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RESEARCH ARTICLE

Spatial and temporal patterns of dissolved organic matter quantity and quality in the Mississippi River Basin, 1997–2013

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Abstract

Recent studies have found insignificant or decreasing trends in time-series dissolved organic carbon (DOC) datasets, questioning the assumption that long-term DOC concentrations in surface waters are increasing in response to anthropogenic forcing, including climate change, land use, and atmospheric acid deposition. We used the weighted regressions on time, discharge, and season (WRTDS) model to estimate annual flow-normalized concentrations and fluxes to determine if changes in DOC quantity and quality signal anthropogenic forcing at 10 locations in the Mississippi River Basin. Despite increases in agriculture and urban development throughout the basin, net increases in DOC concentration and flux were significant at only 3 of 10 sites from 1997 to 2013 and ranged between −3.5% to +18% and −0.1 to 19%, respectively. Positive shifts in DOC quality, characterized by increasing specific ultraviolet absorbance at 254 nm, ranged between +8% and +45%, but only occurred at one of the sites with significant DOC quantity increases. Basinwide reductions in atmospheric sulfate deposition did not result in large increases in DOC either, likely because of the high buffering capacity of the soil. Hydroclimatic factors including annual discharge, precipitation, and temperature did not significantly change during the 17-year timespan of this study, which contrasts with results from previous studies showing significant increases in precipitation and discharge over a century time scale. Our study also contrasts with those from smaller catchments, which have shown stronger DOC responses to climate, land use, and acidic deposition. This temporal and spatial analysis indicated that there was a potential change in DOC sources in the Mississippi River Basin between 1997 and 2013. However, the overall magnitude of DOC trends was not large, and the pattern in quantity and quality increases for the 10 study sites was not consistent throughout the basin.

KEYWORDS

atmospheric deposition, climate, dissolved organic carbon, land management, land-use, Mississippi River Basin, specific ultraviolet absorbance, trends, waste water treatment, WRTDS

1 | INTRODUCTION

Dissolved organic carbon (DOC), a major constituent of aquatic dissolved organic matter, plays several important ecological and biogeochemical roles in freshwater ecosystems. DOC serves as a pH buffer (Weishaar et al., 2003), provides an energy source for aquatic organisms (Cole & Caraco, 2001; Lu et al., 2013), and absorbs ultraviolet radiation (Amon & Benner, 1996). From a water management perspective, increases in DOC concentrations may be problematic because DOC-rich water can produce carcinogens when chlorinated (Gallard & von Gunten, 2002), and organic matter serves as a ligand in the export of toxic metal complexes (Ravichandran, 2004; Senesi, Xing, & Huang, 2009). Increases in DOC concentrations or fluxes may indicate increased (a) carbon losses from the terrestrial environment, delivered via surface or groundwater flow paths, thus reducing potential terrestrial carbon sequestration (Aufdenkampe et al., 2011; Cole et al., 2007), (b) *in situ* photosynthetic production, in response to changing flow rates (Power et al., 1988), nutrients

(Dodds, 2006) and light (Young & Huryn, 1996) availability, or (c) influence of wastewater treatment plant effluent (Griffith, Barnes, & Raymond, 2009).

Increases in lake and river DOC concentrations have been widely reported from the United Kingdom, Europe, and the eastern USA and Canada over the past three decades. These studies have linked trends to specific drivers, with a heavy focus on the decline in atmospheric sulfate deposition (Burns, McHale, Driscoll, & Roy, 2006; Dawson, Malcolm, Middlemas, Tetzlaff, & Soulsby, 2009; De Wit, Mulder, Hindar, & Hole, 2007; Evans, Chapman, Clark, Monteith, & Cresser, 2006; Halliday et al., 2012; Monteith et al., 2007). Hydroclimatic factors leading to increased DOC concentrations and fluxes in freshwater systems include increased air temperatures (Evans et al., 2006; Laudon et al., 2013), increased streamflow (Erlandsson et al., 2008; Sarkkola et al., 2009), and drought (Lepistö, Futter, & Kortelainen, 2014; Pärn & Mander, 2012; Worrall, Burt, & Adamson, 2006). Land management has also been implicated in DOC increases (Chen & Driscoll, 2009; Clutterbuck & Yallop, 2010; Evans et al., 2007; Worrall et al., 2006). Although many studies have documented positive trends, a number of other studies have also reported insignificant trends or significant decreases in both DOC concentration and flux (Apsite & Klavins, 1998; Arvola, Räike, Kortelainen, & Järvinen, 2004; Clair, Dennis, Vet, & Laudon, 2008; Fahey et al., 2005; Jennings et al., 2010; Navrátil, Norton, Fernandez, & Nelson, 2010; Räike, Kortelainen, Mattsson, & Thomas, 2012; Rodríguez-Murillo, Zobrist, & Filella, 2015).

Several studies that reported increases in DOC have focused on smaller watersheds (<30 km^2) draining acid, organic-rich soils (Dawson et al., 2009; Evans et al., 2006; Halliday et al., 2012; Laudon et al., 2013; Sarkkola et al., 2009; Worrall et al., 2006), but the objective of this study was to test the hypothesis that changes in DOC concentrations and fluxes are also signals of climate or anthropogenic disturbances in large river systems. We tested our hypothesis in the Mississippi River Basin (MRB), where DOC represents 25% to 35% of total C export to the Gulf of Mexico (Stets & Striegl, 2012). We selected this basin because it is the largest watershed in North America (3.3×10^6 km^2), draining 41% of the land surface area of the conterminous USA (Benke & Cushing, 2005). The mainly north–south flow of the river across the continent traverses a considerable climate gradient, with the Upper Mississippi River extending from its headwaters at Lake Itasca in northern Minnesota to its confluence with the Missouri River. The Lower Mississippi River begins at the confluence with the Ohio River and extends to the outlet on the coast of the Gulf of Mexico (Benke & Cushing, 2005). Increases in upper MRB streamflow (regardless of attribution) have been documented at 100-year time scales (1890–2010) (Gupta, Kessler, Brown, & Zvomuya, 2015; Hirsch & Ryberg, 2012; Raymond, Oh, Turner, & Broussard, 2008; Ryberg, Lin, & Vecchia, 2014; Schilling, Chan, Liu, & Zhang, 2010), and recent results from a coupled hydrological–biogeochemical model show increases in DOC in the lower MRB between 1900 and 1980 as a result of changes in land management practices (Ren et al., 2016), with climate and extreme events such as droughts and floods explaining much of the interannual variability in carbon flux from the basin (Tian et al., 2015).

A challenge when interpreting temporal trends in water quality is the dependence of concentration and loads on year-to-year variability in streamflow (Eimers, Watmough, & Buttle, 2008). To address this issue, we used the weighted regressions on time, discharge, and season (WRTDS) (Hirsch, Moyer, & Archfield, 2010) model to produce flow-normalized (FN) DOC concentrations and fluxes. The time frame for reporting trends in this study spans 1997 through 2013, as publicly available DOC concentration data in the MRB were available from 1996 onward. Previous studies have combined the analyses of DOC quantity and quality to illuminate how changes in organic matter affect fundamental river processes (Dawson et al., 2009; Erlandsson et al., 2008). In this study, the quality metric was specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), an indicator of DOC aromaticity. We hypothesize that the application of WRTDS to document changes in both DOC and $SUVA_{254}$ over space and time will allow inferences related to sources, transport, and turnover of DOC throughout the MRB. Finally, we examine causative mechanisms for changes in DOC, including anthropogenic forcing factors such as climate, land-use, and acid deposition, to attribute potential DOC trend patterns among the sites.

