

1 **Nitrate-N trends in Mississippi and Atchafalaya River Basin Watersheds:**  
2 **Exploring correlations of watershed features with nutrient transport components**  
3 **2000-2020.**

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## 15 1. Abstract

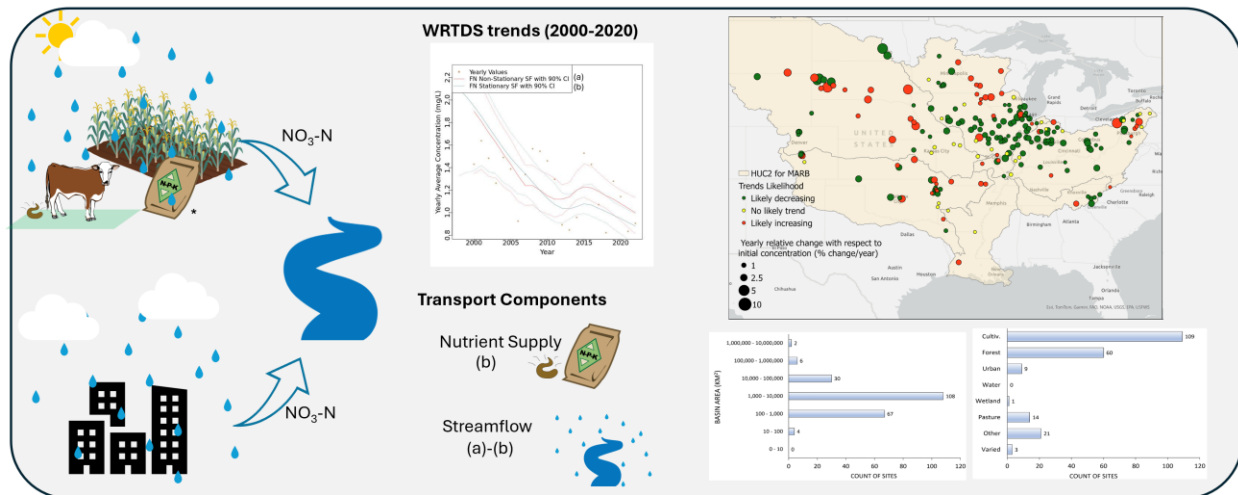
16 Nutrient reduction strategies in the Mississippi and Atchafalaya River Basin (MARB) have been  
17 implemented since mid-2010's to attenuate the impacts of non-point source pollution to the Gulf  
18 of Mexico. Of all nutrients, nitrate represents the largest threat due to its extended presence  
19 throughout the basin and its high solubility in water. To evaluate the performance of state  
20 reduction strategies, long-term changes of riverine nitrate should be identified. The objective of  
21 this study was to estimate the flow-normalized (FN) nitrate-N concentration and yield trends for  
22 the 2000-2020 period across the MARB. A harmonization and in-depth screening of paired  
23 nitrate-N and streamflow datasets resulted in a robust water quality monitoring network of 217  
24 sites. Trends magnitude and likelihood were computed using the Weighted Regression on Time,  
25 Discharge, and Season (WRTDS) coupled to a bootstrap test, and trends results were  
26 correlated with basin features and initial values. Nutrient supply and flow components of trends  
27 were computed through the stationary and non-stationary flow normalization. Results indicated  
28 that 59.4% of the 217 sites had likely decreasing trends, while 27.6% likely increased, and the  
29 remaining 12.9% had no likely change detected. Reductions in riverine FN nitrate-N were  
30 clustered in the north central region of the MARB, with watersheds dominated by cultivated  
31 cropland having relatively high FN concentrations and yields in 2000 followed by likely  
32 downward trends. For the vast majority of sites, the streamflow component contributed to  
33 increased FN nutrients, but the nutrient supply component was more dominant than the  
34 streamflow component.

35 Keywords: Nutrient trends, Nitrate-N, Streamflow, Nutrient supply, Mississippi and Atchafalaya  
36 River Basin, Weighted Regressions on Time, Discharge, and Season model (WRTDS).

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## 2. Graphical Abstract



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\*Maize, Fertilizer, Cow, Feces, & Weir illustrations from Jane Thomas, Tracey Saxby & Jane Hawke at Integration and Application Network ([jan.umces.edu/media-library](http://jan.umces.edu/media-library))

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## 3. Introduction

42 Anthropogenic nutrient pollution from cultivated and urban land in the Mississippi and  
 43 Atchafalaya River Basin (MARB) is the main cause of the 16,000 km<sup>2</sup> hypoxic zone in the  
 44 northern Gulf of Mexico (Piske and Peterson, 2020). Of all nutrients transported to the Gulf of  
 45 Mexico, nitrate is the principal cause of the low-oxygen levels at the Gulf (Rabalais and Turner,  
 46 2019). Sources of this nutrient include inorganic N fertilizers, manure, soil organic matter,  
 47 biological N fixation, municipal wastewater and atmospheric deposition (McIsaac et al., 2002,  
 48 Stackpoole et al., 2021). The MARB has one the most productive farming regions worldwide  
 49 (Goolsby and Battaglin, 2001), making cultivated land the most significant source of nitrate. The  
 50 implementation of tile drainage in cultivated land has also played a main role on nitrate transport  
 51 within the MARB (David et al., 2010).

