (2020b). All data are available in Jones et al. (2020a).

Datasets

Statewide reservoirs. During May–August of 1997–1999, 2004–2007, and 2009–2016, DOC was measured in surface samples (~0.25 m depth) collected from a near-dam location as part of a statewide reservoir monitoring program, wherein 3–4 samples were collected from individual reservoirs in a given summer season (May–Aug; Jones, Thorpe, and Obrecht 2020b). This dataset includes 4425 individual DOC samples from 203 reservoirs (Figure 1a), with 3 to 58 samples per reservoir (median = 16) across 1 to 15 summer seasons. The statewide reservoir dataset is the foundation of DOC characterization in Missouri; all other datasets supplement understanding of spatiotemporal variability.

15 Plains reservoirs. Weekly collections from 15 Missouri reservoirs located in the northwestern quadrant of the state (Figure 1b) during 2004 are detailed in Jones et al. (2016). These reservoirs span much of the trophic state range within the state, with mean TP ranging from 9 to 100 µg/L (Jones et al. 2008b, 2016). This dataset provides the best available information on seasonal patterns in DOC among reservoirs ($n=734$ measurements).

Lake Woodrail (Figure 1b). This 4 ha reservoir is located in a wooded catchment with suburban homes within the limits of Columbia, Missouri; DOC and trophic state metrics were measured daily from March 1995 to December 1996 ($n=658$; Jones, Pollard, and Obrecht 2022b). The Lake Woodrail dataset provides information on daily variation in reservoir DOC.

Lake of the Ozarks (Figure 1b). Data come from a long-term summer monitoring program where 8 sites were sampled on 4 occasions during July and August (Jones and Kaiser 1988, Jones, Obrecht, and Thorpe 2022a), with DOC data available from 2007 to 2014. Data from Truman Lake, located upstream, and the principal inflow to Lake of the Ozarks (Figure 1b), come from the statewide inventory (statewide reservoirs dataset).

The Lake of the Ozarks dataset provides information on the influence reservoir inflows have on DOC.

Statewide streams (Figure 1c). Stream data were compiled from Pollard (2008), with an inventory of 88 streams sampled during low to moderate flow conditions in 2008 and 2009 (Figure 1c). The statewide stream data provide a snapshot of DOC in Missouri's lotic systems.

Hinkson Creek (Figure 1c). Daily samples and streamflow measurements were collected between 6 February 1995 and 31 January 1996 (Parris 2000; $n=357$) at a US Geological Survey site within the municipal limits of Columbia, Missouri (US Geological Survey Station 06910230). Land use in the Hinkson Creek watershed is 34% forest, 38% agriculture, and 25% urban (Kellner and Hubbart 2017). The outflow from Lake Woodrail is a tributary of Hinkson Creek. The Hinkson Creek dataset provides information on daily variation in stream DOC, and allows direct comparisons with changing streamflow conditions.

Watershed features

In addition to water quality variables, in reservoir watersheds ($n=203$) we also measured hydrologic, land use, and edaphic features that can contribute to DOC. Approaches for catchment delineation, basin slope, and current and presettlement land cover were described in Jones et al. (2009) and Bhattacharya et al. (2022). Mean runoff (catchment water export) was interpolated from data in the Missouri Water Atlas (Missouri Department of Natural Resources 1987). There is a 4-fold range in annual runoff in the state along a northwest to southeast axis (10 to 40 cm), while precipitation increases by about 50% over the same range. Both drainage ratio (watershed area/surface area) and flushing rate (calculated using mean annual runoff, watershed area and volume) were used to evaluate the role of hydrology on DOC. Dam heights, the available estimate of reservoir depth, were taken from the National Inventory of Dams (USACE 2020) and are collectively referred to as “depth” in the text (data were unavailable for 8 reservoirs). Watershed delineation, estimation of hydrological flow paths, and percent slope (Slope) were conducted with

ArcInfo geographical information systems (Environmental Systems Research Institute 1997) using 1 m resolution aerial photography and 10 m resolution digital elevation data from 2010 (Missouri Spatial Data Information Service 2011). Reservoir watershed characteristics of land cover were based on 30 m imagery from the LANDSAT thematic mapper developed by the Missouri Resource Assessment Partnership (Jones et al. 2004, Jones, Knowlton, and Obrecht 2008a). Major land cover classes were cropland, forest, grassland, urban, and wetland. The percent soil organic matter (OM) content, permeability (Perm), and soil erodibility (K-factor) were derived from the US Department of Agriculture Natural Resources Conservation Service Soil Survey Geographic Database (USDA NRCS 2023) soils tables and 1:25000 spatial data at the Geographic Resources Center, University of Missouri.

Data analysis

This regional analysis of DOC followed that of Jones, Knowlton, and Obrecht (2008a) by combining data from sites located in the Osage and Glacial Plains (hereinafter referred to as Plains) and sites located in the Ozark Highlands and Ozark Border (hereinafter referred to as Highlands), which combines similar landforms. A hierarchical approach was used to assess the reservoir datasets, as appropriate given available data. Analyses started with DOC in individual samples (e.g., 1 of 4 summer samples collected in statewide reservoirs dataset) and scaled up to the summer means for each reservoir (e.g., by averaging across the 4 collections), and subsequently across the summer means to arrive at a long-term average for a given reservoir. For the statewide streams, available samples were averaged to represent conditions in a given system. Mean values across all streams in the Plains and Highlands are also presented. The analysis of Hinkson Creek data focused on individual samples. Means are geometric calculations to minimize the influence of any one site or sample.

Data analyses, including correlation and regression (simple and stepwise) to assess geographic patterns and drivers of DOC, and one-way

analysis of variance (ANOVA) to determine statistically significant differences, were performed on \log_{10} -transformed data or logit transformation for percentages (which includes land cover and slope), unless otherwise noted. A value of 0.003 was added to the proportion of land cover to account for zero values in the dataset. Regression included coefficients of determination (r^2) and partial r^2 values. Acceptable significance was set at a P value of ≤ 0.01 for correlation, regression, and ANOVA analyses. Regression was used to identify variables accounting for variation in DOC and not for prediction; these models are described but not shown. Correlation (r) was used to assess the strength of monotonic relations between variables. Variation in DOC, specific conductance, and trophic state variables was characterized using the coefficient of variation ($CV = 100 \times [\text{standard deviation}/\text{mean}]$); CV values greater than 100 indicate that the standard deviation exceeded the mean value. To further assess variation in DOC and other variables of interest, the maximum seasonal mean from the most frequently sampled reservoirs (10 to 15 seasons) was compared as a simple ratio with the minimum value for that reservoir. DOC values from 15 Plains reservoirs were normalized by using Z scores ($(\text{observation} - \text{mean})/\text{standard deviation}$) to illustrate seasonality across these systems. Statistical analyses were conducted using SPSS (v. 27).