2 | METHODS

2.1 | Data assimilation

The study included four main stem Mississippi River sites and five tributaries (Table 1, Figure 1). We also estimated fluxes from one distributary site on the Atchafalaya River, which receives 30% of the Mississippi River flow through Old River diversion structure. Full site names and abbreviations are shown in Table 1. All sites are a part of the U.S. Geological Survey (USGS) national fixed-site stream monitoring network (http://cida.usgs.gov/quality/rivers/about). Water quality variables included DOC mg L^{-1} (as C), sulfate mg L^{-1} (as SO_4^{2-}), and alkalinity mg L^{-1} (as $CaCO_3$). $SUVA_{254}$ was calculated as the absorbance coefficient a_{254} (cm^{-1}) divided by the DOC concentration multiplied by 100 and reported in units of L mg C^{-1} m^{-1}. We applied a regression equation to correct for artificially high absorbance values from iron interference: $Absorbance_{corrected} = Absorbance_{measured} - (0.0653*\text{iron concentration [mg } L^{-1}])*100$ (Poulin, Ryan, & Aiken, 2014). The mean number of water quality samples per year varied between 10 and 16 for each site and were obtained from the USGS National Water Information System database (http://waterdata.usgs.gov/nwis).

Water quality samples were analyzed at the National Water Quality Laboratory (NWQL, http://nwql.usgs.gov/). The analytical methods for DOC and $SUVA_{254}$ did not change during 1997–2013 (Brenton & Arnett, 1993). The NWQL switched the total organic carbon (TOC) analyzer in August 1999, from Dohrmann DC-180 (Dohrmann, Santa Clara, CA, USA) to a Tekmar Dohrmann Phoenix 8000, (Teledyne Tekmar, Mason, Ohio, USA) but an unpublished NWQL validation study verified that there were no significant differences in the results between the Phoenix 8000 and its predecessor (Duane Wydoski, Supervisory Chemist NWQL, personal communication, 8/15/2013). The analytical methods for the absorption coefficient at 254 nm, sulfate, alkalinity, and iron remained constant throughout the study period.

The water quality datasets were screened for extreme values. We removed any values that fell outside of the interval [Q1–3*IQR,

TABLE 1 Study site abbreviations, USGS site numbers, USGS site names, and drainage area

Site abbreviation	USGS site number	Site name	Drainage area10^3 km^2
MISS-CL	05420500	Mississippi River at Clinton, Iowa	222
IOWA-WAP	05465500	Iowa River at Wapello, Iowa	32
ILLI-VC	05586100	Illinois River at Valley City, Illinois	69
MISS-GR	05587455	Mississippi River below Grafton, Illinois	443
MEZZ-HE	06934500	Missouri River at Hermann, Missouri	1353
MISS-TH	07022000	Mississippi River at Thebes, Illinois	1847
OHIO-GRCH	03612500	Ohio River at Dam 53 near Grand Chain, Illinois	526
ARKA-LR	07263620	Arkansas River at David D Terry L&D below Little Rock, Arkansas	410
MISS-FR	07373420	Mississippi R near St. Francisville, Louisiana	2914
ATCH-MEL	07381495	Corps of Engineers (COE) Atchafalaya River at Melville, Louisiana	241

Note. USGS = U.S. Geological Survey.

Q3 + 3*IQR], where IQR is the interquartile range and Q1 and Q3 are the first and third quartiles, or the 25th and 75th percentiles (McDonald, Stets, Striegl, & Butman, 2013). This resulted in the removal of 64 DOC values, 45 $SUVA_{254}$ values, 2 sulfate values, and 4 alkalinity values so that final datasets contained 2,427 DOC; 1,497 $SUVA_{254}$; 2,652 sulfate; and 2,505 alkalinity values. No DOC samples were collected between 2002 and 2003 at Iowa River at Wapello, Iowa (IOWA-WAP) and 2002 and 2006 at Illinois River at Valley City, Illinois. Initial publications using WRTDS recommended at least 20 years of data with daily streamflow values and >200 samples per site (Hirsch et al., 2010), but more recent studies have successfully implemented the model using smaller calibration datasets (Corsi, De Cicco, Lutz, & Hirsch, 2015; Medalie, Hirsch, & Archfield, 2012). The threshold set for this study was 150 water quality samples over 15 years (Tables SI-1 to SI-4). $SUVA_{254}$ values were only available from 1999 to 2013, and three sites had too few samples for $SUVA_{254}$ trend analysis (IOWA-WAP, ILLI-VC, and Mississippi River below Grafton, Illinois (MISS-GR).

Streamflow (m^3 s^{-1}) values for all sites, except Mississippi River near Francisville, Louisiana (MISS-FR) and Corps of Engineers Atchafalaya River at Melville, Louisiana (ATCH-MEL), were obtained from National Water Information System. Streamflow data for the USGS MISS-FR and ATCH-MEL sites were obtained from the Army Corps of Engineers (http://www.mvn.usace.army.mil/). USGS streamflow is subject to a rigorous quality assurance/quality control (QA/QC) process, and each daily streamflow value is tagged with a qualifier indicating if the value has been approved. Approval indicates that actual streamflow measurements have been used to reevaluate the stage-discharge relationships and the estimated daily streamflow values over the course of the year. Over 99% of the approximately 55,000 streamflow values used in the trend analysis were qualified as approved. The other 0.3% were provisional, which indicates the data were subject to revision. The Army Corps of Engineers has a similar review process. For these reasons, an independent error analysis was not performed on discharge measurements. The range of all discharge

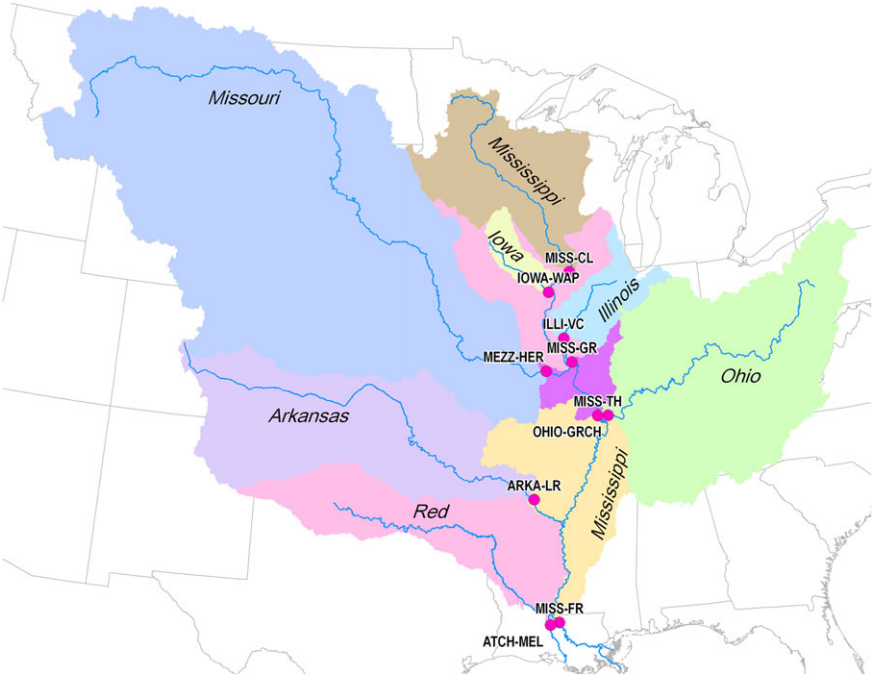

FIGURE 1 Location of the 10 study sites in the Mississippi River Basin

values compared to the range of discharge values during DOC sampling is represented in Figure SI-1.