52 Federal, state, and local agencies have implemented nutrient reduction strategies to reduce the  
 53 amount of pollutants entering streams (Mississippi River Gulf of Mexico Watershed Nutrient  
 54 Task Force, 2008). Analyses of long-term changes in the nitrate loads and concentrations in

55 streams across the MARB allow the identification of regions having the largest reductions and  
56 increases of nutrient contribution over time. Goolsby and Battaglin (2001) investigated the long-  
57 term change on the average nitrate flux in the MARB, finding 1980-99 nitrate-N flux to be three  
58 times larger than that of 1955-70. This increase coincided with increased use of N fertilizer as  
59 well as an increase in precipitation and river flow. Donner et al. (2002) used models to estimate  
60 that 25% of the increase in nitrate load was due to increased streamflow. Distinguishing the  
61 influences of changing nutrient source management from climate factors on river loads is an  
62 ongoing challenge.

63 To increase the amount of information extracted from riverine concentration time series, and  
64 reduce the impact of year-to-year streamflow variations on long-term trends analysis, the  
65 Weighted Regression on time, discharge, and season (WRTDS) was proposed (Hirsch et al.,  
66 2010). This method was applied to estimate nutrient trends up to 2012 for the MARB (Oelsner et  
67 al., 2017, Crawford et al., 2019), and up to 2020 for 110 USGS water quality monitoring sites  
68 across the U.S. (US Geological Survey, 2024). A further development of the WRTDS method  
69 allowed the computation of trends considering the non-stationarity of flow (Choquette et al.,  
70 2019, Hirsch, 2018). This advancement permitted the separation of streamflow driven transport  
71 component from all other non-streamflow components that could impact the fate and transport  
72 of nutrients (Murphy and Sprague, 2019), hereafter named nutrient supply transport component.

73 Transport and retention of nutrients are mainly controlled by the advective processes occurring  
74 as water flows throughout the watershed, and the availability of these non-point source  
75 pollutants in watershed compartments (Speir et al., 2021). Both flow and nutrient supply  
76 components are influenced by watershed features. Land use, soil, topography, and  
77 climatological conditions determine rainfall to runoff conversion, infiltration, and  
78 evapotranspiration processes, all of these influencing water volumes and residence times  
79 (Goyette et al., 2019). Land use is the main driver of nutrient supply, linked to fertilizer and

80 manure application and legacy nitrogen from current and historical agricultural land (Stackpoole  
81 et al., 2021), and to point sources from urban areas. Furthermore, basin area influences the  
82 complexity of the river system being studied. Small catchments often allow the clear  
83 identification of sources contributing to measured loads, as opposed to large watersheds (i.e.,  
84 larger than a couple of hundreds of square kilometers), in which diverse interconnected systems  
85 regulate the fate and delivery of nutrients at the outlet (Alexander et al., 2002), making nutrient  
86 reduction strategies tougher to implement and assess.

87 The objective of this paper is to conduct a methodologically consistent trend analysis of riverine  
88 Nitrate-N concentration and yield (load/drainage area) across the MARB from 2000 to 2020 and  
89 estimate the relative influences of streamflow and nutrient supply component on trends results  
90 using screened nitrate-N and streamflow datasets across the MARB. The correlation of trends  
91 results and watershed features (i.e., drainage area, relief, upstream dam storage, and historical  
92 dominant land use) was analyzed. An analogous analysis was performed for Total Phosphorus  
93 (Botero-Acosta et al., In preparation).

#### 94 4. Materials and Methods

95 The trend period selected for this analysis provided the largest number of sites meeting data  
96 requirements to allow for a meaningful study across the MARB. A 20-year trends period (2000-  
97 2020) with 2-year additional periods at starting and ending periods, to improve the accuracy for  
98 2000 and 2020 estimations, was used. In addition, formal state nutrient loss reduction strategies  
99 were implemented from mid-2010's, making this period of particular interest to evaluate the  
100 performance of the selected approaches.

## 101 4.1. Data harmonization and screening

102 A riverine nitrate-N concentration dataset was compiled from all records having nitrate or  
103 nitrate+nitrite concentrations in filtered or unfiltered water samples in the US Water Quality  
104 Portal (National Water Quality Monitoring Council et al., 2021). This definition was based on the  
105 reported minor concentrations of nitrite with respect to nitrate and the marginal difference  
106 between filtered and unfiltered samples (Oelsner et al., 2017). Records from sites linked to the  
107 same stream segment were unified to increase the time series length at these locations. This  
108 process was done through the COMID feature of the National Hydrograph Dataset Plus (EPA,  
109 2022). Nitrate-N data was harmonized and screened. The harmonization of the observed  
110 dataset plays a major role when analyzing historical changes of nutrient loads (Sprague et al.,  
111 2017). Representatives and documentation from the various reporting agencies were consulted  
112 to clarify methods and units of ambiguous records. For nitrate data, 12% of records with  
113 ambiguous form (elemental or molecular) or units were clarified by contacting the reporting  
114 organization, while 32% were solved through the reported analytical method.