Results

Reservoirs

Statewide reservoirs

Individual samples. During summer (May–Aug), DOC in individual samples collected from reservoirs statewide ranged from <1.0 to 15.9 mg/L ($n=4425$; Table 1), with a mean of 5.8 mg/L and 75% of samples between 4.9 to 7.5 mg/L. Monthly means varied by only $\sim 1.05\%$, indicating there was not a strong temporal trend during summer across systems and years. Values averaged 5.7 mg/L in May ($n=745$), 5.8 mg/L in June and July ($n=1581$ and 1293, respectively), and 6.0 during August ($n=806$). Variation among individual DOC samples ($CV = 34\%$) was slightly less than

Table 1. Summary statistics for select water-quality and hydrologic, land cover, and edaphic watershed features in 203 Missouri reservoirs sampled routinely during May–Aug 1997–1999, 2004–2007, and 2009–2016. Water-quality summary statistics are presented for individual samples and reservoir means. Specific conductance is abbreviated as KSP.

	<i>n</i>	Minimum	Geometric mean	Median	Maximum
Individual samples					
DOC (mg/L)	4425	0.4	5.8	6.1	15.9
TN (µg/L)	4630	<50	705	740	7430
TP (µg/L)	4632	2	36	38	740
Chl (µg/L)	4632	0.1	14.8	16.1	772.6
KSP (µS/cm)	4627	16	169	183	673
Reservoir means					
DOC (mg/L)	203	1.6	6.1	6.5	10.8
TN (µg/L)	203	100	740	795	2077
TP (µg/L)	203	5	40	45	388
Chl (µg/L)	203	0.6	16.0	48.7	114.5
KSP (µS/cm)	203	22	164	181	548
Hydrologic variables					
Depth (m)	195	4.3	12.2	11.9	76.8
Surface area (ha)	203	2.0	29.1	19.8	21,778
Drainage ratio	203	3.9	20.5	17.6	591.8
Runoff (cm)	203	10.2	20.4	18.8	44.5
Flushing rate (/yr)	196	0.1	1.2	1.0	85.8
Slope (%)	203	1.6	8.7	9.3	28.5
Land cover variables					
Cropland (%)	203	0	6.8	14.9	74.0
Grassland (%)	203	0	28.4	34.5	77.0
Forest (%)	203	0	13.1	16.7	99.0
Wetland (%)	203	0	0	0.2	4.1
Surface water (%)	203	0	6.4	7.5	33.0
Urban (%)	203	0	2.4	3.2	71.0
Edaphic variables					
Permeability	203	0.33	0.72	0.66	3.34
Erodibility (K-factor)	203	0.25	0.33	0.34	0.45
Organic matter (%)	203	0.19	0.75	0.73	1.63

specific conductance (42%), about half that of TN (62%), around one-third of TP (104%), and one-quarter of Chl (132%).

Reservoir mean values. Among reservoir means, DOC ranged from 1.6 to 10.8 mg/L with an overall mean of 6.1 mg/L, and 75% of values ranged from 5.3 to 7.9 mg/L ($n=203$; Table 1). The smallest mean value was measured in a flood control reservoir in the Highlands (Clearwater Lake; Jones et al. 2008b) that receives considerable inflow from springs; the watershed is primarily forested (83%), with permeable soils of low organic content. The largest mean value was measured in a reservoir at the northern edge of the Highlands that is managed for recreational fisheries (Dairy Lake 1; Jones, Pollard, and Obrecht 2022b). In an adjacent reservoir (Dairy Lake 3), where TP was the highest value in the dataset (388 µg/L, Table 1), DOC was 9.3 mg/L. For reservoirs with DOC measured from 10 to 15 seasons the maximum summer mean averaged 1.8 times the minimum ($n=40$). In comparison, this ratio averaged 2.0 for specific

conductance, 2.7 for TN, 3.6 for TP, and 7.4 for Chl.

Regional patterns. There was a distinct statewide pattern of reservoir DOC increasing with latitude going from the Highlands to the Plains (Table 2). Regional means were 4.7 ($n=66$) and 7.0 mg/L ($n=137$), respectively, which is a statistically significant difference of 49% (ANOVA $F=86.01$). In comparison, regional differences were greater for trophic state metrics; the difference for TN was 90% (470 in the Highlands vs. 914 µg/L in the Plains; Table 2), more than 160% for TP (21 vs. 55 µg/L), and 200% for Chl (7.6 vs. 22.8 µg/L). For specific conductance the difference was 28% (139 vs. 178 µS/cm). Among these reservoirs, DOC was most strongly correlated with TN ($r=0.81$), while correlations with TP and Chl were weaker ($r=0.66$ and 0.60, respectively, $n=203$, log transformed). The correlation between DOC and specific conductance was not statistically significant ($P = -0.095$).

In regression analysis, latitude explained 40% of cross-system variation in DOC (untransformed;

Table 2. Summary statistics for select water-quality and hydrologic, land cover, and edaphic watershed features in Missouri Plains and Highlands reservoirs. Water-quality data are presented as reservoir means. Specific conductance is abbreviated as KSP.

	Minimum	Geometric mean	Median	Maximum
Highlands reservoirs				
Water-quality variables (<i>n</i> = 66)				
DOC (mg/L)	1.6	4.7	4.8	10.8
TN (µg/L)	101	470	495	1917
TP (µg/L)	5	21	19	387
Chl (µg/L)	0.6	7.6	6.9	72.6
KSP (µS/cm)	22	139	166	548
Hydrologic variables (<i>n</i> = 61 to 66)				
Depth (m)	4.6	14	14.2	76.8
Surface area (ha)	2.4	31.3	20.8	20,774
Drainage ratio	3.9	25.3	18.8	591.8
Runoff (cm)	17.8	31.5	34.8	44.5
Flushing rate (/yr)	0.2	1.7	1.3	85.8
Slope (%)	4.6	11.3	12.3	28.5
Land cover variables (<i>n</i> = 66)				
Cropland (%)	0	0.9	1.0	52
Grassland (%)	0	18.1	25.7	75
Forest (%)	0	30.2	45.8	99
Wetland (%)	0	0	0.1	4
Surface water (%)	0	5.3	7.3	33
Urban (%)	0	1.4	2.8	34.0
Edaphic variables (<i>n</i> = 66)				
Permeability	0.37	1.21	1.36	3.34
Erodibility (K-factor)	0.25	0.3	0.3	0.45
Organic matter (%)	0.19	0.52	0.53	1.00
Plains reservoirs				
Water-quality variables (<i>n</i> = 137)				
DOC (mg/L)	3.6	7	6.9	10.5
TN (µg/L)	310	914	944	2076
TP (µg/L)	10	55	51	197
Chl (µg/L)	2.1	22.8	24.8	114
KSP (µS/cm)	61	178	185	448
Hydrologic variables (<i>n</i> = 133 to 137)				
Depth (m)	4.3	11.4	11.0	38.4
Surface area (ha)	2.0	28	19.0	21,778
Drainage ratio	4.0	18.5	17.0	89.6
Runoff (cm)	10.2	16.6	17.0	28.2
Flushing rate (/yr)	0.1	1.0	1.0	7
Slope (%)	1.6	7.8	7.7	18.1
Land cover variables (<i>n</i> = 137)				
Cropland (%)	0.0	17.9	25.6	74
Grassland (%)	7.0	35.2	37.9	77
Forest (%)	0.0	8.7	11.2	82
Wetland (%)	0.0	0.0	0.3	4.0
Surface water (%)	1.0	7	7.5	32
Urban (%)	0	3.2	3.2	71.0
Edaphic variables (<i>n</i> = 137)				
Permeability	0.33	0.56	0.52	1.90
Erodibility (K-factor)	0.3	0.35	0.35	0.41
Organic matter (%)	0.47	0.89	0.82	1.63