Mean annual temperature and precipitation estimates for each watershed were derived from the parameter-elevation relationships on independent slopes datasets (Daly et al., 2008) (http://www.prism.oregonstate.edu/). Mean annual wet sulfate deposition (kg ha^{-1}) was derived from the National Atmospheric Deposition Program/ National Trends Network sites annual maps (http://nadp.sws.uiuc.edu/NTN/annualmapsByYear.aspx), which represent interpolations of about 100-point data sample locations within the MRB. Land cover was based on the National Water-Quality Assessment Program Wall-to-Wall Anthropogenic Land Use Trends dataset (hereafter referred to as the land-use dataset) (Falcone, 2015), which provides estimates of various land uses at 60-km resolution every 10 years, starting in 1974. The time period that best encompasses our water quality dataset were the decades spanning from 1992 to 2002 and 2002 to 2012. The six land use classes are aggregates of the 19 schemas used in the National Land Cover Database: *Water* class includes water and wetlands, the *Developed* class includes high and medium density residential, commercial, and transportation, and the *Semi-developed* class describes areas that are less built up than those of the *Developed* class, but have some of the same land uses. The *Production* class includes agriculture, mining, and timber activities, the *Conservation* class refers to protected lands, and the *Low-use* class describes area with no evidence of consistent human use.

Major sewage facilities information, including the number and flow rate, was included in the GAGES II database (Falcone, Carlisle, Wolock, & Meador, 2010). These data were derived from the U.S. Environmental Protection Agency's Permit Compliance System and Integrated Compliance Information System (https://www.epa.gov/enviro/geospatial-data-download-service). Soil order information was derived from the State Soil Geographic Database. Soil quality data was derived from the Soil Survey Geographic database (Soil Survey Staff, 2009), using methods similar to those in Bliss, Waltman, West, Neale, and Mehaffey (2014).

2.2 | Modeling and statistical analysis

The WRTDS model was used to estimate FN DOC concentrations and fluxes and changes in $SUVA_{254}$ values over time. WRTDS is implemented in the R package EGRET (Hirsch & De Cicco, 2015). Concentration was modeled as

$$\ln(c) = \beta_o + \beta_1 t + \beta_2 \ln(Q) + \beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t) + \varepsilon, \quad (1)$$

where ln is natural log, c is concentration, β_i are fitted coefficients, Q is daily mean streamflow, t is decimal time, and ε is the unexplained variation. Using WRTDS, we determined a unique set of coefficients for this equation at all points on a regular grid of Q and t values for the period of record. The coefficient weights were based on the distance in time, streamflow, and season between the data point and the location in Q, t space. This approach allowed the relationship between streamflow and concentration, as well as the seasonal pattern in this relationship, to gradually evolve over time.

The estimates from the WRTDS model were summarized into calendar years; 17 years of concentration and flux (DOC, sulfate, and alkalinity) results (1997 through 2013) and 15 years of $SUVA_{254}$ results (1999 through 2013). The model output also included a flux bias statistic, which is a dimensionless description of the sum of the estimated fluxes on all sampled days minus the sum of the true fluxes on all sampled days. A value near zero suggests that the model is nearly unbiased. We multiplied the bias statistic by 100 (Tables SI-1 to SI-4).

The bootstrap test for the model is available in EGRETci (Hirsch, Archfield, & De Cicco, 2015). The wBT function in this package enables the user to implement hypothesis tests for trends in FN concentration and fluxes and provide *p*-values and 95% confidence intervals for the magnitude of trends (Hirsch et al., 2015). We ran the bootstrapping function (wBT) for DOC, $SUVA_{254}$, sulfate, and alkalinity trend analyses using the following parameters: nboot = 100, bootbreak = 100, and blockLength = 200. A *p*-value < 0.02 in Table 2 should be interpreted as a strong evidence to reject the null hypothesis that there was no significant trend in DOC concentration or flux over time. In general, we interpret a p-value of < 0.001 from a statistical analyses as overwhelming evidence for rejecting the null hypothesis. In the case of the wBT, it would take an excessive amount of computer time to get a result like "p<0.001" because the function is computationally intensive. For example, running the MISS-CL DOC calibration data for 100 iterations provided a p-value of <0.02 for rejection of the null hypothesis that the FN DOC concentration trends is different than zero, but 200 iterations were needed to produce a p-value of <0.01. More detailed information about the implementation of the EGRETci package for this study can be found in the Supporting Information. The Mann–Kendall trend test was used to detect significant monotonic trends in mean annual wet atmospheric sulfate deposition and the minimum-, mean-, and maximum-annual discharge for 10 sites during 1997–2013.

3 | RESULTS

3.1 | DOC trends

FN DOC concentrations and fluxes increased significantly in the upper part of the MRB but not in the lower part during 1997–2013. Significant increases occurred at the main stem site Mississippi River at Clinton, Iowa (MISS-CL) and two tributaries (ILLI-VC and Missouri River at Hermann, Missouri), but there were no significant changes in FN DOC concentrations or fluxes at the other main stem sites (MISS-GR, MISS-TH, and MISS-FR), the other tributaries (IOWA-WAP, Ohio River at Dam 53 near Grand Chain, Illinois (OHIO-GRCH), and Arkansas River at David D Terry L&D below Little Rock, Arkansas), or the distributary site (ATCH-MEL) (Figure 2, Table 2).

Annual DOC concentration (Figure 2a, open circles) had more variability than the FN DOC concentration (lines), and we detected a subtle but coherent spatial pattern in the FN DOC concentrations for three of the upper basin sites. For example, MISS-CL, IOWA-WAP, and ILLI-VC FN concentrations increased from 1997 to 2007 but decreased from 2008 to 2013. FN DOC concentrations and fluxes are presented with 95% confidence intervals in parenthesis. FN DOC concentration for the time period 1997 to 2007 were 1.4 (1.1, 1.6)

TABLE 2 WRTDS model results for 10 sites in the MRB

Site Abbreviation	Mean streamflow $m^3 s^{-1}$	1997 FN DOC Conc mg C L^{-1}	FN DOC conc change mg C L^{-1}	*p*-value	1997 FN DOC Flux 10^6 kg yr^{-1}	FN DOC flux change 10^6 kg yr^{-1}	*p*-value	1997 FN DOC yields g C m^{-2} yr^{-1}	1999 FN $SUVA_{254}$ L mg^{-1} C m^{-1}	FN $SUVA_{254}$ change L mg^{-1} C m^{-1}	*p*-value
MISS-CL	1590 (340)	5.9	**1.1 (0.4, 1.8)**	**<.02**	312	**60 (21, 95)**	**<.02**	1.41	3.2	0.1 (−0.2, 0.4)	.58
IOWA-WAP	300 (130)	3.8	-0.1 (−0.6, 0.3)	.62	39	−3 (−8, 3)	.37	1.22	NA	NA	NA
ILLI-VC	710 (250)	4.5	**0.5 (0.1, 0.9)**	**<.02**	98	**17 (7, 28)**	**<.02**	1.42	NA	NA	NA
MISS-GR	3650 (1060)	5.6	0.3 (−0.3, 1.1)	.34	642	30 (−37, 131)	.42	1.45	NA	NA	NA
MEZZ-HE	2530 (910)	3.9	**0.5 (0.1, 0.8)**	**.02**	337	**41 (11, 72)**	**<.02**	0.25	2.0	**0.9 (0.6, 1.3)**	**<.02**
MISS-TH	6770 (2030)	4.8	0.3 (−0.2, 0.8)	.20	1067	51 (−63, 183)	.44	0.58	2.3	**0.9 (0.6, 1.2)**	**<.02**
OHIO-GRCH	8230 (1640)	2.8	0.2 (−0.05, 0.4)	.13	772	29 (−26, 79)	.35	1.47	2.8	0.0 (−0.1, 0.2)	.47
ARKA-LR	1280 (600)	4.1	0.3 (−0.2, 0.6)	.17	173	10 (−14, 31)	.36	0.42	2.8	0.1 (−0.3, 0.5)	.60
MISS-FR	14670 (2860)	3.7	0.0 (−0.2, 0.3)	.74	1753	-7 (−116, 128)	.96	0.60	2.6	**0.2 (0.1, 0.4)**	**<.02**
ATCH-MEL	6240 (1250)	3.7	0.0 (−0.1, 0.3)	.66	745	-5 (−37, 52)	.93	3.09	2.6	**0.2 (0.1, 0.4)**	**<.02**

WRTDS = weighted regressions on time, discharge, and season; MRB = Mississippi River Basin; FN DOC = flow normalized dissolved organic carbon; $SUVA_{254}$ = specific ultraviolet absorbance at 254 nm.

