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*Non-linear multi-decadal trends in organic matter dynamics in Midwest reservoirs are a function of variable hydro-climate*

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Running Head: Reservoir organic matter trend & controls

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**Abstract**

Dissolved and particulate organic matter can influence biogeochemical processes in aquatic systems. An understanding, however, of the source, composition, and processes driving inland reservoir organic matter cycling at a regional scale over the long-term is currently unexplored. Here, we quantify decadal patterns (>20 years) of dissolved organic matter (DOM) quantity and composition and particulate organic matter (POM) in 40 reservoirs in the midcontinent USA. We built 184 Random Forest models to identify how the relative influence of watershed characteristics and limnological parameters on organic matter dynamics may vary over time and in synchrony with hydro-climatic anomalies. The reservoir organic matter quantity and composition varied non-monotonically through time and in contrast to lake browning observed in the northern hemisphere. Reservoir DOM composition switched from humic and aromatic during wet summers to aliphatic, potentially autochthonous DOM during particularly prolonged dry summers in the mid-2000s. The shift in reservoir DOM quantity and composition could be attributed to the change in time-varying control of watershed and limnological factors mediated by the hydro-climatic conditions. Watershed control (e.g., percent crops) was predominant during wet summers, while the effect of reservoir morphology (e.g., maximum depth) and water quality parameters (e.g., Secchi depth, Chlorophyll-*a*) were evident during dry summers. Thus, future predictions of drier conditions may promote "greening" with negative implications for reservoir water quality and treated drinking water. Considering the non-linear nature of reservoir organic matter dynamics and its controls will help to better mitigate water quality issues in these constructed systems increasingly impacted by global changes.

*1. Introduction*

Dissolved organic matter (DOM) is a complex mix of aromatic and aliphatic organic compounds originating from terrestrial or aquatic sources, with significant influence on aquatic biogeochemistry (Fellman et al. 2010). DOM serves as a source of nutrients, including carbon (C) and nitrogen (N) to the lakes; where an increased influx can trigger microbial respiration and increase greenhouse gas emissions from lakes (Sadro and Melack 2012), and may diminish in-lake primary productivity by limiting light (Lennon et al. 2013). The complex DOM molecules may also be photo-oxidized, and the resulting breakdown products can further serve as a nutrient source for algal growth and potentially advance toxin-producing cyanobacterial blooms (Orihel et al. 2017; Reinl et al. 2022). Similarly, particulate organic matter (POM), either transported from the watershed or produced autochthonously, can be remineralized and contribute to the aquatic C cycle (Piirsoo et al. 2018).

Dissolved and particulate organic matter cycling in freshwater lakes is sensitive to global climate change and anthropogenic activities (Tranvik et al. 2009; Williamson et al. 2015). Climate-induced increases in hydrological extremes, such as high precipitation events and droughts along with anthropogenic alteration of land cover can shift the balance between terrestrial and autochthonous DOM in inland systems with severe water quality implications (Solomon et al. 2015). For instance, the progressive humification or "browning" of lakes in the northern hemisphere has been attributed to the increasingly wetter climate and the associated loading of terrestrial DOM (Roulet and Moore 2006; De Wit et al. 2016). During droughts, a reduction in terrestrially derived DOM and POM into lakes is expected. In particular, in forested, snow-dominated lakes in Canada, Dillon and Molot (2005) observed a reduction in catchment derived DOM quantity, measured as dissolved organic carbon (DOC) during drier conditions. Additionally, Schindler et al. (1997) found that in Boreal lakes, droughts can promote in-lake processes, such as autochthonous DOC generation, and microbial and photo-degradation of terrestrial DOC, with subsequent water quality implications. Global precipitation intensity and droughts will likely become more severe in the future (Cook et al. 2014). Improved understanding of organic matter composition and quantity and the complex interacting factors influencing them is essential for effective management of inland resources. Such insight will inform global C cycling and water quality under projected climate extremes.

Reservoirs are ubiquitous and increasing globally (Zarfl et al. 2014), yet organic matter source, processing, and its influence on water quality in these constructed systems are understudied. Reservoirs are hotspots for processing large amounts of C, making them an integral part of the global C budget (Tranvik et al. 2009). Despite the importance of reservoirs on C cycling, few studies have investigated both organic matter composition and quantity in impounded water, as routine water quality monitoring efforts typically focus on organic matter quantity. However, optical property based measures of DOM composition, such as aromaticity and molecular weight can provide insights regarding DOM source, underlying driving processes, and water quality implications (Weishaar et al. 2003; Del Vecchio and Blough 2004). Among the few reservoir focused studies, Hestir et al. (2014) observed high variability in DOC concentration, DOM quantity and molecular weight across six reservoirs in SW Australia (Table 1). They alluded to the potential role of watershed characteristics in driving DOM variability. A recent study explored DOC and DOM quantity in inland waters across the land use gradient in

Minnesota, USA (Olmanson et al. 2020). Although Olmanson et al. (2020) do not discuss the DOM cycling in reservoirs specifically, they report higher DOC and DOM quantity in the lakes and reservoirs in the forested, northern regions of the state than in the agricultural, southern regions. Another study that compiled the optical characteristics of inland waters in Brazil, including six reservoirs, showed that reservoirs had low DOM concentrations due to low terrestrial inputs (da Silva et al. 2021). The above studies provide critical insights on reservoir DOM characteristics but are limited as they generally focus on a small number of reservoirs over a short duration (<2 years; Table 1). As such, these studies do not address variability in watershed and reservoir characteristics and hydro-climate on DOM dynamics over large spatio-temporal scales. The importance of watershed characteristics including land cover and morphology along with the hydro-climatic regime on DOM fluxes and within river DOM processing is well recognized in fluvial systems (Raymond and Saiers 2010; Bhattacharya and Osburn 2020, 2021). Similarly, an understanding of DOM dynamics over long temporal scales can establish baseline conditions, detect deviations from the baseline and associated trends, as shown by the long term C studies in other aquatic systems (Jaffé et al. 2008; Bhattacharya et al. 2016; Singh et al. 2016), and may help in effective water resource management. Thus, there remains a need to investigate the regional variability in reservoir DOM source, composition, and key drivers over multi-decadal scales.

Our work aims to investigate how spatial variability in watershed and limnological characteristics may interact with hydro-climatic conditions to affect organic matter composition and quantity in 40 reservoirs over two decades (1990-2016) in Missouri, USA. We assessed organic matter dynamics by analyzing DOM optical properties (via absorbance), and DOC and POM concentrations. Further, we used machine learning-based multivariate models to quantify the time-varying influence of watershed and lake-specific controls on DOM in reservoirs. The characterization of reservoir organic matter dynamics and its drivers at multi-decadal scales will be useful for developing effective management strategies for these inland systems undergoing global changes.

## *2. Methods*

### *2.1 Study sites*

We sampled 40 reservoirs across Missouri, USA (Fig. 1) through a long-term (1990–1992 and 1997–2016) water quality monitoring program. These reservoirs span the major land cover gradients in the state. Land cover is predominantly agricultural in the north and forested in the south. This statewide land cover pattern also leads to a gradient in reservoir trophic status (Jones et al. 2004, 2008, 2020; Petty et al. 2020).

Watershed delineation, estimation of hydrological flow path and % slope (Slope) were conducted with ArcInfo geographical information systems (ESRI. Enviromental Systems Research Institute. ARC/INFO version 7.1. Enviromental Systems Research Institute, Redlands 1997) using 1-m resolution aerial photography and 10-m resolution digital elevation data from 2010 created by the Missouri Resources Assessment Program. Reservoir watershed characteristics including land cover, % soil organic matter content (OM), permeability (Perm), and soil erodability (K) were based on 30-m imagery from the LANDSAT thematic mapper developed by the Missouri Resource Assessment Partnership (Jones et al. 2004, 2008). Major land cover classes were: cropland, forest, grassland, urban, and wetland (Fig. 1). For this study, we grouped the watersheds based on % land cover. Watersheds with >50 % crop, forest, or grassland were identified as "agricultural", "forested", and "grassland" watersheds, respectively. Watersheds with no predominant land cover (<50 %) were identified as "mixed" watersheds. Wetland (0–3%) and urban areas (0.1–6 %, except for three watersheds with 11–31 %) were minor contributions to land cover and were therefore not considered unique land cover groups (Fig. 1). Morphological data including reservoir volume (Vol), average runoff (Runoff), maximum depth (Depth), and the ratio between watershed and lake area ($W_{area}$:$L_{area}$) were obtained from Missouri Department of Natural Resources (MDNR, 1986; 2019). Changes in prominent land cover across the state of Missouri were also assessed using the National Land Cover Database (NLCD; Homer et al. 2007; Yang et al. 2018; See supporting information [SI] SI Table 1), which showed only ~2 % change in cropland, including pastures, from 2001–2016. No other land cover groups showed substantial changes (> 1 %) during this time period. Due to the relatively small change over time, land cover was treated as a static variable for all statistical analyses in this study. Finally, to assess broad-scale hydro-climatic patterns, the long-term record of summer Palmer Drought Severity Index (PDSI) from 1990–2016 were obtained for the four regions (NE, NW, SE, & SW) in Missouri (NOAA 2019). PDSI is prominently used for quantifying long-term droughts globally (Dai et al., 2018). The index utilizes estimates of soil moisture balance by integrating the antecedent and current temperature, precipitation, and evapo-transpiration anomalies. Positive PDSI values represent wet conditions and negative values represent droughts, where the greater absolute values indicate the severity of wet or dry conditions (Cook et al. 2014).