Figure 2); longitude, however, did not significantly explain residual variation. Regression showed runoff was negatively related with latitude (partial $r^2 = 0.86$, $n=203$) and increased with longitude (partial $r^2 = 0.11$), which reflects increasing values to the southeastern corner of the state where rainfall is greater and soils are more permeable. Given this strong statewide pattern, a quadratic relation between runoff and DOC explained an amount of variation similar to that for latitude (39%).

Soil properties in reservoir watersheds showed strong regional patterns along a largely north-west–southeast axis ($n=203$). Permeability decreased in a quadratic pattern with latitude ($r^2 = 0.60$), while both K-factor erodibility and organic matter increased to the northwest as measured by latitude and longitude ($r^2 = 0.37$ and 0.57 , respectively). As detailed previously (Jones et al. 2008b, 2009), percent row crop showed a quadratic increase with latitude ($r^2 = 0.38$), while percent forest cover decreased

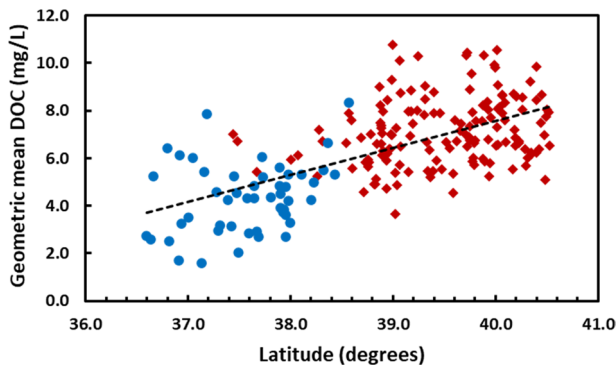


Figure 2. Relation between latitude and geometric mean of dissolved organic carbon (DOC) concentrations in reservoirs located in the Highlands (blue circles) and Plains (red diamonds) regions of Missouri.

($r^2 = 0.19$). Percent grassland increased in a quadratic pattern with longitude ($r^2 = 0.26$), while basin slope decreased with longitude ($r^2 = 0.26$). Among the hydrologic features of depth, area, and drainage ratio, the statewide pattern with latitude and longitude either was not significant (depth) or accounted for 4 to 8% of cross-system variation, which reflects the diversity of reservoir size and depth within the state (Table 2; Jones et al. 2008b).

Statewide regression relations for DOC. When latitude and longitude were not considered (to avoid multicollinearity), 64% of variation in DOC was explained by permeability, depth, and drainage ratio (negative coefficients, partial $r^2 = 0.39$, 0.11, and 0.07, respectively), followed by percent cropland and percent grassland (positive coefficients, partial $r^2 = 0.05$ and 0.02, respectively, $n=195$). Similar variation in DOC (58%) was explained by these variables when the analysis was limited to drainage ratios <30 (eliminating the upper quartile reservoirs, $n=148$), which indicates rapidly flushed reservoirs did not strongly influence the cross-system pattern. The results were similar when flushing rate was substituted for drainage ratio.

When soil properties were excluded, 61% of variation in DOC was accounted for by percent cropland (positive coefficient, partial $r^2 = 0.29$), depth and drainage ratio (negative coefficients, partial $r^2 = 0.18$ and 0.12, respectively), and percent grassland (positive coefficient, partial $r^2 = 0.02$, $n=195$). Permeability was negatively related with both percent cropland and percent grassland

($r=-0.58$ and -0.37 , respectively) and positively correlated with percent forest ($r=0.54$, $n=203$). When agricultural land cover was excluded, percent forest entered (negative coefficient) with depth and drainage ratio to explain 57% of the variation in DOC. Percent cropland and percent forest were negatively correlated among these watersheds ($r=-0.65$, $n=203$).

Regional regression relations for DOC. Among Highlands reservoirs mean DOC ranged from 1.6 to 10.8 mg/L (Table 2; CV = 39%, $n=66$). Regression analyses show 71% of the variation in DOC in Highlands reservoirs was accounted for by drainage ratio, depth (partial $r^2 = 0.40$ and 0.22, respectively, negative coefficients), and percent row crop (partial $r^2 = 0.13$, positive coefficient, $n=61$).

Among Plains reservoirs, mean DOC ranged from 3.6 to 10.5 mg/L (Table 2; CV = 19%, $n=137$). About 45% of the variation in DOC was accounted for by depth (partial $r^2 = 0.29$), with percent urban, permeability, and percent surface water (partial $r^2 = 0.04$ to 0.07, all negative coefficients, $n=131$), adding modest improvement to the amount of variance explained. There was a strong negative correlation between percent surface water and drainage ratio among these watersheds ($r=-0.74$, $n=137$), indicating the relative area of small ponds decreases as watershed area increases. Noteworthy is that the lowest DOC value in the Plains (3.6 mg/L) was in the reservoir with the highest (71%) urban area (Lake Tapawingo, Jones et al. 2008b). When reservoirs with ≥ 18 to 71% urban area ($n=9$, mean % urban area = 29%) were removed from the analysis, 38% of the variation in DOC was accounted for by depth, permeability, and percent surface water (all negative coefficients). Among these reservoirs, urban area averaged 3%.