Mean streamflow (1 standard deviation), FN DOC concentration and flux values in 1997, estimated changes between 1997 and 2013 with 95% confidence intervals, and *p*-value associated with trend analysis. The final three columns show $SUVA_{254}$ values in 1999, estimated changes between 1999 and 2013, and *p*-values. *P*-values <.02 are indicated in bold and NA = not available.

mg·C·L^{-1} for MISS-CL, 0.07 (−0.3, 0.7) mg·C·L^{-1} for IOWA-WAP, and 0.7 (−0.2, 1.1) mg·C·L^{-1} for ILLI-VC. Changes in FN DOC concentrations for the time period 2008 to 2013 were −0.23 (−0.7, 0.2) mg·C·L^{-1} for MISS-CL, −0.13 (−0.5, 0.2) mg C L^{-1} for IOWA-WAP, and −0.1 (−0.6, 0.5) mg C L^{-1} for ILLI-VC. The initial increases in FN DOC concentrations at MISS-CL and ILLI-VC for the first 10 years of the record were large enough to produce an overall positive trend for the entire reporting period (1997 to 2013), despite decreases in the latter part of the record. The MISS-GR site, which integrated the surface waters from MISS-CL, IOWA-WAP, and ILLI-VIC, showed a similar FN DOC concentration pattern over time. FN concentrations increased by 0.2 (0.0, 0.7) mg C L^{-1} during 1997–2003 and then decreased by −0.1 (−0.3, 0.1) mg C L^{-1} during 2004–2007.

The MEZZ-HE site was the only MRB site having a significant monotonic increase in FN DOC concentration trend during 1997–2013; the estimated increase was 0.5 (0.1, 0.8) mg C L^{-1}. However, below the Missouri River's confluence with the main stem Mississippi, there were no significant changes in either FN DOC concentration or flux, even at the site immediately downstream from MEZZ-HE, the MISS-TH site (Figures 2a and 2b). There was no significant change in the river DOC export to the Gulf of Mexico during 1997–2013 either. The average DOC export value, which was approximated by summing the average FN DOC fluxes from the MISS-FR and ATCH-MEL, was 2.4 Tg C yr^{-1}. DOC fluxes normalized by land surface at the two most upstream sites on the main stem of the Mississippi River were twice those (1.4 and 1.5 g C m^2 yr^{-1}) at the two more downstream sites, which had yields of 0.6 g C m^2 yr^{-1} (Table 2, Figure 3).

3.2 | Concentration versus discharge relationship

The three panels in Figure 4 each represent 4 years of concentration-discharge results from the early, middle, and late periods of the annual trend analysis record: 1998–2001, 2005–2008, and 2010–2013. An imagined vertical line through the WRTDS contour plot (Figure 4) indicates how concentration varies with streamflow at a given point in time, while a horizontal line shows the variation in concentration throughout the year for a given streamflow. The MISS-CL results are highlighted here because this site had the most significant trends out of the 10 MRB sites. High flows in April and May at MISS-CL were driven by snowmelt, and from 1998 to 2001, the highest DOC concentrations (>8 mg L^{-1}) appeared near the tail end of peak streamflow, typically July, at discharges >2000 m^3 s^{-1}. By 2005, high DOC in the late spring and early summer was associated with all flows ranging from 800 to 3000 m^3 s^{-1}. By 2010, DOC concentrations at flows <1000 m^3 s^{-1} decreased slightly compared to 2005–2008, but the season of high DOC lengthened from spring all the way through the end of the fall.

3.3 | DOC aromaticity

Despite sizable and significant trends in FN DOC concentrations and fluxes at MISS-CL, we did not detect any significant change in FN $SUVA_{254}$ at that site, but it did have the highest $SUVA_{254}$ value (3.2 L mg^{-1} C m^{-1}) (Table 2). In contrast, significant increases in FN

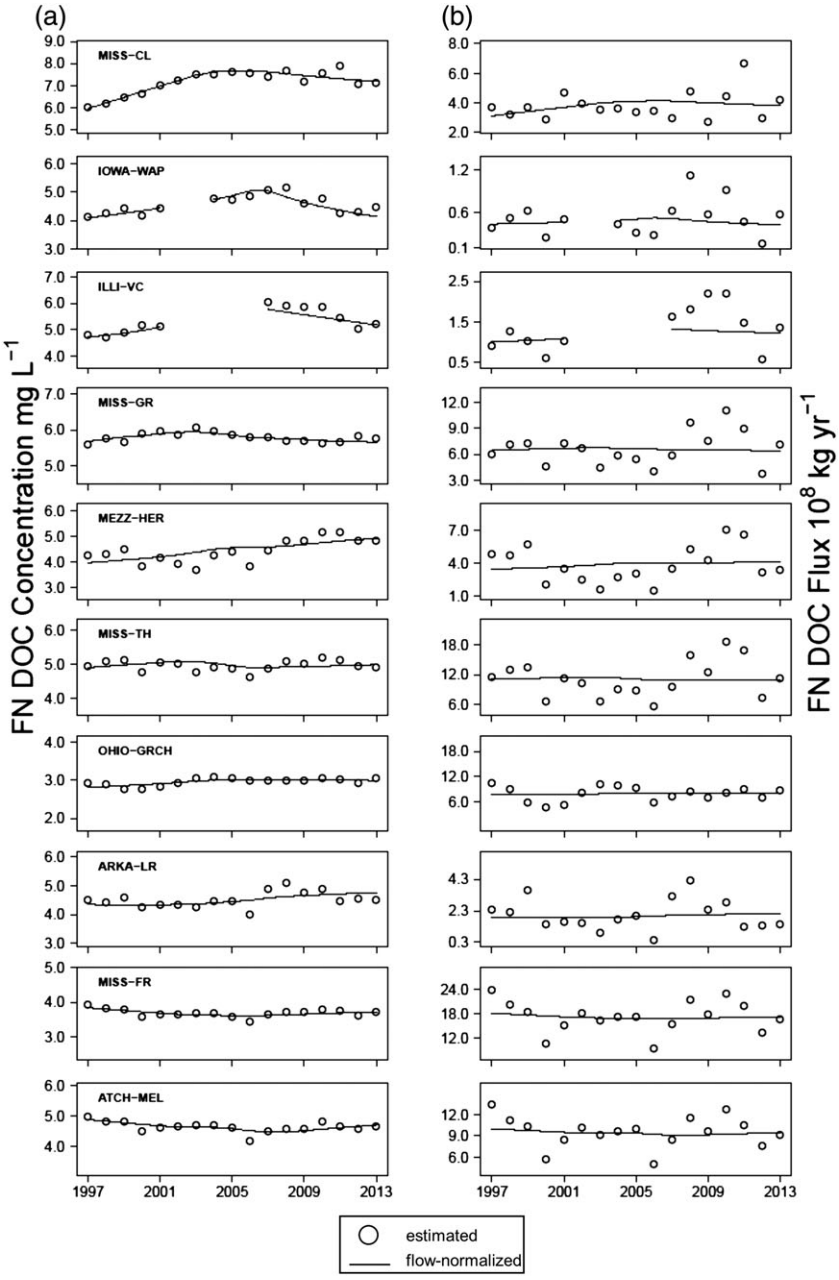

FIGURE 2 (a) Annual mean estimated and flow normalized dissolved organic carbon (FN DOC) concentration, and (b) total annual estimated and flow-normalized DOC flux from 1997 to 2013

DOC concentrations were coupled with significant increases in FN $SUVA_{254}$ at the MEZZ-HE site (Figure 3). Significant increases in $SUVA_{254}$ were evident at the lower basin site, MISS-TH, and the MISS-FR and MISS-MEL sites, although these were lower in magnitude.