115 Harmonized concentration data were included in trend calculations only after various screening  
116 criteria were met. Initially, a record screening identified and solved duplicates and censored  
117 records. Missing, zero, negative, and outlier records were removed from the analysis, as well as  
118 composite, control and field analyzed samples. Subsequently, site screening removed sites that  
119 had more than 50% of left-censored data, less than 70% quarterly coverage for the 2000-20  
120 period, and less than 10% of decadal WQ data on days with high flow regime (SF>85  
121 percentile).

122 Streamflow (SF) sites located upstream or downstream of WQ sites were selected from the  
123 USGS gage network when basin areas had a maximum difference of 10% and no dams were  
124 located in between the sites. Data of dams built before 2013 were extracted from EPA (2022).

125 SF data screening identified missing, zero and negative flow values. Missing records were filled  
126 for years having no more than 3 consecutive and 30 total missing records using the FillMiss  
127 function (USGS, 2016). All SF sites with no consecutive records for the 1998-2022 water year  
128 periods were discarded. From the screening and harmonization procedure, 217 sites were  
129 identified for which flow normalized nitrate concentration and load trend analyses between 2000  
130 and 2020 were conducted.

## 131 4.2. Nitrate-N trends

132 The Weighted Regression on Time, Discharge and Season (WRTDS) (Hirsch et al., 2010)  
133 method was implemented to compute the flow normalized (FN) concentration and loads from  
134 observed data. The performance of the WRTDS method was evaluated through the Pearson  
135 correlation coefficient, the extrapolation metric and the flux bias statistics. In addition, a visual  
136 inspection of residuals was performed to remove sites with step changes in concentrations, not  
137 reproduced by the WRTDS method (Oelsner et al., 2017).

138 Flow normalization was calculated by two methods: 1) normalized to average flow distribution  
139 observed for the period of observation (stationarity assumption); and 2) normalized to a moving  
140 window of flow distributions (non-stationarity assumption or generalized normalization). The  
141 difference between these two estimates is considered the change due to non-stationary flow.  
142 The rest of the change is due to all other factors, including changes in point and non-point  
143 sources, legacy nutrients, land cover and management. For brevity, Murphy and Sprague  
144 (2019) use the term “management component”, which may not adequately convey the role of all  
145 other factors such as legacy nutrients and inaccuracies in WRTDS flow normalized estimates,  
146 and may understate the impacts of management practices on water flow. Rather than  
147 “management component” we use the term “nutrient supply component”, but acknowledge that  
148 we have not quantified specific nutrient supplies such as fertilizer inputs or point sources, etc.

149 Our use of the term “nutrient supply” is a catchall term that refers to all factors other than  
150 changes in average streamflow, which is a proxy for nutrient sources and sinks. All TP  
151 concentration and yield values referred to in the results section correspond to flow normalized  
152 values.

153 Trends were determined by the difference between estimated FN concentration or load for 2020  
154 and 2000. To reduce the impacts of streamflow random variations on resulting nutrient time  
155 series, the flow-normalized values of the obtained time series were used to estimate long term  
156 trends (Murphy and Sprague, 2019, Hirsch et al., 2010). WRTDS has been widely used to  
157 characterize trends of nutrient loads (e.g., McIsaac et al. (2023), US Geological Survey (2024)),  
158 and to estimate the impacts of management practices and flow on resulting trends (Murphy and  
159 Sprague, 2019). Analyses were conducted using the R statistical software program (R Core  
160 Team, 2017) and the EGRET R-package (Hirsch, 2018, Hirsch and De Cicco, 2015).

161 To compare trends results among sites with varied characteristics, concentration trends were  
162 weighted by the flow normalized concentration at the beginning of the trends period (2000) and  
163 divided it by the number of years, which provided a percent change of concentration per year  
164 (Murphy and Sprague, 2019). Likewise, load trends were weighted by the drainage basin area  
165 (USGS, 2024) to identify the yearly nutrient yield expressed in kilograms per square kilometer  
166 and year. Analyzing both relative and absolute changes will provide insights about basin specific  
167 processes impacting nutrient concentrations during the trends period as well as allow the  
168 identification of those basins that might be larger contributors of nutrient loads.