*2.2 Sampling and analysis*

Long-term trends in limnological parameters and organic matter composition and quantity were assessed on 40 reservoirs over the duration of 23 years (1990–1992 and 1997–2016). Reservoirs were sampled 3 or 4 times during summer (May–August) annually from 1990–2016, except during 1993–1996. Surface water temperature (temp) and Secchi disk depth (Secchi) were measured on each sampling occasion from an open water location directly in front of the dam. Temp was measured using YSI multi parameter sondes (models 50B [1990–2000], 85 [2000–2006], and 550A [2006–2016]) with accuracy of +/- 0.1–0.30 °C and resolution of 0.10 °C at <0.5 m lake depth. Surface water samples for all subsequent analyses were collected from the same location as temp and Secchi. Samples were collected immediately beneath the surface (~0.25 meter) to exclude neuston and surface film (http://limnology.missouri.edu/sops/index.html).

Water samples were stored on ice until reaching University of Missouri Limnology Laboratory. Whole water samples were refrigerated for less than 24 hours before partitioning for total nitrogen (TN), total phosphorus (TP), and turbidity analysis. The TN concentrations were measured on whole water samples using the persulfate oxidation method (APHA, 1985) and TP concentrations were measured on whole water samples using the ascorbic acid colorimetric method (APHA 1985). Samples for TN and TP were analyzed with a Spectronic Genysis 2 UV/VIS spectrophotometer with an accuracy of +/- 1 nm and precision of +/- 0.5 nm using a 5 cm quartz and glass cuvette, respectively. Turbidity was measured using the Hach 2100N Turbidimeter with an accuracy of +/- 2 % of reading with stray light from 0–10000 NTU and resolution of 0.01 NTU. Three replicates per sample were used for TN and TP analysis and two replicates per sample for turbidity analysis.

A subset of the water sample was filtered on the day of collection using a 1.2 $\mu$m glass fiber filter (GFF). Duplicate filters were analyzed for chlorophyll-*a* (corrected for degradation products; Chl-*a*) measured fluorometrically using USEPA Method 445.0 (Arar and Collins 1997), modified for heated ethanol extraction (Sartory and Grobbelar 1984) and a Turner Design 700 fluorometer with a detection limit of 0.3 µg $L^{-1}$. The filtrate was analyzed for dissolved organic carbon (DOC) concentrations and CDOM spectrophotometric measurements including absorbance at 440 nm ($a_{440}$) and specific visible absorbance by CDOM at 440 nm ($SVA_{440}$), respectively. The DOC analysis was conducted using the high temperature combustion method (APHA 5310 B, 1985) on a Shimadzu TOC-$V_{CPH}$ analyzer with a detection limit of 0.2 mg $L^{-1}$ of C. Prior to DOC analysis, filtrate was acidified (pH < 3) with 1 N $H_2SO_4$. The samples were air sparged for 7.5 minutes to ensure the removal of background dissolved inorganic C. The DOC values were an average of three injections with two replicates per sample. CDOM quantity and composition were assessed by spectrophotometric measurements. Absorbance at a given wavelength (λ) in nm was measured on a Genesys 2 spectrophotometer with a 5 cm quartz cuvette blanked on deionized water. Blank corrected Napeirian absorption coefficient $a_\lambda$ was calculated

$$a_\lambda = \frac{2.303 \times A_\lambda}{l}$$

where $A_\lambda$ is the blank corrected spectrophotometer absorbance at a wavelength and $l$ is the pathlength in meters (Kirk 1994). Decadic $SVA_{440}$ was then calculated as a ratio between absorbance at 440 nm and DOC concentration. The $a_{440}$ is a good indicator of CDOM quantity, often allochthonous and humic in nature (Helms et al. 2008). Higher $SVA_{440}$ has been shown to be an indicator for aromatic CDOM, whereas lower values indicate lower quantities of allochthonous and aliphatic CDOM (McKnight et al. 1997; Reche and Pace 2002). UV-absorbance at 254 nm ($a_{254}$) and SUVA at 254 nm ($SUVA_{254}$) were also calculated for all study reservoirs during 2005–2010 ($n$=900), using the methods described. Strong correlations of $a_{440}$ and $SVA_{440}$ with $a_{254}$ and $SUVA_{254}$, respectively ($r$=0.93; $p$<0.001; SI Fig. 1) showed that $a_{440}$ and $SVA_{440}$ can be good indicators of CDOM quantity and composition for our study.

We also measured particulate organic matter (POM) concentrations, which is typically an indicator of fresh, autochthonous organic particulates (Jones et al. 2008). POM concentrations are reported as the difference in weight between total suspended solids (TSS) and particulate inorganic matter (PIM). TSS concentrations were determined by filtering a known volume of surface water through 1.5µm Whatman 934-AH GFFs that were pre-rinsed with de-ionized water, dried (105 °C), ashed (550 °C), and tared (APHA, 1985). PIM concentrations were determined by weighing material on the filter paper before and after ashing for TSS.

### *2.3 Statistical analyses*

To identify the major factors influencing organic matter quantity ($a_{440}$, DOC), composition ($SVA_{440}$) and POM concentrations were compared to a) limnological parameters, including TN, TP, Chl-*a*, turbidity, Secchi, and Temp; and b) watershed and lake morphometric characteristics, including % land cover, $W_{area}$:$L_{area}$, Vol, Depth, OM, K, average run-off, and Slope, and 3) hydro-climate patterns utilizing the long-term record of Palmer Drought Severity Index (PDSI) for the four regions (NE, NW, SE, and SW) in Missouri (NOAA 2019).

Random Forest modeling, a machine learning technique (Breiman 2001) was used to rank the relative importance of watershed and lake morphometric characteristics annually from 1990–1992 and 1997–2016. Although linear regression-based approaches have been used effectively to understand the relationship between explanatory and response variables, some limitations remain such as collinearity, outlier sensitivity, and data normality (Cutler et al. 2007). A nonparametric modeling approach, such as Random Forest models accounts for these limitations (Breiman, 2001). Random Forest models are also suitable for a large number of predictors and address the uncertainty in model selection because variable selections are based on the agreement of several model runs. Our approach resulted in 184 Random Forest models; each model was then run 25 times, and the model with the highest variance explained was used to compute the variable importance rankings (Singh et al. 2018). The importance of each explanatory variable was assessed by permuting variables one at a time against all the other variables and recording the mean square errors (MSE). A greater increase in percent MSE indicated greater importance of the permuted variable. Only those variables that tiered in the top 5 in importance rankings with a frequency greater than or equal to 5 were selected as important (Singh et al. 2018). Random Forest modeling was conducted with “randomForest 4.6-12” package (Liaw and Wiener 2002).