3.4 | Drivers

Of the 30 streamflow trend tests conducted (minimum-, mean-, and maximum-annual discharge for 10 sites), only one, ARKA-LR annual minimum stream flow, showed a statistically significant trend at p 0.05 (Table 3). There were no significant changes in mean annual precipitation or temperature either (Table 3), and there was no significant correlation between mean annual precipitation versus FN concentrations and mean annual temperature versus FN concentration for any of the sites (Table SI-5).

The average annual atmospheric sulfate deposition rates significantly decreased for the basins associated with all 10 MRB sites during 1997–2013, with concurrent significant decreases in FN surface water sulfate concentrations for six of the 10 MRB sites (Table 4), but significant increases in surface water alkalinity occurred at only two sites. The relatively large reductions in atmospheric sulfate deposition and surface water FN sulfate concentrations coupled with smaller positive changes in FN alkalinity (Table 4) indicate that the MRB is well buffered.

Decadal changes in land-use from 1992 to 2002 and from 2002 to 2012 showed reductions in the Low Use category by 1.24 to 0.13%, except for ILLI-VC from 1992 to 2002, which showed a slight increase of 0.08%. Increases in *Semi-Developed* and *Developed* classes ranged between 0.01% to 1.26%, but the percent increase in the *Water* and *Conservation* classes was narrower and values fell between 0.0% and 0.03% (Table 5). *Production* both increased and decreased among the 10 basins included in the study, and the direction of

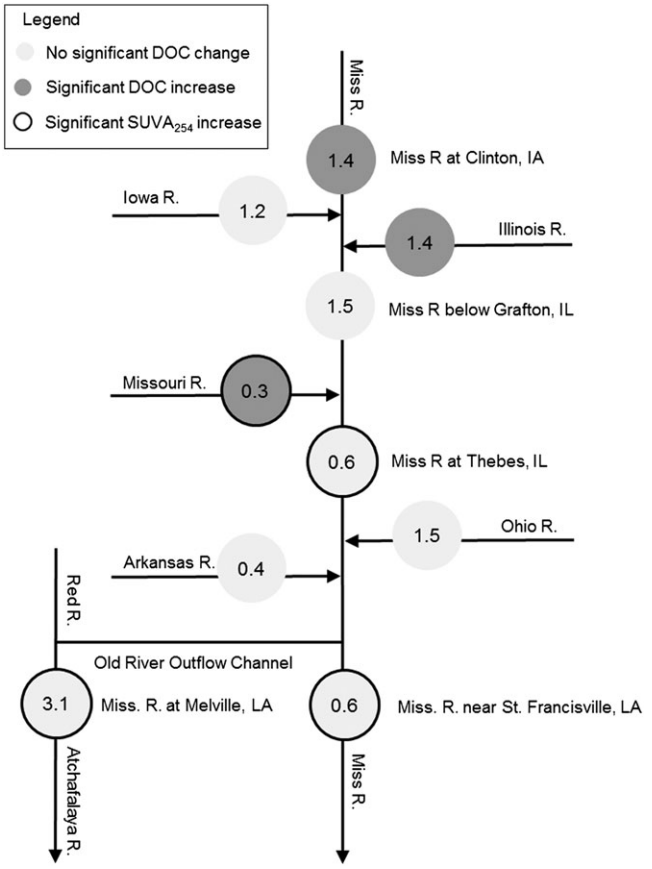

FIGURE 3 Dissolved organic carbon (DOC) yields (g C m2 yr-1) from 1997 and trends from 1997 through 2013 for main stream Mississippi River sites and major tributaries

change often varied for a particular basin during 1992 through 2002 as compared to 2002 through 2012. The MISS-CL site had the greatest increase in FN DOC concentration among the 10 study sites, and the basin showed a 1.04% reduction in *Low Use* during 1992–2002, with conversions to *Production* (0.55% increase), *Semi-developed* (0.33% increase), and *Developed* (0.16% increase). However, the MISS-CL sites had a decrease in *Production* from 2002 to 2012 (0.13%). In contrast, the Illinois River Basin, which also showed a significant increase in FN DOC concentration, showed decreases in *Production* for both time periods, and increases were mainly in the *Semi-developed* and *Developed* categories. The land-use change patterns for the MEZZ-HE basin provided yet another contrasting scenario. This basin, which had significant increases in both FN DOC concentrations and $SUVA_{254}$, showed a decrease in *Production* (0.3%) from 1992 to 2002, but an increase of 0.19% during 2002–2012, with increases in the *Semi-Developed* and *Developed* land-use categories of 0.07% and 0.08%, respectively. The highest rate of land-use change for the MEZZ-HE site occurred between 2002 and 2012, with a reduction of *Low Use* at a rate of 0.41%. The density and flow rates for sewage treatment facilities represent long-term totals, and the Illinois River Basin had the highest density and highest flow rates, while the Missouri River Basin had the lowest density and lowest flow rates (Table 6).

4 | DISCUSSION

4.1 | DOC fluxes and concentrations

Only three sites of the 10 study sites had significant increases in FN DOC concentrations and fluxes for the time period 1997 to 2013. The largest change occurred at MISS-CL, with an increase of 1.1 mg C L^{-1} over the 17-year time period, which translated to 0.07 mg C L^{-1} yr^{-1}. The 0.5 mg L^{-1} increase at ILLI-VC and MEZZ-HE was equivalent to 0.03 mg C L^{-1} yr^{-1}. This value was smaller than previously reported non-flow normalized DOC concentration increases of 0.2 and 0.58 mg C L^{-1} yr^{-1} (Clutterbuck & Yallop, 2010; Dawson et al., 2009; Hruška, Krám, McDowell, & Oulehle, 2009). Other studies in the United Kingdom, Czech Republic, and Finland reported increasing trends of DOC or proxies for DOC, such as chemical oxygen demand, but of a much lower magnitude, ranging from 0.06 to 0.11 mg C L^{-1} yr^{-1} (Neal, Robson, Neal, & Reynolds, 2005; Oulehle & Hruška, 2009; Sarkkola et al., 2009; Worrall & Burt, 2004). Trend studies in the eastern USA reported changes of 0 mg C L^{-1} yr^{-1} for a small catchment in Maine (Navrátil et al., 2010), 0.06 mg C L^{-1} yr^{-1} for two streams in the Adirondacks (Burns et al., 2006), and 0.22 mg C L^{-1} yr^{-1} for the Hudson River Basin (Findlay, 2005). Of these reported studies, only the results for the Adirondack streams were normalized for annual variability in flow conditions.

The smaller magnitude of change during 1997–2013 at MISS-GR (0.3 mg C L^{-1}) compared to MISS-CL (1.1 mg C L^{-1}) indicated that

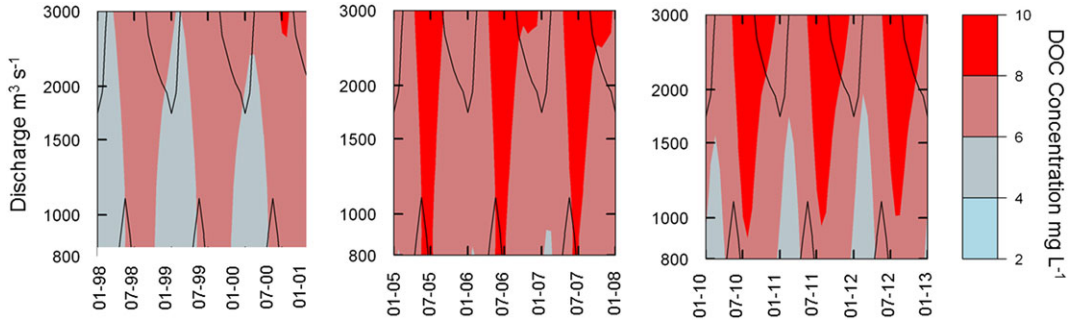

FIGURE 4 Contour plots of estimated MISS-CL dissolved organic carbon (DOC) concentration (mg L-1). Lower black line represents the 5th percentile of flow; upper black line represents the 95th percentile of flow. Three plots for the early, middle, and late periods of analysis by month and year