169 A likelihood-based approach, the block bootstrap method (Hirsch et al., 2015), was used to  
170 estimate the likelihood of the total trends for concentration and yield (values normalized under  
171 the non-stationary flow assumption). This method runs multiple replicates of WRTDS using  
172 randomly selected subsamples from the observed data and computed the fraction of replicates  
173 with positive trend ( $\sigma$ ). A positive replicate fraction of 0.66 or larger would indicate a likely



174 upward trend, while an estimate of positive replicates of less than 0.33 would indicate a likely  
175 downward trend, and fractions between 0.33 and 0.66 would correspond to no likely trend since  
176 similar number of replicates were found to have increasing and decreasing trend (Yates et al.,  
177 2022, Hirsch et al., 2015). Positive replicate fractions > 0.90 and <0.10 were considered highly  
178 likely upward and downward trends, respectively.

179 The dominance of one trend component vs the other (e.g., flow vs. nutrient supply) was  
180 established based on the factor of exceedance. A transport component was identified as  
181 dominant if it was at least 1.5 times the other component (using absolute values). The  
182 percentage of influence of each transport components (flow or nutrient supply) was computed  
183 as:

$$184 \quad \% \text{ Influence component } A = \frac{\text{abs}(\% \text{ change component } A)}{\text{abs}(\% \text{ change component } A) + \text{abs}(\% \text{ change component } B)} \quad \text{Eq.1}$$

185 Influence of Nutrient Supply and Streamflow components on load trends are equivalent to the  
186 influences of both components on yield trends.

### 187 4.3. Watershed features

188 Data for basins associated with the nitrate-N trends sites was analyzed along with the trends  
189 results. Basin area, land use, elevation, and upstream dam storage information were extracted  
190 from publicly available data. Dominant land uses for years 2001, 2011, and 2019 were identified  
191 from National Land Cover Dataset (NLCD) maps and the combined land use categories (Table  
192 1) covering the largest area of the drainage basin (Stets et al., 2020). The dominant land use for  
193 the 2000-2020 trend period was identified for those basins having the same dominant land use  
194 category prevailing for the 2001, 2011, and 2019 NLCD maps. When the dominant category  
195 changed during the 2000-2020 period, the label “Varied” was assigned. In addition, changes of  
196 percentage coverage from 2001 to 2019 for each land use category were computed and

197 correlated with riverine nitrate trends. A proxy of basin slope was included in our analysis as the  
 198 relief per area unit (m/km<sup>2</sup>). Relief was computed as the difference between the maximum and  
 199 the minimum elevation within the basins draining to trends sites from a 5x5 degree DEM.  
 200 Finally, dam storage information was extracted from the National Hydrography Dataset Plus  
 201 (NHD-Plus) (EPA, 2022).

202 **Table 1. National Land Cover Database (NLCD) categories grouped for watershed feature**  
 203 **analysis.**

Adapted land use categories	NLCD Category ID#	Description
<b>Cultivated (tilled land)</b>	82	Cultivated Crops -areas used to produce annual crops, such as corn, soybeans, vegetables, tobacco, and cotton, and perennial woody crops such as orchards and vineyards. Crop vegetation accounts for greater than 20% of total vegetation. This class also includes all land being actively tilled.
<b>Forest</b>	41	Deciduous Forest
	42	Evergreen Forest
	43	Mixed Forest
<b>Urban</b>	22	Developed, Low Intensity
	23	Developed, Medium Intensity
	24	Developed High Intensity
<b>Water</b>	11, 12	Water
<b>Wetlands</b>	90, 95	Wetlands
<b>Pasture/Hay</b>	81	Pasture/Hay
<b>Other</b>	21	Developed, Open Space- areas with a mixture of some constructed materials, but mostly vegetation in the form of lawn grasses.
	31	Barren Land (Rock/Sand/Clay)
	52	Shrub/Scrub
	71	Herbaceous

204

205 Watershed features were analyzed through Pearson correlation (r) matrices to evaluate the  
 206 direction and the degree of collinearity between variables. The statistical significance of  
 207 correlations was evaluated by testing the null hypothesis of no correlation with an alpha value of  
 208 0.05.