15 Plains reservoirs

DOC in individual samples collected from 15 northwestern reservoirs over 49 wk in 2004 ranged from 2.7 to 12.4 mg/L ($n=734$) with an overall mean of 6.3 mg/L (Table 3); reservoir mean DOC ranged from 4.1 to 9.1 mg/L with a median of 6.0 mg/L ($n=15$). As in the statewide dataset, the CV for DOC (25%, $n=734$), was similar to specific conductance (23%), about half

Table 3. Summary statistics for select water-quality and hydrologic, land cover, and edaphic watershed features in 15 Plains reservoirs sampled weekly during 2004. Water-quality data are given for individual samples from the 15 reservoirs during the study and as mean values among the reservoirs. Specific conductance is abbreviated as KSP.

	Minimum	Geometric mean	Median	Maximum
Individual sample information (<i>n</i> = 734)				
DOC (mg/L)	2.7	6.3	6.1	12.4
TN (μg/L)	210	775	840	2210
TP (μg/L)	4	34	33	252
Chl (μg/L)	0.6	11.6	12.1	195.2
KSP (μS/cm)	111	207	207	348
Reservoir mean values (<i>n</i> = 15)				
DOC (mg/L)	4.1	6.5	6.0	9.1
TN (μg/L)	317	838	829	1500
TP (μg/L)	8.9	42	42	100
Chl (μg/L)	1.7	14.4	15.0	32
KSP (μS/cm)	148	213	211	303
Hydrologic variables (<i>n</i> = 15)				
Depth (m)	6.1	13.9	15.2	23.5
Surface area (ha)	10.3	56.9	45.7	408
Drainage ratio	4.0	13.1	13.4	39.0
Runoff (cm)	10.9	14.1	14.5	19.3
Flushing rate (/yr)	0.1	0.4	0.4	2.1
Slope (%)	5.1	9.1	9.7	15.1
Land cover variables (<i>n</i> = 15)				
Cropland (%)	1.0	11.8	15.8	54.0
Grassland (%)	19.0	40.9	42.8	77.0
Forest (%)	2.0	10.4	12.7	61.0
Wetland (%)	0	0	0.9	2.0
Surface water (%)	4.0	9.7	9.1	32.0
Urban (%)	1.0	3.1	3.1	18.3
Edaphic variables (<i>n</i> = 15)				
Permeability	0.33	0.51	0.42	0.96
Erodibility (K-factor)	0.31	0.35	0.34	0.37
Organic matter (%)	0.57	0.91	0.75	1.63

that of TN (42%), one-third of TP (76%), and less than one-fourth of Chl (115%). These reservoirs represent nearly the full range of DOC in the Plains region, half the range of TP and Chl, and about two-thirds the range of TN (Tables 2 and 3).

During summer (May–Aug) overall mean DOC in these 15 reservoirs was 6.7 mg/L (*n* = 255), which amounts to about a 4% increase over the annual mean (Figure 3a). The general seasonal pattern shows an increase in spring concurrent with rainfall (about 20 cm between April and June), which indicates allochthonous input. Subsequently, values were elevated during summer, indicating autochthonous sources and mineralization. There was a modest decline during fall destratification (Figure 3a). In these reservoirs the maximum DOC value (*n* = 12 reservoirs) or

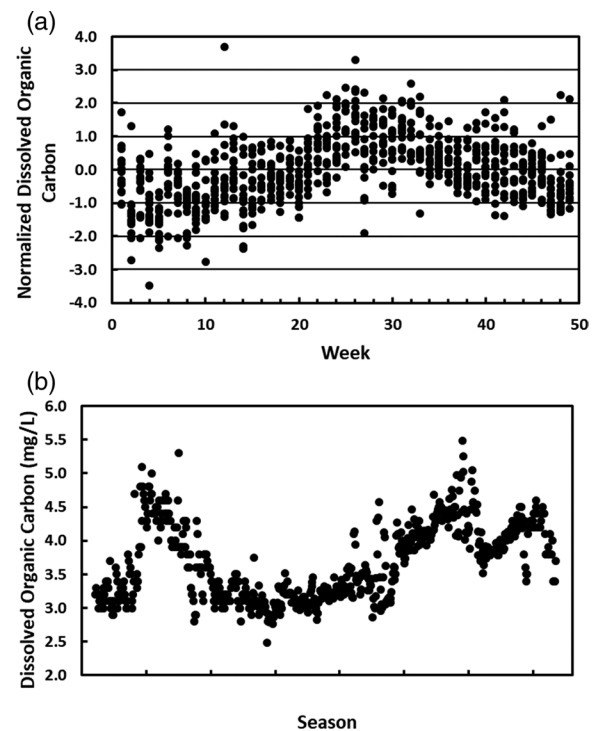


Figure 3. Seasonal patterns in dissolved organic carbon (DOC) in (a) 15 Plains Missouri reservoirs sampled for 49 consecutive weeks in 2004 (data were normalized [observation – mean/standard deviation]) and (b) Lake Woodrail, sampled daily from Mar 1995 to Dec 1996.

second highest value (*n* = 3 reservoirs) was collected during June to August. A cross-system comparison showed mean summer and mean 49 week DOC values were highly correlated ($r = 0.99$, $n = 15$); in each reservoir summer means exceeded the overall mean by an average of 0.3 mg/L (from <0.1 to 1.1 mg/L). Noteworthy is that in cross-system analyses ($n = 15$ reservoirs), these modest seasonal differences were positively correlated with reservoir-mean TP ($r = 0.78$) and TN ($r = 0.67$) and negatively correlated with depth ($r = -0.80$); these metrics are indicators of trophic state. About 91% of mean summer DOC was explained by the drainage ratio (positive coefficient, partial $r^2 = 0.74$, $n = 15$) and slope (negative coefficient, partial $r^2 = 0.17$, $n = 15$).

These 15 reservoirs were also represented in the long-term statewide dataset. Reservoir mean DOC values were similar in both datasets; regression showed a slope of unity and the intercept indicated 2004 values were ~0.1 mg/L larger than the long-term mean DOC value in the statewide inventory ($r^2 = 0.85$, $n = 15$). The northwestern location of this subset of 15 Plains reservoirs

(Figure 1b) results in lower average runoff (14.1 vs. 16.7 cm) and flushing rates (0.4 vs. 1.0/year) relative to elsewhere in the Plains. These reservoirs also had smaller drainage ratios (13.2 vs. 18.5) relative to others in the region.