TABLE 3 Results of Mann–Kendall trend test on minimum-, mean-, and maximum-annual streamflow ($m^3\ s^{-1}$), mean annual precipitation (cm), and temperature (°C) for 1997 through 2013

Site	Annual minimum streamflow ($m^3\ s^{-1}$)	Mean annual streamflow ($m^3\ s^{-1}$)	Annual maximum streamflow ($m^3\ s^{-1}$)	Mean annual precipitation (cm)	Mean annual air temperature (°C)
MISS-CL	0.28 (0.09)	−0.08 (0.68)	−0.19 (0.27)	−0.09 (0.65).	0.09 (0.65)
IOWA-WAP	0.17 (0.33)	0.09 (0.63)	0.03 (0.89)	0.04 (0.84)·	0.03 (0.90)·
ILLI-VC	−0.17 (0.32)	0.14 (0.45)	0.03 (0.88)	0.31(0.09)	0.13 (0.48)
MISS-GR	−0.18 (0.28)	0.08 (0.68)	0.21 (0.21)	0.10 (0.59)	0.06 (0.77)
MEZZ-HE	−0.08 (0.65)	0.01 (1.0)	−0.02 (0.89)	0.10 (0.59)	0.00 (1.0)
MISS-TH	−0.05 (0.78)	0.08 (0.68)	0.11 (0.53)	0.10 (0.59)	0.00 (1.0)
OHIO-GRCH	−0.09 (0.60)	0.06 (0.77)	−0.16 (0.37)	−0.44 (0.59)	0.19 (0.30)
ARKA-LR	0.38 (0.03)	−0.22 (0.22)	−-0.02 (0.94)	−0.29 (0.84)	0.1 (0.59)
MISS-FR	0.11 (0.53)	−0.02 (0.89)	−0.09 (0.58)	-0.03 (0.11)·	0.00 (1.0)
ATCH-MEL	0.12 (0.46)	−0.11 (0.45)	−0.13 (0.45)	−0.19 (0.30)·	0.15 (0.43)

Note. The tau value is presented, and the associated *p*-value is in parentheses.

upstream DOC may be processed along the intervening river reach by mineralization, adsorption, or photolysis (Creed et al., 2015). However, it is also important to consider that there was a 40% increase in streamflow between the three upstream sites and MISS-GR, and this site integrated fluxes from smaller tributaries for which the DOC trend patterns were unknown (Table 2). Because of this data gap, we could not determine if the smaller magnitude of change in the main stem MISS-GR site reflected nonconservative transport between the upstream study sites and MISS-GR, or conservative mixing of significant increases from our upstream study sites (MISS-CL and ILLI-VC) with insignificant increases from the intervening tributaries.

Approximately 40% of the streamflow for MISS-TH comes from MEZZ-HE. The MISS-TH site, which reflected the mixing of MISS-GR (no trend) and MEZZ-HE (positive trend) water, did not show a significant change in FN DOC export. Estimated fluxes (circles) showed large oscillations in the lower basin, but the FN results were characterized by limited variability and indicated insignificant DOC trends over time (lines) (Figure 2b, Table 2). The MISS-TH site represented about 45% of the streamflow to the MISS-FR site. The MISS-TH site, along with the OHIO-GRCH and the ARKA-LR tributaries, did not show significant changes in FN DOC concentrations or fluxes. Therefore, it was not surprising that the MISS-FR site, which integrated waters from MISS-TH, OHIO-GRCH, and ARKA-LR, did not show significant FN DOC changes.

Freshwater DOC export can impact nutrient loads and food web dynamics in adjacent aquatic ecosystems, including coastal wetlands and estuaries (Bianchi, 2011). Our study indicated no significant change in river DOC export to the Gulf of Mexico from 1997 to 2013. The average DOC export value, approximated by summing the average FN DOC fluxes from the MISS-FR and ATCH-MEL, was 2.4 $Tg\ yr^{-1}$. The dominant signal for the FN DOC fluxes in the main stem MISS-FR site, which is channelized with artificial levees and has little contact with adjacent floodplains (Shen, Fichot, & Benner, 2012), was likely the upstream main stem DOC fluxes from MISS-TH with smaller intervening tributaries (Cai, Guo, Wang, & Aiken, 2015; Duan et al., 2007) exerting less influence (Aiken, Spencer, Striegl, Schuster, & Raymond, 2014). The MISS-TH, OHIO-GRCH, and ARKA-LR sites accounted for approximately 75–85% of the streamflow and DOC

TABLE 4 Results of Mann–Kendall trend test on atmospheric sulfate deposition rates and WRTDS results of surface water FN sulfate concentrations and surface water FN alkalinity concentrations for the time period 1997 through 2013

Site	Sulfate deposition in 1997 kg ha^{-1}	Tau annual sulfate deposition	FN sulfate conc in 1997 mg L^{-1}	FN sulfate conc change mg L^{-1}	*p*-value	FN alk conc in 1997 mg L^{-1}	FN alk conc change mg L^{-1}	*p*-value
MISS-CL	7.6	−.70*	25.5	−0.3 (−5.6, 3.3)	.91	150	−6.6 (−32.0, 0.9)	.36
IOWA-WAP	10.2	−.67*	37.1	−4.3 (−6.1, −1.9)	<.02	161	16.7 (7.6, 29.2)	<.02
ILLI-VC	16.2	−.72*	67.0	−7.3 (−12.4, −0.8)	<.02	182	8.1 (−8.6, 22.4)	.23
MISS-GR	10.2	−.76*	34.8	−2.1 (−5.4, 0.1)	.07	156	0.8 (−10.3, 12.6)	.74
MEZZ-HE	4.2	−.62*	180	−27.2 (−56.2, −5.1)	<.02	167	−6.7 (−19.7, 3.8)	.20
MISS-TH	6.0	−.71*	90.6	−8.5 (−20.6, 0.7)	.13	155	−2.4 (−15.7, 7.2)	.60
OHIO-GRCH	22	−.81*	37.0	0.4 (−2.9, 5.0)	.72	75	7.1 (2.3, 9.3)	<.02
ARKA-LR	8.0	−.76*	66.2	−27.1 (−35.1, −10.4)	<.02	90	3.7 (−18.3, 25.6)	.55
MISS-FR	9.8	−.83*	54.1	−7.8 (−14.0, −1.6)	<.02	110	0.26 (−4.1, 4.1)	.94
ATCH-MEL	14	−.66*	50.8	−9.3 (−18.0, −4.2)	<.02	93	5.4 (−14.6, 14.6)	.36

Note. WRTDS = weighted regressions on time, discharge, and season; FN = flow-normalized.

*indicates a *p*-value <.0001.