Principal component analysis (PCA), an ordination method, was used as a complementary way to visualize the temporal relationship between organic matter composition and quantity, with PDSI and only the important limnological and watershed characteristics that were selected by Random Forest models. Annual summer averages for each year (*n*=23) were calculated for every parameter and normalized, scaled and centered for the PCA. The PCA was interpreted using the bi-plot, where the first PCA axis explains the main direction of variation in the data; whereas the second axis explains the variables which are completely uncorrelated with the first axis (ter Braak, 1994). The vectors of environmental variables are represented as arrows on the PCA bi-plot. The vectors with longest arrows and smallest angles to the first or second PCA axis are more strongly correlated and therefore, have greater weight in determination of each axis (ter Braak, 1994). The PCA was conducted using the “vegan 2.3−1” package (Oksanen, 2015). Two-way analysis of variance (ANOVA) was also conducted on annual averages for each year (*n*=23) to test significant differences in organic matter quantity and composition, and limnological parameters with land cover groups and wet and dry summers based on PDSI. A nonparametric Mann-Kendall trend test (Mann 1945; Kendall 1975) was then used to test for the presence of trends in the response variables. If a trend was present, the change per unit time (true slope) was estimated using Sen’s slope analysis (Sen 1968). Mann-Kendall and Sen’s slope test were conducted using “trend 1.1.1” package (Pohlert 2018). Changepoint analysis was conducted to test the presence of a prominent shift in organic matter dynamics using the “changepoint 2.2.2” package (Killick and Eckley 2014). The Akaike information criterion (AIC) was used as the penalty criteria to identify any significant changes in mean and variance in the DOM quantity, composition, and POM concentrations. All statistical analyses were conducted in R statistical software.

## *3. Results*

### *3.1 Spatial patterns in watershed characteristics, limnological parameters, and organic matter quantity and composition*

Watershed and lake morphological characteristics, as well as limnological parameters varied across the 40 sampled reservoirs (SI Table 2). The average runoff, permeability, $W_{area}$:$L_{area}$, and Slope decreased from forested, grassland, mixed, and agricultural watersheds. In contrast, soil erodability (K) and soil organic matter content (OM) were highest in agricultural and lowest in forested watersheds (SI Table 2). Forested reservoirs (average maximum depth=9.9 m, SD=8.6) were about twice as deep as agricultural reservoirs (average maximum depth=4.7 m, SD=2.0). Lake volumes also varied 14 fold from forested reservoirs (average Vol= 4.0E+07 $m^3$, SD=8.0E+07) to mixed land cover (average Vol=7.0E+08 $m^3$, SD=1.9E+09; SI Table 2). The average values of TN, TP, and Chl-*a* were 3 times greater in the agricultural reservoirs than in forested reservoirs (SI Table 2). Average turbidity was 4–5 times greater in agricultural reservoirs (6.7 NTU, SD=11.3) than in forested (1.7 NTU, SD=3.1) and grassland (1.3 NTU, SD=1.9) reservoirs. Subsequently, the average Secchi was about 2.5 times deeper in forested reservoirs (2.1 m, SD=0.94) than agricultural reservoirs (0.9 m, SD=0.19; SI Table 2).

The organic matter quantity and composition, including average $a_{440}$, $SVA_{440}$, DOC, and POM concentrations, varied significantly with land cover ($p$ <0.05; SI Table 3). The greatest values were observed in agricultural reservoirs, followed by mixed, with forested and grassland reservoirs having the lowest values (SI Table 2). DOC and POM concentrations varied by ~1–1.5 times between agricultural reservoirs and both forested and grassland reservoirs (SI Table 2). The $a_{440}$ values were more variable, average $a_{440}$ was 3–4 times greater in agricultural than forested and grassland reservoirs. Similarly, the average $SVA_{440}$ was almost 2 times greater in agricultural than forested and grassland reservoirs (SI Table 2).

*3.2 Temporal patterns in PDSI, limnological parameters and organic matter quantity and composition*

We used summer PDSI values for the 4 regions (NE, NW, SE, and SW) during each summer from 1990–2016 to assess the influence of wet versus dry summers (Fig. 2A). The PDSI patterns indicated that 1990–1999 summers were relatively wet, with the exception of drier conditions in 1991, 1992, and 1996 (Fig. 2 A). Summers of 2000–2007 were predominantly dry, with exceptional droughts observed in 2000, 2003, and 2006 interjected by wet summers in 2001, 2002, and 2004. The next long-duration wet period was 2008–2016. These wet summers were interspersed by droughts in 2012 and 2014 (Fig. 2 A). Temporal changes in most limnological parameters varied with PDSI, with significant differences between wet and dry summers ($p$< 0.05; SI Table 3). Average turbidity ranged between 1.2–7.3 NTU across years, where average values were about 3–4 times larger during wet summers than dry summers. Average TN varied between 600 to 800 $\mu g\ L^{-1}$ and TP between 33 to 52 $\mu g\ L^{-1}$. In wet summers, average TN and TP concentrations were about twice that of dry summers. Average Secchi ranged between 1.3–1.8 m and depths were significantly deeper during dry compared to wet summers ($p$< 0.001; SI Table 3). Average Chl-*a* concentrations varied between 11.4 to 30.4 $\mu g\ L^{-1}$, although significant differences were not observed between wet and dry years, higher values were observed during droughts in the mid-2000s. Average surface water Temp measured in these survey collections did not vary significantly among years and ranged from 23.5–28.5 °C.

The average $a_{440}$ ranged between 1.43–5.62 $m^{-1}$, with 4 times greater averages during wet summers than values observed during droughts (Fig. 2 A; Fig.1 B; SI Table 3). Although no significant increasing or decreasing trend over time was observed for $a_{440}$ ($\tau$=-0.083, Sen's slope= -0.007, $p$> 0.05), multiple changepoint analyses showed $a_{440}$ was statistically lower during the dry summers (Fig. 2 A; SI Table 3-4). Similar changes in $a_{440}$ values were seen across all reservoirs. For example, average $a_{440}$ values in an agricultural reservoir were twice that of a forested reservoir, and the difference in $a_{440}$ variability between wet and dry summers was apparent (SI Fig. 2). Average $SVA_{440}$ varied between 0.1–0.4 $m^{-1}$ L $mg^{-1}$ (Fig 2 C), where the lowest averages were observed during the prolonged dry summers of 2003–2007, and later in 2012 and 2014 (Fig. 2 C). Highest average values were observed during the wet summers of 1999 and 2010 (Fig. 2 C). No significant increasing nor decreasing trend was identified in $SVA_{440}$ values ($\tau$=-0.183, Sen's slope= -0.007, $p > 0.05$), but changepoints were observed in 2004 and 2007. These temporal patterns in $SVA_{440}$ were consistent with the PDSI (Fig. 2 A). ANOVA indicated that average $SVA_{440}$ values were significantly different ($p < 0.001$; SI Table 3) in wet summers (0.2 $m^{-1}$ L $mg^{-1}$), with values about twice that of dry summers (0.1 $m^{-1}$ L $mg^{-1}$). Average DOC varied temporally between 4.2–6.9 mg $L^{-1}$ (Fig. 2 D). No prominent monotonic trend ($\tau$=0.20, Sen's slope= 0.086, $p > 0.05$) was observed for DOC, and a changepoint was observed in 2007 (Fig. 2 D). Significant differences in DOC were also observed during wet and dry summers (SI Table 3). Further, temporal patterns in average POM concentrations varied from 2.7–4.38 mg $L^{-1}$ with two significantly distinct changepoints in 2003 and 2007 (Fig. 2 E).

### *3.3 Limnological and watershed controls on inter-annual variability in organic matter quantity and composition*

Random Forest models indicated that 45–95 % of variance in $a_{440}$ was explained by limnological parameters. The $a_{440}$ variance explained by watershed characteristics ranged from 40–82 % (SI Fig. 3 A). Turbidity, Secchi, TN, TP, and Chl-*a* were ranked as important; however, their relative importance varied across years. Temp had less than 5 % frequency of occurrence and thus was not considered important. Turbidity ranked most important almost every summer, approximately 96 % of the time, except in 2004 when TN ranked highest. Secchi and TP were generally second- and third- ranked in variable importance. The importance of Secchi, however, decreased with a subsequent increase in importance for TN during the dry summers between 2003–2007. Chl-*a* ranked as the fifth most important variable most summers, except during droughts, when Chl-*a* was of greater importance (third or fourth in ranking, Fig. 3 A-B).

Among the watershed characteristics including 4 land cover groups (SI Table 2), soil erodibility (K), % agriculture, $W_{area}$:$L_{area}$, Depth, and % forest primarily explained temporal patterns in $a_{440}$ (Fig. 3 G-H). Soil erodibility (K) was most important ~60 % of the time (Fig. 3 G-H), and % agriculture ranked as most important 25 % of the time and second ~40 % of the time. These two variables ranked as first and second during wet summers and ranked fourth and fifth during the dry summers of 2003–2007 and relatively dry summers of 2012 and 2014. Consequently, the relative importance of Depth and $W_{area}$:$L_{area}$ increased to 1$^{st}$ and 2$^{nd}$ ranked in variable importance during dry summers, particularly in mid-2000s. The % forested land cover was usually ranked fourth or fifth in terms of variable importance 25 and 50 % of the time. Variables with less than 5 % frequency of occurrence were not included.