Lake Woodrail

Measured DOC in Lake Woodrail during 1995–1996 ranged over 2-fold from 2.5 to 5.5 mg/L in individual samples ($n=658$, interquartile range 3.2 to 4.1 mg/L), with a mean of 3.6 mg/L, which is within the lower third measured among Highlands reservoirs (Table 2). The seasonal pattern shows an increase in spring followed by maxima of ~4.5 mg/L for several weeks during both summers, followed by declining concentrations (Figure 3b). The seasonal increase in 1995 coincided with 48 cm of rainfall between April and early June (70 days, maximum 76 mm), with DOC increasing from ~3 to >4.5 mg/L; this increase was concurrent with a 20% decline in specific conductance (from ~190 to 150 $\mu\text{S}/\text{cm}$). Chl was <5 to 10 $\mu\text{g}/\text{L}$ during this inflow period and subsequently increased to >20 $\mu\text{g}/\text{L}$. DOC averaged 3.9 mg/L during May–August 1995 ($n=123$), which was significantly larger than the average of 3.1 mg/L during other months that year ($n=181$, ANOVA $F=296.1$). During spring 1996, DOC increased following a 5.5 cm rainfall in late April and several subsequent events (70 day total = 26.6 cm); concurrently, Chl increased from ~5 $\mu\text{g}/\text{L}$ to more than 35 $\mu\text{g}/\text{L}$ with only a modest change in specific conductance. DOC averaged 4.2 during May–August 1996 ($n=123$), which was significantly larger than the average of 3.6 mg/L during other months that year ($n=231$, ANOVA $F=149.9$). These seasonal increases, concurrent with rainfall, indicate allochthonous input increased DOC during both springs, with autochthonous activity potentially contributing to DOC concentrations during summer. The epilimnion of this reservoir is largely isolated from surface inflow, which enters as an interflow during peak stratification (Jones, Pollard, and Obrecht 2022b).

Most day-to-day changes in DOC in Lake Woodrail were modest when expressed as a proportion of the overall mean. In 15% of sequential samples there was no change, in 70% the absolute difference was $\leq 5\%$ of the mean and in

3% of samples the change was more than $\pm 20\%$. As in the cross-system analyses of Missouri reservoirs, the CV for DOC (15%, $n=658$) in Lake Woodrail was similar to that for specific conductance (13%), less than half that of TN (38%), about one-third that of TP (48%) and about one-sixth of the Chl value (98%).

Lake of the Ozarks

Summer DOC data averaged across 8 sites on Lake of the Ozarks showed a quadratic pattern with discharge during May through August (Figure 4). Discharge explained 90% of temporal variation in DOC among seasonal averages, which differed by only 1.6 mg/L, or 1.4-fold (from 4.2 to 5.8 mg/L, mean of 5.0 mg/L, $n=8$ seasons). For individual sites, discharge explained from 79 to 93% of temporal variation ($n=8$ seasons); mean DOC varied by about ~0.5 mg/L among the sampling sites, with values gradually declining along the reservoir mainstem. During this period DOC in Truman Lake, located on the Osage River immediately above Lake of the Ozarks, averaged 5.1 mg/L and showed a strong, positive correlation with reservoir discharge ($r=0.80$, $n=7$ seasons, no 2008 data).

Streams

Statewide streams

Under low flow conditions, DOC ranged between 1.9 and 12.9 mg/L among 122 sampled streams, with a mean of 6.3 mg/L (Fig 1c, Table 4). Unlike

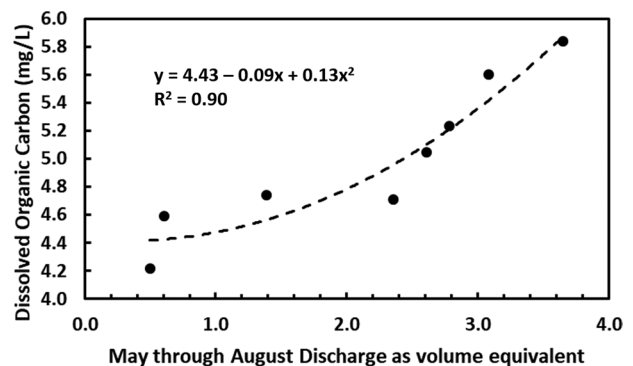


Figure 4. The relation between May through Aug discharge from Lake of the Ozarks (presented as seasonal volume divided by lake volume; unity would be one equivalent volume flushing) and seasonal geometric mean dissolved organic carbon concentrations averaged across 8 sampling sites during Jul–Aug 2007–2014.

Table 4. Summary statistics for select water-quality measures, slope, and land cover in Missouri Plains and Highlands streams. Specific conductance is abbreviated as KSP.

	Minimum	Geometric mean	Median	Maximum
Plains streams (<i>n</i> =117)				
DOC (mg/L)	2.8	6.4	6.2	12.9
TN (µg/L)	195	585	570	3745
TP (µg/L)	33	91	81	553
Chl (µg/L)	1.3	6.9	6.9	34.9
KSP (µS/cm)	211	350	357	569
Slope (%)	2.2	7.9	8.0	15.0
Cropland (%)	2.4	21.2	24.2	83.4
Grassland (%)	10.0	46.4	50.2	78.0
Forest (%)	0.7	11.4	11.1	67.8
Wetland (%)	0.2	2.1	2.3	5.1
Open water (%)	0.1	3.0	3.5	8.8
Urban (%)	0.8	1.9	1.9	5.3
Highlands streams (<i>n</i> =5)				
DOC (mg/L)	1.9	4.0	4.6	6.1
TN (µg/L)	185	480	485	910
TP (µg/L)	44	66	72	113
Chl (µg/L)	2.7	5.5	5.9	11.6
KSP (µS/cm)	319	367	366	402
Slope (%)	8.2	9.5	9.7	10.7
Cropland (%)	7.6	18.7	17.4	45.6
Grassland (%)	33.5	42.1	44.8	48.5
Forest (%)	16.1	28.2	32.1	40.2
Wetland (%)	0.7	1.3	1.3	2.4
Open water (%)	0.5	1.1	1.3	2.0
Urban (%)	1.5	1.8	1.6	2.3

the reservoir pattern, the relation with latitude among these streams was comparatively weak, accounting for only 4% of variation. As in reservoirs, variation in DOC (CV = 27%) was less than for TN (65%), TP (62%), and Chl (50%) but larger than for specific conductance (18%). Among these streams DOC was positively correlated with TP, TN, and Chl ($r=0.55$, 0.53 , and 0.24 , respectively, $n=122$) and negatively correlated with specific conductance ($r=-0.53$, $n=34$). Mean DOC was 4.0 mg/L in the Highlands ($n=5$) and 6.4 mg/L in the Plains ($n=117$), which follows the regional pattern in reservoirs, with slightly lower averages (Table 4).

Using regression analysis, over 60% of among-system variation in DOC was explained by percent forest (partial $r^2 = 0.34$), watershed area (partial $r^2 = 0.08$), and slope (partial $r^2 = 0.08$, all negative coefficients), with percent wetland entering the regression with a positive coefficient (partial $r^2 = 0.11$). No other variables entered to explain more than 3% of residual variation. Similar variation was explained when percent cropland was substituted for percent forest (negative coefficient). Noteworthy is

that among the 5 Highland streams in the dataset, DOC ranged from 1.9 to 6.1 mg/L, with percent wetland (0.7 to 2.4%, untransformed) explaining 99% of the increase in a quadratic fit.