TABLE 5 Decadal percent change in land-use from the NWALT dataset, 1992–2002 and 2002–2012

Site	Year	Water	Developed	Semi-developed	Production	Low use	Conservation
MISS-CL	1992–2002	0.00	0.16	0.33	0.55	−1.04	0.00
	2002–2012	0.03	0.27	0.25	−0.13	−0.43	0.00
IOWA-WAP	1992–2002	0.00	0.17	0.13	0.08	−0.39	0.00
	2002–2012	0.00	0.26	0.01	0.11	−0.39	0.00
ILLI-VC	1992–2002	0.00	0.79	0.16	−1.09	0.08	0.06
	2002–2012	0.03	0.98	0.16	−0.69	−0.48	0.00
MISS-GR	1992–2002	0.00	0.28	0.21	0.03	−0.53	0.01
	2002–2012	0.02	0.41	0.20	−0.24	−0.38	0.00
MEZZ-HE	1992–2002	0.00	0.07	0.06	−0.03	−0.13	0.03
	2002–2012	0.01	0.08	0.07	0.19	−0.41	0.06
MISS-TH	1992–2002	0.00	0.12	0.12	−0.01	−0.26	0.02
	2002–2012	0.01	0.17	0.11	0.08	−0.41	0.04
OHIO-GRCH	1992–2002	0.00	0.36	1.26	−0.40	−1.24	0.01
	2002–2012	0.00	0.38	0.80	−0.12	−1.10	0.03
ARKA-LR	1992–2002	0.00	0.13	0.12	0.23	−0.64	0.16
	2002–2012	0.00	0.17	0.24	0.13	−0.56	0.02
MISS-FR	1992–2002	0.00	0.17	0.34	−0.08	−0.47	0.04
	2002–2012	0.01	0.21	0.26	0.03	−0.55	0.03
MISS-MEL	1992–2002	0.01	0.08	0.21	0.35	−0.65	0.00
	2002–2012	0.01	0.13	0.11	0.06	−0.31	0.00

Note. The sum of each row is zero

NWALT = National Water-Quality Assessment Program Wall-to-Wall Anthropogenic Land Use Trends.

TABLE 6 Number and flow rate from major sewage treatment facilities normalized to watershed area

Site	Number of major sewage treatment facilities per10^4 km^2	Sum of flow rate for sewage treatment facilities10^6 m d^{-1}
MISS-CL	4	12
IOWA-WAP	8	7
ILLI-VC	20	159
MISS-GR	8	36
MEZZ-HE	1	4
MISS-TH	3	13
OHIO-GRCH	11	28
ARKA-LR	3	8
MISS-FR	4	15
ATCH-MEL	4	7

fluxfrom the MRB. River yields at the MISS-TH and MISS-FR sites were equal at 0.6 g C m^2 yr^{-1}, despite the inputs from the OHIO-GRCH (Figure 3). The distributary site (ATCH-MEL) had much higher carbon yields than MISS-FR (Table 2) because it included the influence of the Red and Atchafalaya Rivers, which are less channelized and likely reflected DOC inputs from adjacent floodplains (Shen et al., 2012).

4.2 | Concentration versus discharge relationships

The contour plot for the site with the largest DOC increase (MISS-CL) illustrated the dynamic nature of concentration as a function of streamflow over several annual cycles spanning a total of 17 years, an insight often absent from long-term trend analyses. Winter precipitation is dominated by snow at the MISS-CL site, and winter snow packs often accumulate on organic-rich soils. High flows in April and May at MISS-CL were driven by snowmelt, and from 1998 to 2001, the highest FN DOC concentrations (>8 mg L^{-1}) appeared near the end of peak streamflow in July. This concentration-discharge (C-Q) pattern has been associated with DOC transported from near-surface soil runoff or overland flow from near-stream peat lands, often during high precipitation events (Inamdar, Christopher, & Mitchell, 2004). By 2005, high FN DOC concentrations were associated with all flows ranging from 800 to 3000 m^3 s^{-1}. Additionally, the highest FN concentrations (10 mg L^{-1}) shifted to earlier in the season, late spring and early summer, during peak flows. The increases in FN DOC concentrations during this period indicated that DOC increases were not just related to either runoff or leaching events but to an increase in the available pool of DOC within the soil profile that was mobilized at all flows (Evans et al., 2006). By 2010, FN DOC concentrations decreased at flows between 800 and 1000 m^3 s^{-1}, while FN DOC concentrations were maintained at higher flows. If the DOC flux were controlled solely by surface runoff in these basins, the C-Q relationship would have been consistent over time. However, the C-Q relationship differed over both annual and seasonal cycles at the MISS-CL site, indicating a potential change in DOC source and/or hydrologic connectivity of terrestrial-aquatic environments (Evans et al., 2006). The IOWA-WAP and ILLI-VC sites also showed FN DOC increases prior to 2007, followed by FN DOC decreases for 2008–2013. This similarity in patterns for the three sites suggests that a driver or suite of drivers may have been influencing surface or groundwater DOC dynamics in the upper MRB.

4.3 | DOC aromaticity

Previous studies have reported river $SUVA_{254}$ values that ranged from 1.8 to 4.8 L mg^{-1} C m^{-1}, with the low end representing less aromatic authochthonous, microbial, or algal sources, and the high end representing more aromatic terrestrial organic matter sources (Spencer, Butler, & Aiken, 2012; Williams, Yamashita, Wilson, Jaffé, & Xenopoulos, 2010). In this study, MISS-CL had the highest $SUVA_{254}$ values (3.2 L mg^{-1} C m^{-1}, Table 2), which may reflect the influence of highly aromatic DOC compounds originating in hydric soils (Ågren et al., 2008), as 10% of this basin wetland area. Despite sizable and significant trends in FN DOC concentrations and fluxes at MISS-CL, no significant change in FN $SUVA_{254}$ was detected.

Both the MISS-CL and MEZZ-HE sites were situated downstream from reservoirs, and longer water residence times and an abundance of direct sunlight provide an environment favorable for in-stream production of DOC (Cai et al., 2015). Microbial-based DOM generally has lower $SUVA_{254}$ values, and the impact of this source on DOC composition was better reflected in a relatively low FN $SUVA_{254}$ value of 2.0 in 1999 at the MEZZ-HE site, rather than the 3.2 value at MISS-CL (Table 3). A low $SUVA_{254}$ value can also indicate loss of aromatic DOC, and the impoundment of water and exposure to intense solar radiation can lead to a reduction of $SUVA_{254}$ values for organic matter of either terrestrial or aquatic origin (Spencer et al., 2012).

From 1999 to 2013, we estimated a 0.9 (0.6, 1.3) L mg^{-1} C m^{-1} increase in FN $SUVA_{254}$ at the MEZZ-HE site. The presence of more fresh terrestrially-derived hydrophobic organic material would lead to a significant increase in FN $SUVA_{254}$. Another explanation for the increasing trend in FN $SUVA_{254}$ is a reduction in phytoplankton production, which could occur because of decreased water clarity resulting from increased terrestrial delivery of suspended sediments to surface waters (Bilotta & Brazier, 2008; Henley, Patterson, Neves, & Lemly, 2000). The increasing FN $SUVA_{254}$ signal was conserved within the lower basin, resulting in significant increasing trends at the MISS-TH, MISS-FR, and ATCH-MEL sites (Table 2). Significant increases in FN $SUVA_{254}$ were coupled with significant increases in FN DOC concentrations at the MEZZ-HE site (Figure 3). The combined shift in both DOC quantity and quality at the MEZZ-HE sites indicates a potential shift in DOC source between 1999 and 2013.

4.4 | Drivers

Despite ample evidence of increases in streamflow at a century scale time frame in the upper MRB (Gupta et al., 2015; Hirsch & Ryberg, 2012; Ryberg et al., 2014; Schilling et al., 2010), there were no significant shifts in precipitation or discharge in the MRB during 1997–2013. We estimated that average annual atmospheric sulfate deposition rates significantly decreased for the basins associated with all 10 MRB sites during 1997–2013, with concurrent significant decreases in FN sulfate concentrations for six of the 10 MRB sites (Table 4). The majority of previous studies relating the reduction in atmospheric sulfate deposition to surface water DOC concentration increases were conducted in small catchments underlain by acidic soils rich in organic matter with low buffering capacity (Evans et al., 2006; Hruška et al., 2009). High sulfate loading increased the acidity and ionic strength of drainage waters, which likely decreased organic matter mineralization rates and solubility in affected soils (Evans, Monteith, & Cooper, 2005; Kalbitz, Solinger, Park, Michalzik, & Matzner, 2000). Recent reductions in atmospheric sulfate deposition have accordingly been linked to increasing DOC solubility and export to surface waters (Erlandsson et al., 2008; Evans et al., 2006; Dawson et al., 2009; Hruška et al., 2009). Inherent differences in soil types between the MRB and previous DOC trend study sites was the most likely explanation for the overall lack of change in FN DOC concentrations in response to widespread reductions in atmospheric sulfate deposition throughout the MRB. The agricultural soils of this region are Mollisols and Alfisols (Falcone et al., 2010), and the high average cation exchange capacity (1,490 meq 100 g^{-1}) coupled with the insignificant trends in alkalinity at the majority of sites (Table 4) indicated that the MRB is well-buffered (Turner & Rabalais, 2003). Therefore, it was not surprising that our results did not provide strong evidence of changes in DOC solubility in response to the significant reductions in acid deposition throughout the basin.