Temporal variability in $SVA_{440}$ was explained more by limnological parameters (27–93 %) than watershed characteristics (23–66 %; SI Fig. 3 B). Among limnological parameters, turbidity was the most important variable, followed by Secchi, TP, TN, and Chl-*a* (Fig. 3 C-D). Turbidity was the most important variable every summer with the exception of 2016. Secchi was the second ~80 % of the time, except during 2005–2007 when TP, TN, and Chl-*a* were ranked as second and third (Fig. 3 D). Among the watershed variables, K, % forest, % agriculture, Depth, and $W_{area}$:$L_{area}$ were most important influencing $SVA_{440}$ (Fig. 3 I-J). During wet summers in 1997–2002 and from 2008–2016, K and land cover, particularly % agriculture were the most important variables (Fig. 3 I). During dry summers (2003–2007), % forest, Depth, and $W_{area}$:$L_{area}$ increased in importance and were ranked in the top three important variables. During the drought of 2012, Depth and $W_{area}$:$L_{area}$ were ranked first and second in importance.

Temporal variability in DOC concentration was explained more by watershed characteristics (50 – 93 %) than limnological parameters (36 – 76 %; SI Fig. 3 C). Among the limnological variables, TN was top ranked 90 % of the times followed by TP, which was ranked second most important variable. Secchi and Turbidity were ranked as third and fourth important, followed by Chl-*a* which was ranked the fifth most important variable 70 % of the time except during the substantially dry years when it was ranked as fourth most important (Fig. 3 E-F). For watershed characteristics, K, and % agriculture were the most prominent watershed variables explaining the variability in DOC concentration, ~90 % of the time (Fig. 3 K-L). Third through fifth in variable importance were soil properties such as soil organic matter (OM) content, runoff, and permeability (Fig. 3 K-L).

Variability in POM concentration was explained more by limnological parameters (42–93 %) than watershed characteristics (64–82 %; SI Fig. 3 D). Among limnological parameters, Chl-*a* was always most important, followed by Secchi, TP, TN, and turbidity (Fig. 3 G-H). During the wet summers of 1992–1998, Secchi was ranked as fourth and fifth in importance, and TN and TP were typically ranked between second and third. During the drier mid-2000s summers, TP ranked as the second most important, followed by Secchi and TN. From 2007–2016, Secchi and TP were ranked second or third, followed by TN and turbidity. Turbidity was consistently ranked fifth ~82 % of time (Fig. 3 G-H). Watershed characteristics explained less variability in POM concentrations than limnological parameters (SI Fig. 3 D). As a result, several watershed variables that ranked within the top five had a low (<5 %) frequency of occurrence and were not listed. Among watershed characteristics, Depth, K, and % agriculture were identified as the most important variables, followed by soil organic matter (OM) and Vol (Fig. 3 O-P). Depth was most important ~90 % of the time, with the exception of a few substantially dry summers in the mid-2000s (Fig. 3 O-P). The % agriculture and K were usually ranked as the second and third, with a few exceptions. The soil organic matter (OM) and Vol were mostly low ranked and were not consistently ranked in the top 5 important variables across summers. For instance, Vol was ranked second and third in importance in the early 1990s and between 2009 and 2016.

### *3.4 Relationship between limnological parameters and dissolved organic matter composition and quantity with PDSI*

Principal Component Analysis (Fig. 4) showed that axes 1 and 2 explained ~ 53 % and 27 % of the variability, respectively. PDSI values were significantly ($p$< 0.0001) correlated with $a_{440}$ ($r$= 0.8), $SVA_{440}$ ($r$= 0.7), turbidity ($r$= 0.8), TN ($r$= 0.6), and TP ($r$= 0.8) with higher values associated with positive PDSI. Positive correlations of $a_{440}$ with $SVA_{440}$ ($r$= 0.9, $p$< 0.001) and DOC ($r$= 0.46, $p$< 0.001) showed similar terrestrial sources for these variables (Fig. 3). POM and Chl-*a* ($r$= 0.7) were significantly ($p$< 0.0001) correlated prominently during dry summers when Secchi depths were deeper. Sample points located on the right, lower quadrant of the PCA bi-plot (Fig. 3) represent the substantially dry summer years marked by low $a_{440}$, $SVA_{440}$, nutrients, turbidity, and deeper Secchi. Morphological parameters Depth, $W_{area}$:$L_{area}$, and Vol were located in the lower right quadrant and closer to samples from dry summer years. Wet summer samples were abundant in $a_{440}$, $SVA_{440}$, and DOC located closer to the vectors of PDSI, and watershed characteristics including agriculture, soil erodibility (K), and soil organic matter (OM). Significant differences in DOM quantity and composition and limnological parameters were also observed during wet and dry summers and with different land cover (SI Table 3).

*5. Discussion*

This is one of few studies to uniquely explore long-term (> 20 years) variation in reservoir organic matter composition and quantity and their relative controls in midcontinent reservoirs at a broad spatial scale in the United States (Table 1). The wide range (8–9 fold) in DOM quantity and composition represented the broad spatial-temporal heterogeneity across our study reservoirs (Table 1). Others report wide ranges in DOM composition, such as in the oligo- to hyper eutrophic lakes in Florida, USA, and across the lakes in Minnesota, Wisconsin, and Northern Michigan, USA (Table 1). The range in trophic gradients, however, did not always translate to the higher quantity or wide ranges in DOM quantity, most notably in the snow-dominated lakes in Northern and Eastern Canada and the tropical inland systems in Australia and Brazil (Table 1). These observations further emphasize the complexity and diversity of factors that may drive the DOM dynamics in inland systems.

Furthermore, the observed non-monotonic patterns in DOM quantity and composition in our study reservoirs contrasted with lake-focused studies in Europe and Northeast USA that report an increase in allochthonous DOM through time (Roulet and Moore 2006; Williamson et al. 2015). Instead, the abundance of terrestrial, humic, and aromatic DOM in reservoirs increased during wet summers (positive PDSI), observed more prominently during 1990–2002 and 2008–2016, but were interjected by significantly lower values during prolonged dry summers (negative PDSI) during 2003–2007. Further, using 184 Random Forest models, we highlight that relative influence of watershed and in-reservoir factors shift in response to PDSI variability. We show the role of watershed characteristics, particularly agricultural land cover and associated soil properties, on organic matter transport during the wet summers, and the influence of morphological features such as lake depth and $W_{area}$:$L_{area}$ on autochthonous organic matter production in dry years.

*5.1 Does wet-dry climate variation drive organic matter quantity and composition?*

Terrestrial DOM was distinctly more abundant in reservoirs during wet summers than during droughts. Greater amounts of $a_{440}$ and $SVA_{440}$ indicate the greater influx of humic and aromatic DOM to reservoirs during periods of increased runoff (Hansen et al. 2016). Similarly, greater abundance of DOC during the wet summers showed that DOM quantity also increases with increased runoff. Studies in riverine ecosystems have shown that high precipitation events or storms can lead to excessive transfer of DOM from watersheds to receiving waters (Raymond and Saiers 2010; Singh et al. 2016; Bhattacharya and Osburn 2021). Surficial and preferential flow-paths during high precipitation events tend to effectively dissolve and transport more soil and plant-derived humic and aromatic organic matter to the receiving waters (Solomon et al. 2015). Low watershed residence times in wet conditions further accelerates downstream transport of unprocessed, humic, organic matter (Creed et al. 2015). Elevated humic and aromatic DOM potentially contributed from rainfall and runoff processes has also been reported in boreal lakes (Schindler et al. 1997; Dillon and Molot 2005), higher altitude lakes (Sadro and Melack 2012), and humid sub-tropical lakes in Florida (Brezonik et al. 2015; Hansen et al. 2016). Wet summers also corresponded to higher reservoir turbidity, TN, and TP concentrations, indicating higher erosion and nutrient export triggered by large precipitation events (Jones et al. 2004, 2008). Due to the coupled nature of C, N and P cycles (Solomon et al. 2015), similar increase in abundance of DOM and dissolved nutrients has been observed in north temperate and boreal lakes experiencing greater terrestrial influx (Dillon and Molot 2005; Seekell et al. 2015).