Hinkson Creek

DOC averaged 3.8 mg/L (interquartile range 2.8 to 4.9 mg/L, $n=354$) with a minimum and maximum of 2.0 and 12.7 mg/L, respectively. The CV for DOC at 40% was lower than for TN (72%), Chl (107%), and TP (142%) and was slightly larger than for specific conductance (37%). Streamflow ranged from unmeasurably low to about 8 m³/s and the flow-weighted average DOC was 5.9 mg/L. Average DOC during above-normal flow conditions (greater than the 75th percentile of 35 yr of daily flow record between 1967 and 2020; US Geological Survey 2016) was 6.2 mg/L, which was nearly double the mean of 3.6 mg/L during below-normal flow conditions (less than the 25th percentile of the 35 yr flow record).

In 20% of sequential samples the change in DOC was <0.1 mg/L or ~3% of the mean, in 60% the absolute difference was <25% of the mean, and in the remaining 20% of samples the change was >25%. The largest day-to-day increase (+6.9 mg/L) was associated with the maximum value observed (12.7 mg/L) and coincided with a 5-fold increase in flow; the following day flow declined by half and DOC declined by 7.9 mg/L, which illustrates the variation related to a single spate. Excluding 12 samples with unmeasurable low flow, discharge explained 40% of temporal variation in DOC ($r^2 = 0.40$, $n=338$). Across all samples, DOC was positively correlated with discharge ($r=0.62$), TP ($r=0.77$), TN ($r=0.74$) and negatively correlated with specific conductance ($r=-0.71$ log transformed, $n=354$).

Discussion

Statewide DOC concentrations

Mean summer DOC in statewide inventories of Missouri reservoirs (Table 1, 1.6 to 10.8 mg/L) and streams (Table 4, 1.9 to 12.9 mg/L) span the lower half of worldwide values (<1 to >30 mg/L; Xenopoulos et al. 2003). These values are also

within the range of most global rivers (1 to 20 mg/L; Meybeck 1982). Lower DOC concentrations would be expected in Missouri, which has clay soils and native vegetation dominated by grasslands and hardwood forests (Rae et al. 2001). The overall mean of 5.8 mg/L among individual reservoir samples matches the median value in a large, multicontinent analysis (Sobek et al. 2007); however, it is about 50% greater than the predicted average for lake water globally (3.9 mg/L; Toming et al. 2020). The mean DOC of 6.3 mg/L among streams, under low-flow conditions, is similar to the global average of 5.7 mg/L (Meybeck 1982).

Regional comparisons for these DOC measurements are limited; individual collections from Missouri reservoirs included in the National Lakes Assessment ranged from 1.1 to 13.0 mg/L and averaged 4.8 mg/L ($n=78$, from 2007, 2012, and 2017; USEPA 2023). Similarly, DOC in 5 Iowa lakes, located north of Missouri, averaged from 4.5 to 12.0 mg/L, with a mean of 6.7 mg/L (Pacheco, Roland, and Downing 2014). Values from both collections compare closely with our findings. Also, stream averages of 4.0 mg/L in the Highlands and 6.6 mg/L in the Plains closely match regional reservoir values of 4.6 and 6.9 mg/L, respectively. The non-flow-weighted mean of 3.8 mg/L in Hinkson Creek is similar to the mean of 3.6 mg/L in Lake Woodrail, which is located in the watershed. The similarity of DOC concentrations in streams and reservoirs, despite differences in study design and period of collection, supports the strong connection between inflows and reservoir DOC observed by Bhattacharya et al. (2022) in Missouri and other studies worldwide (Findlay et al. 2001, Mulholland 2003, Lapierre, Seekell, and del Giorgio 2015). Collectively, these data represent the measured range of DOC concentrations in reservoirs and streams within the state.

Statewide DOC concentrations in reservoirs were similar across the summer months, indicating that sampling occurred during a temporal peak. Data from the 15 Plains reservoirs and Lake Woodrail show seasonal increases in DOC during periods of spring runoff, indicative of allochthonous loading, with a likely autochthonous addition during summer months (Figure 3).

These findings are consistent with autotrophic and related metabolic activity maintaining, or slightly increasing, the DOC pool with labile material during summer (Hanson et al. 2011, Evans et al. 2017, Zhou et al. 2018, Bhattacharya et al. 2022). Among reservoirs statewide, DOC was correlated with both macronutrients and Chl, which is consistent with autotrophic sources of DOC. Further supporting contributions by autotrophic sources is the modest increase between mean summer and mean annual DOC in the 15 Plains reservoirs, which correlated with macronutrients and Chl in a cross-system comparison. The analysis of Bhattacharya et al. (2022) indicates that allochthonous and autochthonous influences on DOC quantity and quality in Missouri reservoirs vary in relation to annual patterns in rainfall and runoff.

Reservoir DOC and watershed features

DOC concentrations are determined by multiple watershed features, along with flow paths and hydrology (Mulholland 2003, Seekell et al. 2014). In Missouri reservoirs, DOC values follow a strong geographical gradient between the Plains of northern and western Missouri and the Highlands region in the south. Along this axis, soil permeability, runoff, slope, and forest cover generally increase from the northwest to the southeast, while soil organic matter, erosion potential, and crop cover decline (Nigh and Schroeder 2002, Jones et al. 2004, Jones, Knowlton, and Obrecht 2008a, 2009). Collectively, these features minimize contact between water and soil organic matter in the Highlands and likely contribute to lower overall DOC levels. The influence of permeability, which explained 64% of cross-system variation in DOC among the statewide reservoirs, illustrates a strong physiographic difference in an edaphic driver (soil influence) between the 2 major natural regions in the state. The result is a distinctive pattern of increasing DOC with latitude (Figure 2). Statewide, permeability was negatively related with agricultural land use (percent cropland and percent grassland) and positively related with percent forest. Consequently, when combined with depth and drainage ratio (negative relations), either land use

type explained from 57 to 61% of variation in DOC (forest negative and cropland positive). This analysis indicates that land use and hydrology explain nearly the same variation in DOC as macronutrient concentrations in these reservoirs (Jones, Pollard, and Obrecht 2022b).