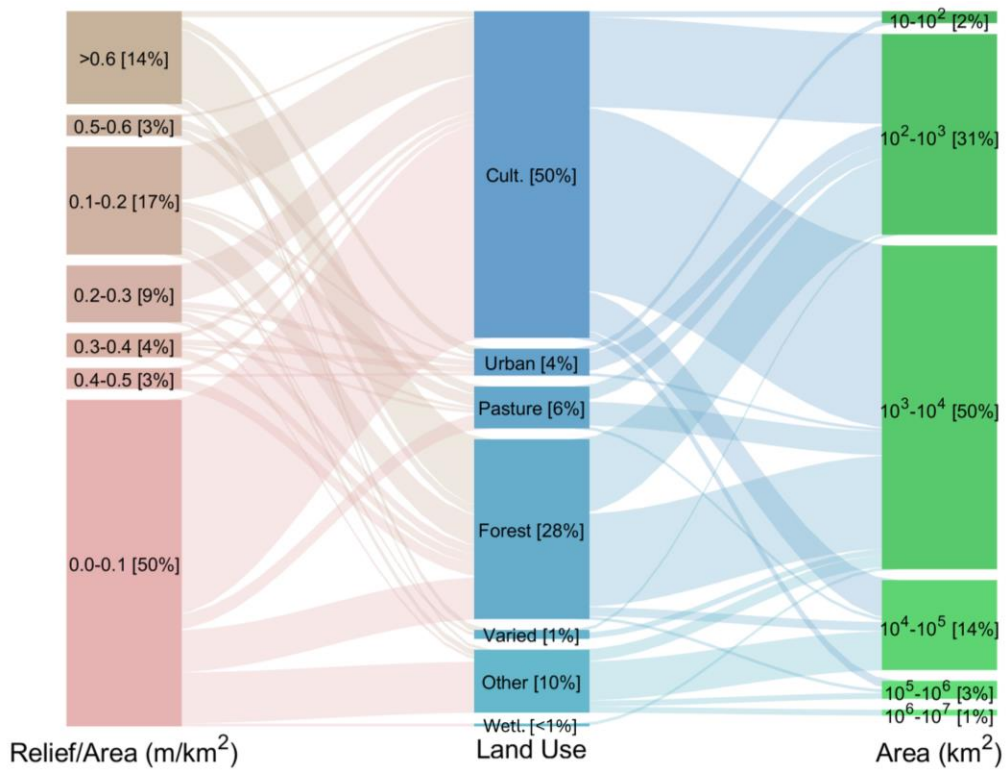
209 5. Results and discussion

210 5.1. Watershed Features

211 The basins associated with the 217 nitrate-N trends sites (Figure A- 1) were characterized as  
212 described in Section 4.3. Cultivated cropland was the dominant land cover for 50% of these  
213 sites, followed by forest (27.6%) (Figure 1, Table 2). It was found that 50% of sites had a Relief  
214 per area between 0 and 0.1 m km<sup>-2</sup>, and a somewhat different 50% of sites had drainage areas  
215 between 1,000 and 10,000 km<sup>2</sup>. Subdivisions of categories of relief per area, land cover and  
216 drainage areas for the sites are illustrated in Figure 1.

217

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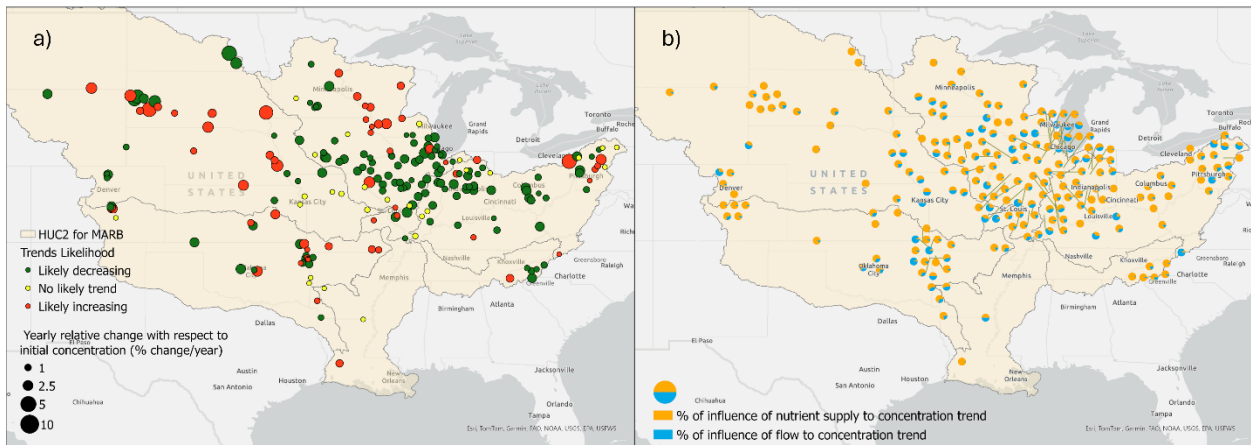