Lower $a_{440}$, DOC, and $SVA_{440}$ during dry summers suggest reduced influx of terrestrial, humic, aromatic DOM and elevated relative abundance of aliphatic DOM. Perhaps with reduction in allochthonous DOM loading, autochthonous DOM production and subsequent microbial breakdown can become a prominent within-reservoir process (Ritchie et al. 2008). In lakes and reservoirs, high quantities of POM and Chl-*a* typically represent increased phytoplankton abundance and thus serve as useful indicators of organic matter production (Boers and Boon 1988; Jones et al. 2004). Previous lake-focused studies have shown that aliphatic, low color absorbing DOM is associated with autochthonous production (De Wit et al. 2016). Thus, the reservoirs are vulnerable to shifts in DOM quantity and composition with a predicted increase in droughts in mid-continental USA. Also, unlike the boreal and high altitude lakes that are experiencing wetter conditions and associated humification/browning of lakes, the DOM dynamics in Midwest reservoirs follow a non-monotonic trend, where wet years are interjected by prolonged dry conditions dominated by within-reservoir processes.

*5.2 Are watershed characteristics important for organic matter quantity and composition?*

The prominent watershed and reservoir morphological characteristics driving organic matter dynamics switched with PDSI variability. During wet summers, watershed characteristics, such as the % agricultural and forested land cover had a substantial influence on organic matter dynamics. Agricultural watersheds in our study had the highest soil OM, possibly because these landscapes were historically prairies (Jones et al. 2008; Jones et al. 2009), with lower slopes that allowed higher soil organic matter accumulation in spite of agricultural activities. These agricultural soils, however, are also prone to erosion (K) due to lack of tree cover and tilling and can, therefore, contribute terrestrial DOM to agricultural reservoirs.

Extensive agricultural activity may also promote autochthonous production and microbial processing of DOM in agricultural streams, and in turn, export higher quantities of microbial, aliphatic DOM to the receiving waters (Williams et al. 2010). In our study, however, higher erosion rates in the agricultural watersheds probably reduced DOM transformation in the agricultural channels and streams draining into the reservoirs and contributed more DOM quantity (DOC, $a_{440}$) and humic, aromatic DOM. Strong watershed influence explained the higher turbidity and nutrients observed in agricultural reservoirs, especially during wet summers. Previous studies in Missouri show that the reservoir trophic state is influenced by external nutrient inputs from agricultural watersheds (Jones et al. 2004, 2009, 2020). The higher $a_{440}$ values (> 10 $m^{-1}$) observed in our study were comparable to eutrophic lakes in Florida that receive substantial agricultural runoff (Brezonik et al. 2015), as well as values commonly observed in predominantly forested, humic lakes in northern USA (Table 1).

In comparison to the agricultural reservoirs the forested reservoirs were at the other end of the nutrient, turbidity, and organic matter continuum (Fig. 3). The forested watersheds in southern Missouri have steeper slopes and lower soil OM storage, thereby contributing lower quantities of organic matter, nutrients, and sediment into the reservoirs (SI Table 2, Fig. 3). Steep watersheds with thinner organic horizons, were also found to transport low quantities of organic matter to northern USA lakes (Rasmussen et al. 1989). Our findings, however, were in contrast to the observations by (Olmanson et al. 2020), as they report substantially greater DOM quantities in the northern forested lakes than the southern agricultural lakes of Minnesota, USA (Table 1). These differences were most likely driven by the relatively greater soil organic matter stores in the forested watersheds than the latter. Similarly, our findings were also in contrast to boreal lakes in Sweden due to greater abundance of watershed-derived DOM and POM in forested lakes (Kothawala et al. 2014).

Reservoir morphological characteristics, such as maximum depth, volume, and $W_{area}$:$L_{area}$ were most strongly correlated with organic matter during drier summers, likely because of their influence on autochthonous C production reflected in greater Chl-*a* and POM concentrations. Reservoirs with lower $W_{area}$:$L_{area}$ generally have increased water residence times and correlated morphological attributes such as volume and depth (Rasmussen et al. 1989). Shallow reservoirs, with small volumes and lower $W_{area}$:$L_{area}$ were typically nutrient replete and abundant in autochthonous DOM and POM, and mostly located in the prominently agricultural section of Missouri. Shallow, small, highly productive agricultural lakes with longer residence times are conducive to in-lake processing of terrestrial DOM and autochthonous production of aliphatic DOM and POM (Cao et al. 2018). Previous studies in Missouri reservoirs indicate the influence of watershed-derived nutrients on Chl-*a* concentrations facilitated by nutrient input and water residence time (Jones et al. 2004, 2005, 2008), with longer residence times being associated with elevated atmospheric C evasion (Jones et al. 2016). Watershed and lake morphological controls on long-term patterns in allochthonous and autochthonous organic matter dominance were in agreement with other studies in boreal lakes (De Wit et al. 2016) and shallow, lowland lakes (Piirsoo et al. 2018).

*6. Conclusions and Implications*

Our understanding of inland organic matter dynamics originates mostly from snow-dominated, often forested, natural lakes. The current study fills the knowledge gaps regarding long-term organic matter dynamics in constructed inland systems located in human-altered landscapes. Our findings highlight the non-monotonic pattern in DOM composition and quantity, indicating the sensitivity of flow-connected reservoirs to hydro-climatic fluctuations and vulnerability to future global changes. Climate predictions expect an increase in droughts for the study region; under these circumstances, Midwest reservoirs will likely undergo "greening" – and respond opposite to lakes located in parts of the world that are experiencing increasing wet conditions resulting in browning of lakes (Roulet and Moore 2006).

Our quantitative assessment shows that the hydro-climatic variability mediates the influence of limnological and watershed controls on reservoir organic matter dynamics. In wet years the organic matter composition is prominently allochthonous and aromatic resulting from greater watershed controls, particularly in agricultural reservoirs. The relative influence of reservoir morphology is highlighted under dry conditions with an increased abundance of aliphatic and potentially algal organic matter.

Dynamic patterns in reservoir DOM and their controls can pose a challenge for effective water resource management. As such, we highlight the necessity to consider long-term trends in both DOM quantity and composition, which are typically sparse for reservoirs (Table 1), to modulate management strategies to accommodate the shifting reservoir versus watershed controls in response to current and future hydro-climatic conditions. Finally, such information can also be integral for predicting the future contribution of reservoirs to organic matter cycling and associated water quality concerns plaguing similar inland water resources in the USA and elsewhere.

**Author contributions:** RB and RN conceived the study. RB analyzed the data, conducted the statistical modeling and wrote the manuscript with feedback from co-authors. Data came from various studies designed and executed by JJ, JG, DO and AT. JH provided watershed-level data.

**Declaration of competing interest:**

The authors declare no competing interests

**Data availability statement:**

Limnological dataset used in the manuscript is available online. See Jones JR, Argerich A, Obrecht DV, Thorpe AP, North RL. 2020. Missouri Lakes and Reservoirs Long-term Limnological Datatset. ver 1. Environmental Data Initiative. https://doi.org/10.6073/pasta/86d8d176e91410566b4de51f44c2624.

Sources for hydroclimatic data are provided in the main text.

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**Figure Captions**

Figure 1 Location of the 40 study reservoirs across the state of Missouri, USA. Inset shows the location of the state of Missouri in USA. Reservoirs are color coded to represent the spatial gradient in average dissolved organic matter quantity estimated by average absorption coefficient at 440 nm wavelength ($a_{440}$) in A) the wet summer of 2013 and B) the dry summer of 2003. White to black scale show low to relatively higher values. The land cover map with major land cover groups for Missouri is also presented (NLCD, 2016). See section 2.1 for more details.

Figure 2 Box and whisker plots show the temporal patterns (1990–1992 and 1997–2016) in A. summer Palmer Drought Severity Index (PDSI) across the four regions (NE, NW, SE, and SW) of Missouri. Positive values reflect wet summers and negative values reflect dry summers. PDSI values ≥ +1.9 represents substantial wet summers and ≤ -1.9 represents substantial droughts (NOAA, 2018), B. dissolved organic matter (DOM) quantity measured as absorbance at 440 nm wavelength ($a_{440}$), C. DOM composition estimated by specific visible absorbance at 440 nm ($SVA_{440}$), D. dissolved organic carbon concentration (DOC), and E. particulate organic matter concentration (POM) in all the study reservoirs (*n*=40). The shaded box indicates the statistically significant changepoints in the temporal data identified via multiple changepoint analyses for $a_{440}$ and POM (2003 and 2007), $SVA_{440}$ (2004 and 2007), and DOC (2007). The box-whisker plots (1 B-E) have been capped at outer bounds of data between $10^{th}$ and $90^{th}$ percentiles. The box-whiskers plots represent the median, $25^{th}$ and $75^{th}$ quartile, minimum and maximum values, and the outliers (< 1.5 times inter quartile range). Horizontal lines indicate averages for each group identified by changepoint analysis.