Land use practices can alter DOC export from watersheds, with differences along land use gradients (Xenopoulos et al. 2021). The negative relation with depth, both statewide and in the 2 physiographic regions, represents in-reservoir loss and dilution, with deeper reservoirs being less productive, reducing the potential for both allochthonous and autochthonous sourced DOC. This finding is consistent with limnological theory and studies of DOC in natural lakes (Rasmussen, Godbout, and Schallenberg 1989, Mulholland 2003). Residual variation accounted for by the negative relation with drainage ratio (or hydrologic flushing), both statewide and among Highlands reservoirs, reflects lower DOC levels in more rapidly flushed reservoirs. This finding also matches global analyses (Sobek et al. 2007, Toming et al. 2020); negative relations have been found in regions where soils release little DOC and flushing rates are high (Canham et al. 2004).

Drainage ratio had a strong positive association with DOC among the 15 Plains reservoirs. By comparison, drainage ratio did not explain a statistically significant amount of variation in DOC among all Plains reservoirs included in the summer statewide inventory; there was a modest negative association among Highlands reservoirs and in the statewide analysis. The literature shows drainage area as a positive predictor of DOC in some regions but not in others (Mulholland 2003, Xenopoulos et al. 2003, Sobek et al. 2007). Several studies show a positive influence in natural lakes (Rasmussen, Godbout, and Schallenberg 1989, Houle et al. 1995, D'Arcy and Carignan 1997, Mulholland 2003, Xenopoulos et al. 2003, Toming et al. 2020), as observed in the 15 Plains reservoirs. These 15 reservoirs were sampled weekly during a single year (2004) and all were subject to similar climatic conditions. Nevertheless, the outcome was equivalent when the long-term reservoir means for these 15 reservoirs were isolated from the statewide dataset and treated separately. These reservoirs were selected to represent the

continuum of reservoir trophic state in the Plains, but the subset would not likely include the full range of driver-response relations influencing DOC. The 15 Plains reservoirs in the subset had smaller drainage ratios and substantially lower runoff and flushing rates than other Plains reservoirs (Tables 2 and 3). Others have shown the importance of region-specific models (Sobek et al. 2007, Seekell et al. 2014), and this example indicates that driver-response relations can differ among heterogeneous reservoirs within a region.

A factor influencing the role of drainage ratio and flushing rate in this cross-system pattern is that large inflows during summer stratification often form density-determined plunging interflows in Missouri reservoirs with little direct effect on the surface layer (Jones et al. 2004, Jones, Pollard, and Obrecht 2022b). Thereby, this event can uncouple the link between watershed loading and surface water chemistry. The influence of inflow timing and volume is outside the scope of this regional characterization but likely contributes to residual variation in the cross-system patterns (Bhattacharya et al. 2022). Data from Lake of the Ozarks (Figure 4) and Truman Lake, the major inflow, support the DOC–inflow linkage commonly shown in the literature (Rasmussen, Godbout, and Schallenberg 1989, D'Arcy and Carignan 1997, Xenopoulos et al. 2003, Sobek et al. 2007, Toming et al. 2020). Unlike other reservoirs in the dataset, most inflow to Lake of the Ozarks is from the epilimnion of an upstream reservoir, which reduces the potential for interflows (Perkins and Jones 2000, Jones, Obrecht, and Thorpe 2022a).

In the Missouri analyses, land cover variables explained similar variability in reservoir DOC as reported in regional studies of northern lakes (Rasmussen, Godbout, and Schallenberg 1989, Houle et al. 1995, D'Arcy and Carignan 1997, Gergel, Turner, and Kratz 1999) and the global analysis of Xenopoulos et al. (2003). In this landscape, the land cover types of row crop, grassland, and forest explained cross-system variation in DOC similar to that for wetlands in North Temperate lakes (Xenopoulos et al. 2003). Soil permeability, however, explained variation similarly to land cover, which is a consequence of multicollinearity among edaphic variables and

land use in the dataset. The similar, but opposite, roles of agricultural land and forest cover in accounting for variation in DOC match the pattern accounting for TP and TN in these reservoirs (Jones et al. 2004, Jones, Knowlton, and Obrecht 2008a, Jones, Thorpe, and Obrecht 2020b). The strong correlations between DOC and nutrients in the statewide and 15 Plains reservoirs indicate that DOC broadly follows the geographic pattern in trophic state.

Agriculture, particularly row crop production, is a continued disturbance to the landscape that increases material loss from the basin, including DOC (Dalzell, Filley, and Harbor 2007, Veum et al. 2009, Tian et al. 2022). Even among Highland reservoirs, cropland accounted for residual variation in DOC, which was also the case in a previous analysis of nutrients (Jones, Knowlton, and Obrecht 2008a). Human-altered landscapes have been shown to enrich both nutrients and DOC (Xenopoulos et al. 2021, Jones, Pollard, and Obrecht 2022b). The increase in DOC with agriculture is consistent with the pattern observed in a comparative analysis of an agricultural watershed (Michigan) and a forested watershed (Connecticut) in the United States (Tian et al. 2022) and in boreal lakes where logging was the major disturbance (Carignan et al., 2000). In contrast, forest cover is modestly disturbed, with low nutrient amendment relative to agricultural land, and relations with DOC in this analyses were negative. Also, the forested landscapes in this dataset have greater permeability and lower organic content.

Among Plains reservoirs, percent surface water (largely farm ponds of <1ha) accounted for a modest, but significant, reduction in DOC. In these watersheds, percent surface water was negatively related to the drainage ratio. Many farm ponds do not have active outlets, which favors long retention times and DOC mineralization (Hanson et al. 2011). Reduction of DOC from landscapes with small agricultural ponds supports their role as active sites of carbon cycling and burial (Downing et al. 2008, Downing 2010, Mendonça et al. 2017, Gilbert et al. 2021, Jones et al. 2023). The negative percent urban–DOC relationship in Plains reservoirs is consistent with other studies in the region (Graham et al. 2010),

and likely is a result of reduced infiltration from impervious surfaces, soil degradation, and bypassing of surface flow with subsurface artificial drainage (Hosen et al. 2014), which is another human disturbance influencing DOC. Although not observed in this analysis, urban features such as stormwater drainage outfalls and retention ponds may be hotspots for DOC influx to waterbodies (Kalev and Toor 2020, Kalev, Duan, and Toor 2021).

The CV for DOC values in Highlands reservoirs was about double that of Plains reservoirs, further documenting differences in DOC variation between regions reported in other studies (Mulholland 2003, Sobek et al. 2007, Seekell et al. 2014). Edaphic and land use features differ between these physiographic provinces. The smallest DOC value in the dataset (1.6 mg/L) was measured in a forested Highlands reservoir with high permeability and low organic matter, which is consistent with conditions in the region. The largest value (10.8 mg/L) was in a northern Highlands reservoir where dairy barn solids were applied in the watershed (Jones, Pollard, and Obrecht 2022b), which seemingly increased soil organic matter. Soil P tests were some 5 to 10 times the local concentration, indicating these applications likely altered background conditions (Jones, Pollard, and Obrecht 2022b). These 2 end members within the same physiographic region may be representative of the least and most disturbed land use extremes in the dataset. As concentrated feeding operations and land applications expand (Jones, Pollard, and Obrecht 2022b), statewide patterns in DOC concentration may change as more reservoirs and streams have these practices in their watersheds, as has been documented for nutrients (Cooke, Welch, and Jones 2011, Welch et al. 2011, Jones, Pollard, and Obrecht 2022b). Land application of biosolids may be another measurable source of human alteration of DOC quantity and composition in agricultural landscapes (Xenopoulos et al. 2021).