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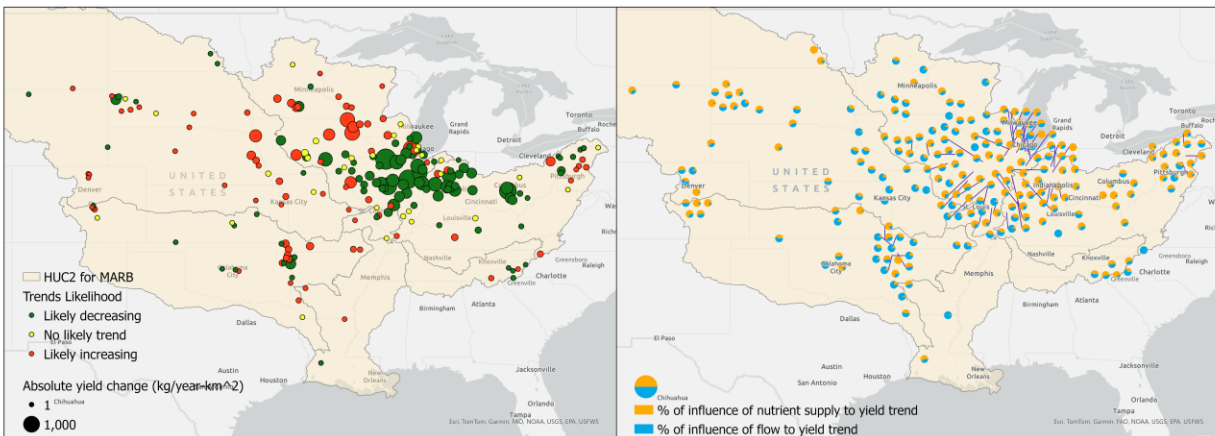
220 **Figure 1. Main watershed features for the 217 nitrate-N trends sites and percentage of**  
 221 **sites for each category.**

222 **5.2. Overall Trends**

223 Flow normalized (FN) nitrate-N concentrations likely decreased at 59.4% of the 217 sites and  
 224 increased at 27.6%, with no likely change detected for the remaining 12.9% (Table 2). FN yields  
 225 likely decreased at 47% of sites, increased at 39.2% of sites and no trend was detected at  
 226 13.8% of sites. Reductions in FN nitrate-N concentration and yield were clustered in the north  
 227 central region of the basin (Figure 2 and Figure 3), much of which is intensively cultivated  
 228 cropland.



229 **Figure 2. a) Nitrate-N concentration trends for the 2000-20 period (n=217). Magnitudes**  
 230 **were set based on absolute values of total trends; colors were set based on trends**  
 231 **likelihood. b) Percent influence of nutrient supply and flow components.**



234

235 **Figure 3. a) Nitrate-N yield trends for the 2000-20 period (n=217). Magnitudes were set**  
 236 **based on absolute values of total trends; colors were set based on trends likelihood. b)**  
 237 **Percent influence of nutrient supply and flow components.**

238 Land cover for slightly more than half of the monitoring locations were dominated by cultivated  
 239 cropland (Figure 1). Of these sites, FN nitrate concentrations likely decreased in 73.4% of the  
 240 sites and FN nitrate yield likely declined in 58.7%. Nationwide trends for the 2002-2012 period  
 241 (Stets et al., 2020) reported decreasing nutrient concentration at 40% of the studied sites  
 242 dominated by cropland. Our results shows an improvement possibly due to increased N use  
 243 efficiency in corn production (Mueller et al., 2019, Haegele et al., 2013) and the implementation  
 244 of nutrient reduction strategies since mid-2010's (Christianson et al., 2018). In contrast, for the  
 245 watersheds dominated by forest cover FN concentration trends were more equally divided  
 246 between likely increasing (43%) and decreasing trends (40%); and a greater percentage had  
 247 likely increasing FN yield trends (56.7%) than decreasing (38.3%) (Table 2).

248 Sites with urban dominated basins (9 sites) showed a predominance on likely decreasing  
 249 concentrations (77.8%) and yield (44.4%). This percentage of sites seems to be larger than the  
 250 one reported by Stets et al. (2020) for urban basins in their national trend analysis for the 2002-  
 251 2012 period (>60%), an indication of the success of implemented management efforts of the  
 252 1972 Clean Water Act for regulating point discharges that, as we evidenced, have continued to  
 253 the 2000-2020 period at the MARB.

254 **Table 2. Distribution of sites by trend likelihood and dominant land cover.**

<i>Dominant Land use</i>	<i>% of sites</i>	<i>Total area (km2)</i>	<i>% of sites for concentration trend categories</i>			<i>% of sites for yield trend categories</i>		
			<i>Likely Increasing</i>	<i>Likely Decreasing</i>	<i>No likely Trend</i>	<i>Likely Increasing</i>	<i>Likely Decreasing</i>	<i>No likely Trend</i>
<i>Varied (3)</i>	1.4%	4932.7	33.3%	33.3%	33.3%	100.0%	0.0%	0.0%
<i>Other (21)</i>	9.7%	3916307.8	42.9%	47.6%	9.5%	38.1%	38.1%	23.8%
<i>Pasture (14)</i>	6.5%	43315.2	35.7%	50.0%	14.3%	64.3%	21.4%	14.3%
<i>Urban (9)</i>	4.1%	3380.7	22.2%	77.8%	0.0%	22.2%	44.4%	33.3%
<i>Forest (60)</i>	27.6%	426003.9	43.3%	40.0%	16.7%	56.7%	38.3%	5.0%
<i>Cultiv. (109)</i>	50.2%	1092838.1	14.7%	73.4%	11.9%	25.7%	58.7%	15.6%
<i>Wetland (1)</i>	0.5%	2563.7	100.0%	0.0%	0.0%	100.0%	0.0%	0.0%