Figure 3 Annual variability in the relative importance of explanatory variables ranked from 1–5 and their % relative frequency of occurrence estimated through Random Forest modeling. The important limnological parameters included Turbidity (NTU), total nitrogen (TN, $\mu g\ L^{-1}$), total phosphorus (TP, $\mu g\ L^{-1}$), Secchi disk depth (Secchi, m), and Chlorophyll-*a* (Chl-*a*, $\mu g\ L^{-1}$). The important watershed characteristics included soil erodibility (K), % agriculture (% Ag), % forest (% For), the ratio between watershed and lake area ($W_{area}$:$L_{area}$), lake depth (Depth, m), lake volume (Vol, $m^3$), soil organic matter (OM, %), average runoff (Runoff, cm), and Permeability (Perm, m/day). Figures A-H, indicate the important limnological parameters and their relative frequency of occurrence, explaining the variability in $a_{440}$, $m^{-1}$, $SVA_{440}$, $m^{-1}\ L\ mg^{-1}$, DOC ($mg\ L^{-1}$), and POM concentrations ($mg\ L^{-1}$), respectively. Figures I-P summarize the important watershed characteristics and their relative frequency of occurrence that explain the variability in $a_{440}$, $SVA_{440}$, DOC, and POM, respectively.

Figure 4. PCA bi-plot between average summer Palmer Drought Severity Index (PDSI) with dissolved organic matter (DOM) quantity measured by absorption at 440 nm wavelength ($a_{440}$), dissolved organic carbon concentration (DOC), average annual DOM composition estimated by specific visible absorbance at 440 nm ($SVA_{440}$), and particulate organic matter concentration (POM). Limnological parameters and watershed characteristics that were identified as important by Random Forest modeling (i.e., shown in Fig. 3) were included in the bi-plot. The sampled years represent the gradient from wet summers (positive PDSI values (black filled circles) to dry summers (negative PDSI; white filled circles). Watershed morphological characteristics are in italics, limnological parameters are underlined, and organic matter composition and quantity variables are in red.

Table 1. The range (minimum [Min] and maximum [Max] values) of terrestrial CDOM quantity measured as absorption at 440 nm ($a_{440}$ [$m^{-1}$]) in lakes and reservoirs reported in different studies. The references (Refs) for each study, along with study location, waterbody type, site description, and study duration have been provided where available.

| **Refs** | **Study Location** | **Waterbody** | **Min** $a_{440}$ ($m^{-1}$) | **Max** $a_{440}$ ($m^{-1}$) | **Site Description** | **Study Duration** |
|---|---|---|---|---|---|---|
| (Thompson et al. 2014) | Mackenzie Delta, NWT, Canada | Lakes | 0.0 | 0.1 | Tundra lakes | Summer 2006, 2007 |
| (Longhi and Beisner 2009) | Quebec, Canada | Lakes | 0.0 | 1.5 | Humid continental, Southern Eastern township and Laurentian Lakes, oligotrophic to eutrophic lakes | Summer 2006, 2007 |
| (Brezonik et al. 2019) | Minnesota, Wisconsin and Northern Michigan, USA | Lakes | 0.0 | 32.5 | Boreal lakes, Northern lakes and forest ecoregion and North-Central hardwood forest | 2014–2018 |
| (Morris et al. 1995) | USA sites (Northeast USA, Alaska, and Colorado), and Argentina | Lakes | 0.03 | 14.3 | Oligotrophic to eutrophic lakes | Summer (year not provided) |
| (Yang et al. 2005) | Yangtze River Floodplain, China | Lake | 0.1 | 0.3 | Subtropical, shallow lake | 2003–2004 |
| (Olmanson et al. 2020) | Minnesota, USA | Lakes & reservoir | 0.1 | 25.5 | Humid continental, all ecoregions of Minnesota. | 2015–2016 |
| (Cuthbert and del Giorgio 1992) | Quebec, Canada | Lakes | 0.1 | 4.7 | Boreal lakes | Summer 1991 |
| (Forsström et al. 2015) | Finland | Lakes | 0.1 | 9.4 | Lapland, subarctic tundra and birch woodland, oligotrophic, high-latitude lakes | Summer 2004 |
| (Zhou et al. 2019) | Yunnan Plateau Lakes, China | Lakes | 0.3 | 2.2 | Subtropical, oligo-eutrophic lakes | 1982–2016; 2017 |

| | | | | | | |
|---|---|---|---|---|---|---|
| (Zhang et al. 2007) | Lake Taihu, China | Lake | 0.3 | 2.4 | Subtropical, eutrophic lake | Summer 2005–2007 |
| (Vachon et al. 2017) | Quebec, Canada | Lakes | 0.3 | 11.1 | Boreal lakes | Summer 2010) |
| (Brezonik et al. 2015) | North & South-central Florida, USA | Lakes | 0.3 | 27.0 | Humid subtropical, oligo to hyper-eutrophic lakes, & low to high acid sensitivity. | 1968–1970; 1978–79 |
| (Brezonik et al. 2015) | Minnesota and Wisconsin, USA | Lakes | 0.2 | 25.1 | Humid continental, oligotrophic to eutrophic lakes | 2013; 1990-2013 |
| (Menken et al. 2006) | Minnesota, USA | Lakes | 0.4 | 11.9 | Humid continental, oligo to eutrophic lakes | Summer 2001 |
| (Watanabe et al. 2009) | Missouri reservoirs, USA | Reservoirs | 0.6 | 6.6 | Humid subtropical, oligotrophic to eutrophic reservoirs | Summer 2002 |
| This Study | Missouri reservoirs, USA | Reservoirs | 0.6 | 36 | Humid subtropical, oligotrophic to eutrophic reservoirs | Summer 1990–1992; 1997–2016 |
| (Bade et al. 2007) | Wisconsin, USA | Lakes | 1.3 | 3.5 | Humid continental, North temperate lakes, oligotrophic to eutrophic lakes | 2001–2002 |
| (Hestir et al. 2014) | Eastern Australia | Reservoirs | ~0.2 | ~2.8 | Alpine to tropical reservoirs | Sep–Nov 2012 Feb–Mar 2013 |
| (da Silva et al. 2021) (and references within) | Brazil | Lakes & reservoirs | 0.1 | 3.8 | Tropical lake and reservoirs, oligo- to hypereu- trophic | Varied from 2013–2018 across many studies |