Stream DOC and watershed features

Stream DOC, measured during low flow, showed negative relations with both slope and watershed area, but unlike for stream macronutrients (Jones,

Thorpe, and Obrecht 2020b), the relation with percent cropland was negative. This finding also differs from the positive relation between DOC and percent cropland in reservoirs, and may indicate land use is less important than hydrology in determining DOC during low-flow conditions in these streams. The significance of percent wetlands in the statewide stream analysis, and particularly in the limited number of Highlands streams ($n=5$), is consistent with wetlands being an important source of DOC in several regional studies, attributable to organic-rich, water-saturated soils and shallow flow paths (Gergel, Turner, and Kratz 1999, Xenopoulos et al. 2003, Kortelainen et al. 2006). In our reservoir analyses, wetland cover did not reduce residual variation in multivariate regression models but accounted for residual variation among streams in the Plains and was strongly related with DOC among a small number of Highland streams ($n=5$). In these systems, wetland cover was associated with large watersheds, grasslands, and modest slope, all characteristics associated with high allochthonous DOC inputs (Mulholland 2003). Others have found that wetlands explain more variability in lotic than in lentic systems (Gergel, Turner, and Kratz 1999), which is consistent with our analysis.

Substantial seasonal variation in stream DOC concentrations during low flow has been observed in some regions of the United States (Tian et al. 2022); however, limited data on growing and fallow season DOC loss from agricultural watersheds in our study region show no temporal pattern in allochthonous input (Veum et al. 2009). Data from Hinkson Creek show lower DOC values in groundwater-dominated low-flow conditions and increasing concentrations with surface water-dominated flow during runoff events, also indicative of the importance of hydrology in determining low-flow DOC concentrations. Further study is needed to assess how land use might influence stream DOC quantity and composition during runoff events and high flows. Large increases and decreases in DOC during spates were measured in Hinkson Creek and after seasonal inflows to Lake Woodrail (Figure 3); these events are likely best measured by high-frequency sensors (Volk et al. 2002). Sensor technology allows insights into DOC quantity

and composition at sub-daily scales, and has the potential to substantially advance process-based understanding of DOC dynamics across a diverse range of landscapes as influenced by hydrologic forcing, biological activities, and water quality conditions (Spencer et al. 2007, Saraceno et al. 2009, Watras et al. 2015).

Temporal variation in DOC and implications for detecting trends

Low temporal variation of DOC relative to trophic state metrics, illustrated by CV calculations, was found in each of the datasets considered in this analysis (reservoirs statewide, 15 Plains reservoirs, Lake Woodrail, and Hinkson Creek datasets, Tables 1–3). This outcome is expected because of both recalcitrance and rapid degradation of organics in this complex pool of material (Hanson et al. 2011, Evans et al. 2017). As expected, variation in DOC was most similar to specific conductance because of the influence of hydrology on both variables. Maximum DOC averaged 1.8 times the minimum summer mean in these reservoirs, which matches previous findings of variation across years (Pace and Cole 2002) and is similar to the ratio for specific conductance.

Small changes measured in daily collections from both Lake Woodrail and Hinkson Creek (during stable flow) indicate modest short-term variation during reservoir stratification and low flow in streams. As such, DOC may be a sensitive indicator of temporal change in these mid-continent systems. Previous research has shown that changes in trophic state metrics (N&P and Chl) are not likely to stand out against ordinary noise unless they are large or rapid (Knowlton and Jones 2006b). Doubling Chl in a given reservoir over 20 yr could be virtually undetectable with routine lake monitoring and it would require a decade to detect similar changes in macronutrients (Knowlton and Jones 2006b). Temporal changes in DOC would likely be detected more rapidly with routine monitoring than nutrient-driven eutrophication because concentrations are less variable. Currently, DOC does not show temporal change in Missouri reservoirs; concentrations have varied nonmonotonically

over past decades, largely in response to runoff (Bhattacharya et al. 2022).

In contrast, increases in DOC have been measured in surface waters worldwide over recent decades, particularly in northern lakes; these changes are related to many factors, including climate parameters and atmospheric deposition (Monteith et al. 2007, Couture, Houle, and Gagnon 2012). The consequences of changing DOC on aquatic systems are complex and include changes in light attenuation, primary production, oxygen demand, and carbon dioxide release, among others (Seekell et al. 2014, Solomon et al. 2015). Current understanding and data to manage affected systems are scarce, and at present, DOC is rarely incorporated in aquatic management criterion (Stanley et al. 2012). In contrast, DOC is of concern in drinking-water treatment and distribution, where removal to reduce taste, odor, and color and prevent disinfection by-product formation is affected by variation in DOC quantity and composition in response to runoff events and seasonal changes (Volk et al. 2002). Understanding influences on DOC quantity and composition can help inform drinking-water management decisions and mitigate potential consequences of changing DOC in lakes and reservoirs.

Conclusions

This statewide DOC analysis illustrates that edaphic features, land use, and hydrology largely account for cross-system variation and are consistent with allochthonous sources determining measured concentrations. Limited data from seasonally sampled reservoirs further indicate a modest autochthonous contribution accounting for marginally higher DOC concentrations during summer. Temporal variation in DOC is less than trophic state metrics, and changes should be more readily detected. This analysis contributes to previous studies of carbon in Missouri reservoirs, which include particulate organics (Jones and Knowlton 2005b), seasonal patterns in carbon dioxide (Jones et al. 2016), sediment organic carbon sequestration (Pittman et al. 2013, Jones et al. 2023), and organic matter quantity and composition (Bhattacharya et al. 2022). Also, it

further landscape-level analyses of factors determining water chemistry and trophic state of reservoirs and streams within the state (Jones, Pollard, and Obrecht 2022b). Despite differences in collection period, mean DOC concentrations in Missouri reservoirs and streams were similar. The summer statewide monitoring program captures the spatial variability and seasonal maxima in DOC concentrations, and general patterns are well represented. More focused studies are required to improve process-based understanding of environmental and temporal drivers in reservoirs and streams throughout the state.

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Disclosure statement

Any use of trade, firm or product names is for descriptive purposes only and does not imply endorsement by the US government. The authors declare no competing interests.

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