<b>MARB (217)</b>	<b>100%</b>	<b>5489342 *</b>	<b>27.7%</b>	<b>59.4%</b>	<b>12.9%</b>	<b>39.2%</b>	<b>46.95%</b>	<b>13.8%</b>
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*\*Total drainage area is larger than the MARB because there are overlapping drainage areas in basins with multiple monitoring locations. For instance, the drainage area of the Mississippi River at Thebes includes all the upstream basins, including the Missouri River at Herman*

255 Mean rates of change in FN nitrate-N concentration over the 2000-2020 period with respect to  
 256 the 2000 value ranged from -0.83% per year for cropland sites to +1.54% per year for a wetland  
 257 dominated watershed (Table 3). The Wetland category was based on one site, Snake River near  
 258 Pine city, MN, receiving drained water from 2563.7 km<sup>2</sup> of which 34.8% is wetlands, 34.1%  
 259 forest, 15.8% pastures, and only 8.8% is dedicated to cultivated crops (USGS, 2019). The FN  
 260 concentration for the beginning of the trends periods at this site was 0.195 mg/l, a relatively  
 261 small value compared to the average (2.8 mg/l) and the maximum (14.09 mg/l) values for all  
 262 217 trend sites. Although this site had an increase of the FN concentration, the large magnitude  
 263 of the relative change with respect to the 2000 value was mainly caused by the small initial FN  
 264 concentration. A substantial amount of literature has reported the property of wetlands in  
 265 reducing nitrate concentration and loads (Hansen et al., 2018, Lin et al., 2008, Cheng et al.,  
 266 2020, Jasper et al., 2014) hence result for this unique site is not representative of this land  
 267 cover and should be further investigated. Minimum and maximum rates of change of FN nitrate-  
 268 N concentration over the 2000-2020 period with respect to the 2000 for individual sites ranged  
 269 between -4.65% and 4.5% per year, occurring at sites with basins dominated by cultivated  
 270 cropland and forest land covers, respectively.

271 Mean rates of annual nitrate-N yield changes ranged from -183 kg N/km<sup>2</sup>-yr for cultivated  
 272 cropland sites to +143 kg N/km<sup>2</sup>-yr for urban sites. Minimum and maximum rates of change  
 273 ranged from -1,379 to 975 kg/km<sup>2</sup>-yr, occurring at sites with basins dominated by cultivated and  
 274 urban land covers, respectively.

### 275 5.3. Nutrient Supply and Streamflow Trend Components

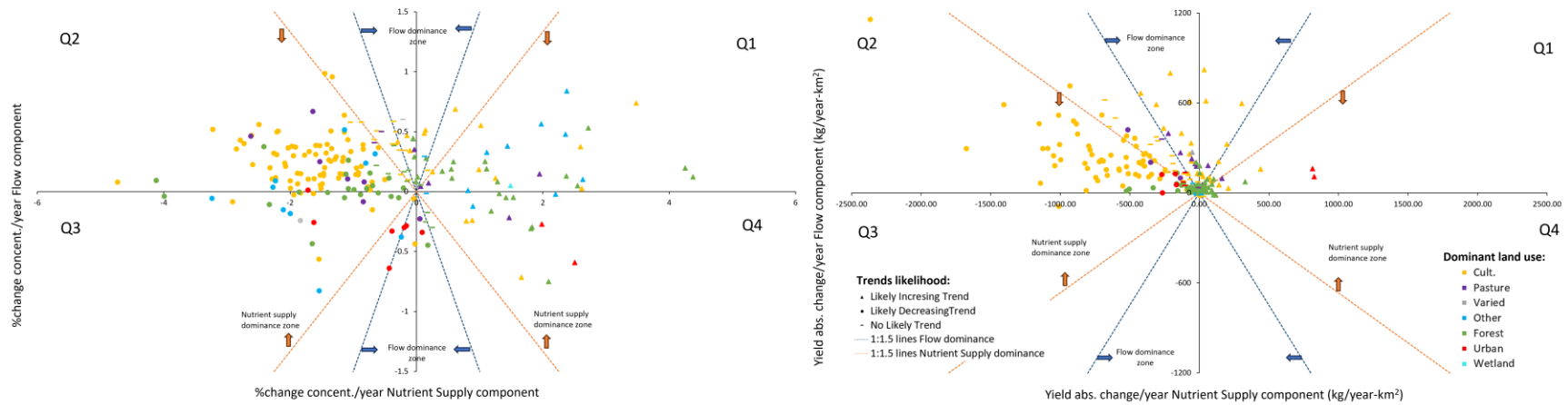
276 The nutrient supply component was the dominant factor at 79% of sites versus 11.5% of sites  
277 where streamflow component was the dominant factor in FN concentration changes (Figure 4,  
278 Figure A- 2). Most sites having a likely decreasing concentration trend had a dominance of the  
279 nutrient component. The change in the streamflow component was greater than zero for 74% of  
280 sites (Figure 4), indicating that increased flow had some role in changing nutrient loads. At some  
281 sites where the flow component was dominant, declining FN concentration (8 sites) may be the  
282 result of dilution from increased streamflow and the depletion of a limited supply (Murphy and  
283 Sprague, 2019).