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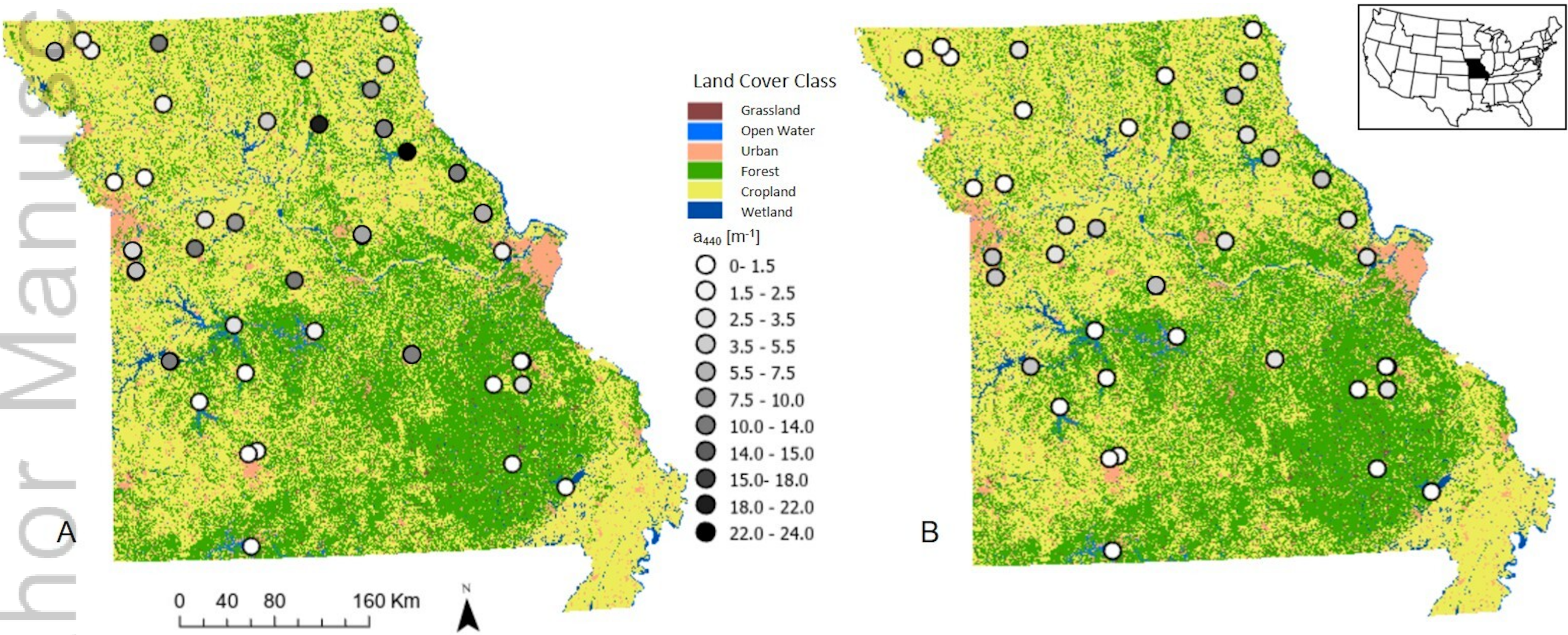
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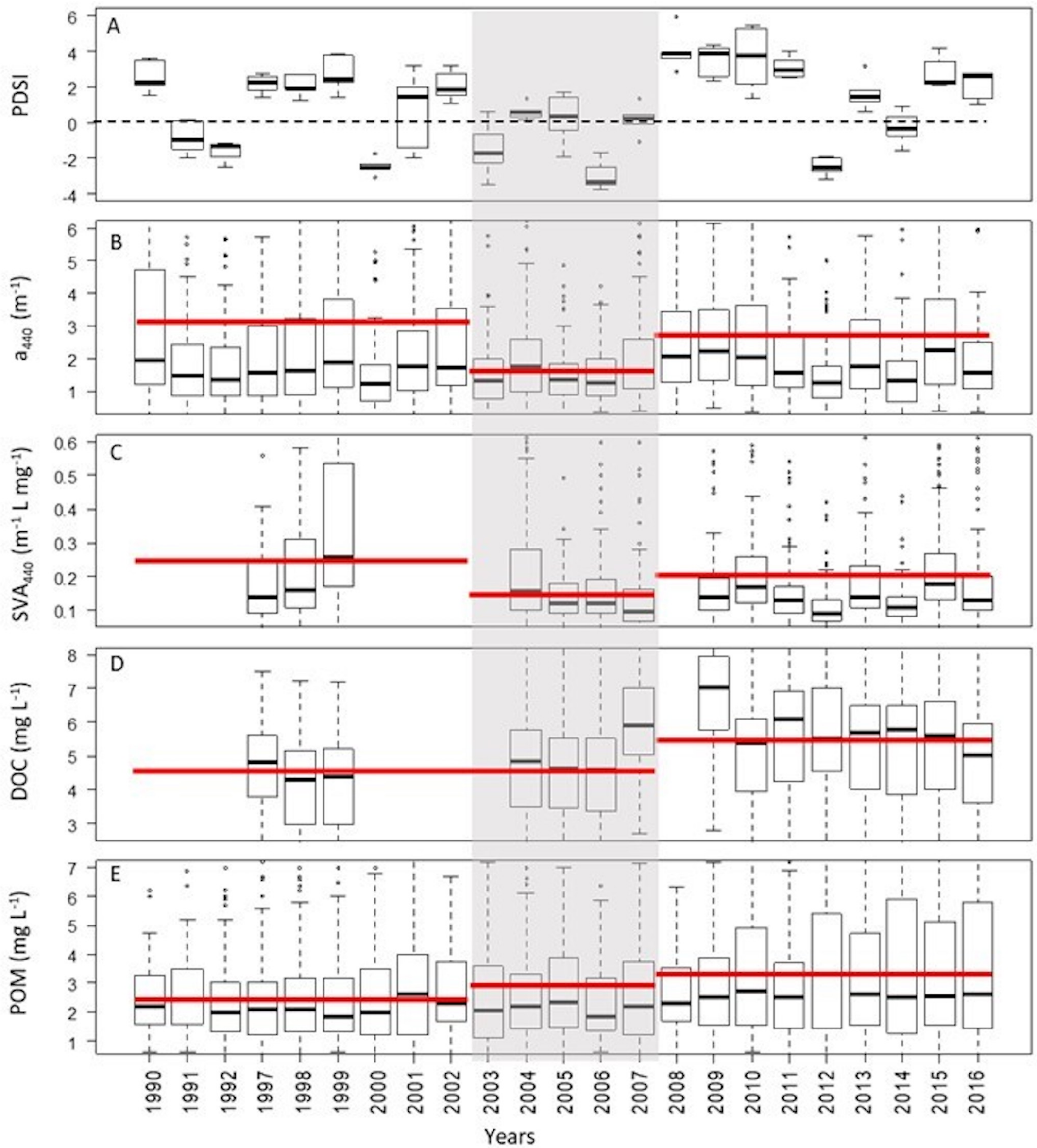
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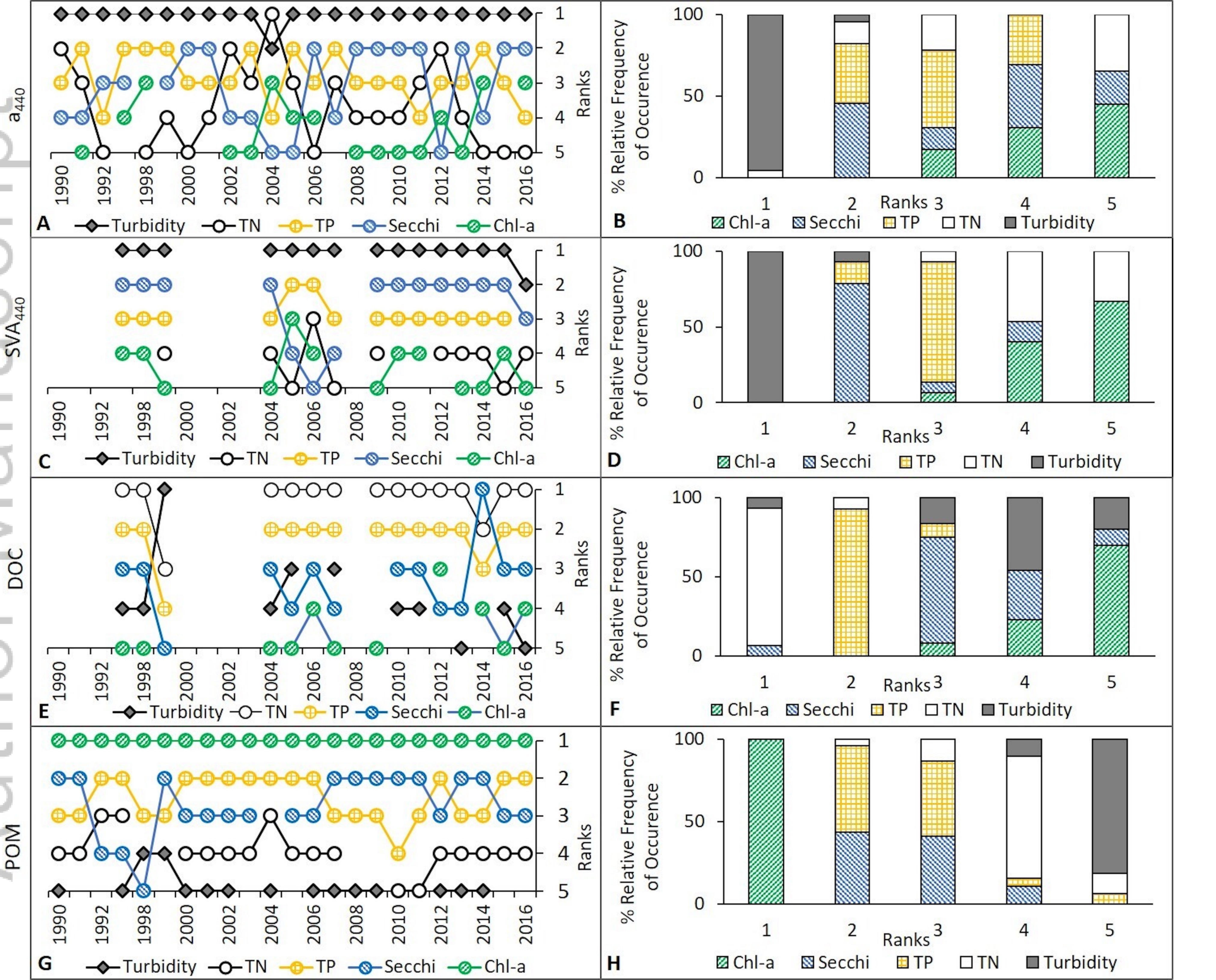