There were consistent temporal changes in land use throughout the MRB. Erlandsson et al. (2008) reported land-use changes of 0.8% and 1.3% in Sweden that were characterized as small, but most likely having an impact on DOC export. The land-use dataset used in this study reported changes between −1.24% and +1.26% for the time period 1992 through 2012 (Table 5). These changes showed a conversion of land use from grasslands into agricultural production, a trend documented in other studies in the Northern Plains for the time period 2006 to 2011 (Johnston, 2013; Wright & Wimberly, 2013). This shift may have played a role in the MISS-CL basin, where the greatest FN DOC increases occurred during 1997–2002. Another consistent land-use change pattern was the conversion of grasslands or other low-use land categories into commercial or residential land use. Even though we found evidence of land-use change throughout the MRB, the impact on DOC quantity and quality was not clear, as significant trends were only found at three sites, and the patterns of the paired DOC and $SUVA_{254}$ trends were variable throughout the basin.

Other land-use factors, particularly in more developed areas of the basin, could also impact water quality in the MRB. For example, urban areas are often associated with high densities of wastewater treatment plants, and wastewater treatment effluent is known to have elevated DOC concentrations (Sickman, Zanoli, & Mann, 2007; Westerhoff & Anning, 2000). All sites in the MRB were likely impacted by wastewater effluent, but the ILLI-VC basin, with a high population density, >150 people km^2 (well above the national average of 31 people km^2) (Stets, Kelly, Broussard, Smith, & Crawford, 2012), also had the highest density of sewage treatment plants and the highest flow rate per unit area of all 10 basins. Increases in wastewater treatment flow due to increased development and may have played a role in the small increases in DOC found in the ILLI-VC, but we did not have an annual-scale time series dataset of land-use change and wastewater treatment flows to make a direct comparison.

Land management practices could also have impacted water quality in the MRB, but publicly available datasets of tillage or fertilization metrics are not currently available at the basin scale. The time frame of

this study overlapped with increased incentives for biofuel production in the conterminous USA and significant increases in conversion of conservation reserve program land to annual row-crop production (Gelfand et al., 2011; Secchi, Gassman, Jha, Kurkalova, & Kling, 2010). These events have been linked to increased soil erosion (Graham, Nelson, Sheehan, Perlack, & Wright, 2007; Robertson et al., 2008) and could explain increasing surface water DOC trends. Soil characteristics, particularly the carbon content, have a strong influence on DOC released to surface waters (Aitkenhead, Hope, & Billett, 1999; Dawson & Smith, 2007), and the significant increases in this study occurred in the basins which have some of the highest soil organic carbon content, between 14 and 20 g C m^{-2} (Bliss et al., 2014; Soil Survey Staff, 2009) of any soils in the conterminous USA (Sundquist et al., 2009). However, the interpretation of the impacts of agricultural land use on river DOC trends is further complicated by the fact that in the same time frame, plantings of genetically engineered crops also increased in the conterminous USA (Fernandez-Cornejo, Wechsler, Livingston, & Mitchell, 2014). The introduction of more genetically engineered crops, specifically herbicide resistant ones, has been linked to reduced tillage (Fernandez-Cornejo et al., 2014), therefore, potentially decreasing erosion and terrestrial carbon loading to rivers. All of these land-use and management factors could impact DOC loading to the MRB, particularly in the upper basin.

We did find evidence of anthropogenic forcing throughout the MRB (sulfate deposition, land-use change, and wastewater treatment effluent), but DOC values showed significant increases at only three of the 10 study sites over the 17-year study period. A recent study by Ren et al. (2016), based on a coupled hydrologic–biogeochemical model, also found insignificant trends for the lower MRB for the time period 1980 to 2010. However, when this same model was applied to a century-scale time frame of analysis (1901 through 2010), significant DOC export increases were found. One explanation for the results from both this and the Ren et al. study is that crop expansion from forest to agricultural lands peaked in the 1950s, and large amounts of DOC may have been be released during the initial cultivation, but organic matter stabilized under cultivation (Delprat, Chassin, Linères, & Jambert, 1997), so that the rate of soil DOC delivery to fluvial environments was unchanging or decreased.

Another possibility is that the surface water DOC response to anthropogenic influences was delayed because of long groundwater residence times, which have been estimated at 10 years for the Ohio River and 4 years for the Missouri River (Michel, 2004), and therefore, several decades may be required to clear the DOC from groundwater reservoirs (Hamilton, 2012). It is also possible that terrestrial DOC loading to rivers did increase between 1997 and 2013, but the DOC was mineralized and converted to CO_2 in shallow water tables or along deeper groundwater flow paths (Baker, Valett, & Dahm, 2000; McMahon & Chapelle, 2008), and therefore that signal was not reflected in surface water DOC concentrations or fluxes. Additionally, it is possible that increased DOC loading to streams could have occurred in headwater regions of the MRB, but the river DOC was subject to *in situ* mineralization or photo-degradation along the intervening river reach and lost to the atmosphere as CO_2 (Butman & Raymond, 2011; Obernosterer & Benner, 2004) and therefore that signal was not reflected in larger river network sites included in this study. Similarly, the mixing of various water sources throughout the river network could have diluted an elevated DOC headwater signal, thus reducing the variability of DOC (Creed et al., 2015).

5 | CONCLUSIONS

The magnitude of change in DOC concentrations and fluxes throughout the MRB was not large and only ranged between −3.5% to +18% and −0.1% to 19%, respectively. The largest DOC increase occurred at the MISS-CL site, and the changes in concentration-discharge patterns between 1997 and 2013 indicated that this may have been due to a shift in DOC sources. The annual DOC trend plots for the three upper basin sites, MISS-CL, IOWA-WAP, and ILLI-VC, were similar suggesting that some similar factor, or a suite of factors, may have been influencing DOC sources in this part of the basin. However, the total drainage area was large (222,000 km^2) and heterogeneous, making the identification of one causal mechanism for DOC increases difficult. We were able to dismiss climate and atmospheric sulfate deposition as possible drivers, but we did document a heavy presence of sewage treatment facilities and multiple land-use changes, specifically the conversion of low-use areas into agriculture or development. We posit that aside from the MISS-CL site, the DOC quantity trend signal throughout the basin was insignificant or weak because (a) the rate and type of anthropogenic forcing documented in this study did not induce any terrestrial or aquatic DOC responses, or (b) a response did occur, but because of DOC turnover in the terrestrial or aquatic environment, mixing of different source waters, or a lag-effect because of long groundwater residence times, the DOC trend signal was muted. The DOC quality trend patterns in the lower basin indicated another potential shift in DOC source, and the more highly aromatic DOC composition found at the MISS-TH, MISS-FR, and MISS-MEL sites later in the period of record likely originated in the Missouri River. The pattern in the lower basin highlighted the importance of upstream waters in structuring the DOC signal in the lower basin, and the most downstream site, MISS-FR, which had less connection to the adjacent landscape, was heavily influenced by upstream and tributary waters. These results contrast with those from smaller scale catchments, where surface waters have shown stronger DOC trends in response to the impacts of climate and land-use change that occur on the adjacent terrestrial landscape.

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