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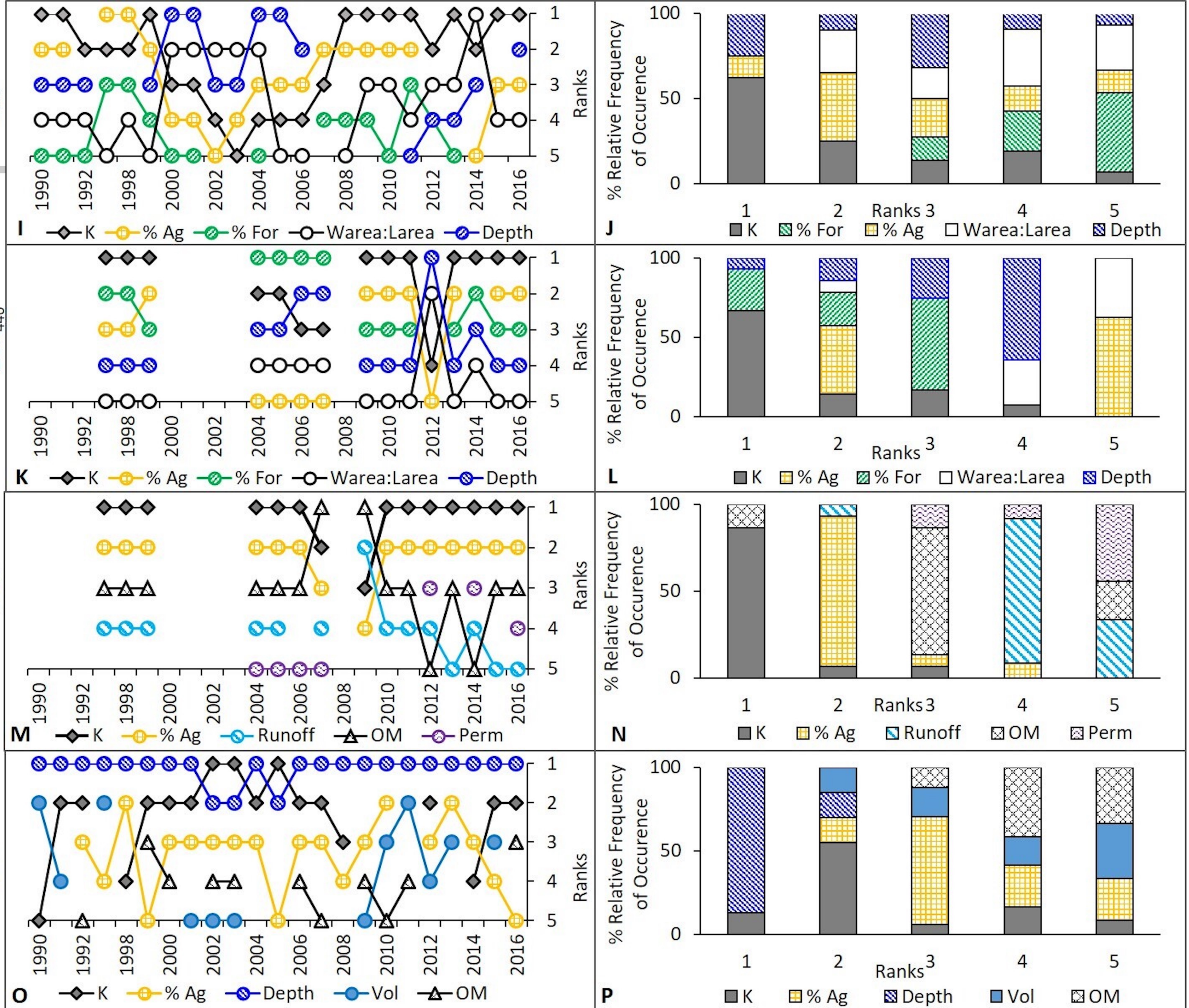

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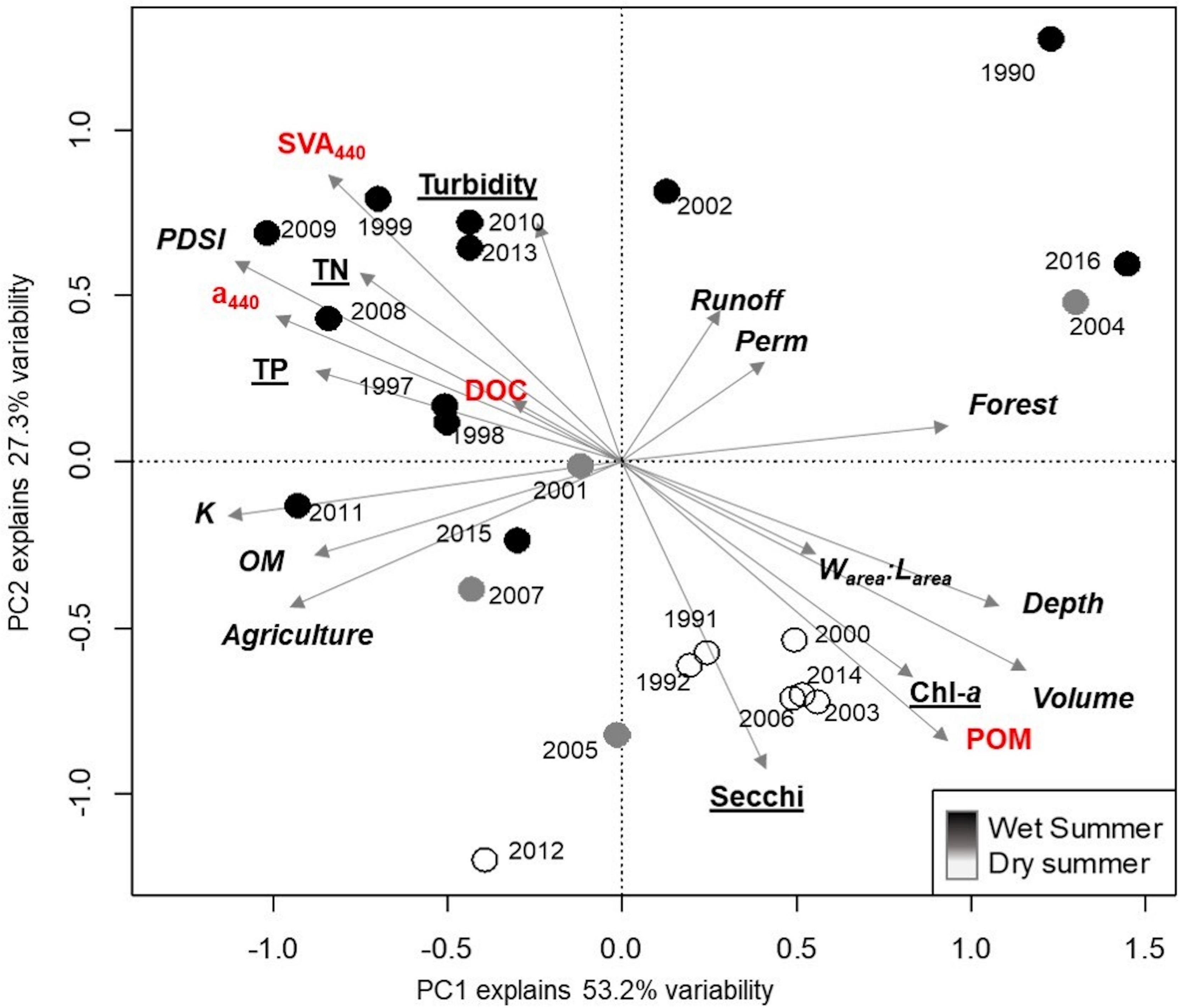

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Agriculture
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Wet Summer
Dry summer
PC2 explains 27.3% variability
PC1 explains 53.2% variability
1.0
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