284 The nutrient supply component of yield trends was dominant at 49.8% of sites while streamflow  
285 component was dominant at 25.3% of sites and mixed dominance was observed at the  
286 remaining 24.9% of sites (Figure 4, Figure A- 3). The change in streamflow component was  
287 greater than zero for 94% of sites. For many sites, there was evidence of declining FN nitrate  
288 yield despite an increased streamflow component (Q2 in Figure 4 and Table 4). These sites  
289 were predominantly found in the nutrient supply dominance zone (Figure 4). Only 2 sites with  
290 flow dominance had a likely decrease on yield trends, while 51 sites had a likely increasing  
291 trend. Our results agree with those reported by Murphy and Sprague (2019) for the contiguous  
292 U.S. in which the management component (equivalent to our nutrient supply component) was  
293 the dominant component for the majority of sites, with some more importance in the yield trends  
294 than in the concentration trends.

295

**Table 3. Mean, maximum and minimum nitrate-N trends for dominant land uses.**

	% change/year Total trend concent. (%/year)			% change/year NS trend comp. concent. (%/year)			% change/year SF trend comp.concent. (%/year)			abs. change/year Total trend Yield (kg/km <sup>2</sup> -yr)			abs. change/year NS trend comp. Yield (kg/km <sup>2</sup> -yr)			abs. change/year SF trend comp. Yield (kg/km <sup>2</sup> -yr)		
	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min
<b>Varied (3)</b>	-0.43	0.39	-2.08	-0.70	-0.05	-1.84	0.27	0.60	-0.24	92.116	220.816	5.090	-13.025	11.832	-51.653	105.141	272.469	4.345
<b>Other (21)</b>	0.11	3.22	-3.29	-0.01	2.63	-3.24	0.12	0.84	-0.83	1.630	48.393	-46.259	-5.292	28.041	-57.987	6.922	63.881	-10.435
<b>Pasture (14)</b>	-0.25	2.10	-2.16	-0.43	1.95	-2.62	0.18	0.67	-0.23	90.371	260.880	-145.698	-106.777	162.666	-513.811	197.148	421.740	33.242
<b>Urban (9)</b>	-0.33	1.91	-1.88	0.01	2.50	-1.72	-0.33	0.01	-0.64	142.921	974.841	-265.551	49.703	826.446	-269.659	93.218	161.764	0.000
<b>Forest (60)</b>	0.12	4.50	-4.03	0.08	4.37	-4.12	0.04	0.53	-0.75	8.594	404.905	-510.699	-28.636	329.698	-524.013	37.230	204.167	-13.088
<b>Cultiv. (109)</b>	-0.83	4.22	-4.65	-1.08	3.48	-4.73	0.25	0.99	-0.72	-182.572	902.155	-1378.930	-429.310	440.309	-2364.865	246.738	1158.301	-90.210
<b>Wetland (1)</b>	1.54	1.54	1.54	1.49	1.49	1.49	0.05	0.05	0.05	8.166	8.166	8.166	-1.705	-1.705	-1.705	9.871	9.871	9.871
<b>MARB (217)</b>	-0.40	4.50	-4.65	-0.55	4.37	-4.73	0.15	0.99	-0.83	-76.104	974.841	-1378.930	-229.089	826.446	-2364.865	152.986	1158.301	-90.210



**Figure 4. Nutrient Supply component vs Flow component for nitrate-N concentration and yield trends. Markers and colors represents the trend likelihood and dominant land use category, respectively.**



**Table 4. Percentage of sites by trend likelihood per quadrant in Figure 4**

	<i>Concentration trend categories (% of sites)</i>				<i>Yield trend categories (% of sites)</i>			
	Likely Increasing	Likely decreasing	No likely trend	Cumulative Quadrant	Likely Increasing	Likely decreasing	No likely trend	Cumulative Quadrant
<b>Q1</b>	16.13%	0.00%	1.38%	17.51%	23.96%	0.00%	0.00%	23.96%
<b>Q2</b>	3.69%	43.32%	9.68%	56.68%	13.82%	43.32%	12.90%	70.05%
<b>Q3</b>	0.00%	14.75%	0.00%	14.75%	0.00%	2.76%	0.00%	2.76%
<b>Q4</b>	7.83%	1.38%	1.84%	11.06%	1.38%	0.92%	0.92%	3.23%

## 5.4. Correlation Analyses

FN concentrations and yields in 2000 tended to be greatest in watersheds dominated by cultivated cropland, and there was a tendency for these high concentrations and yields to decline by 2020, with some exceptions (Figure 5). Crawford et al. (2019), analyzed nitrate trends in MARB subbasins from 2002 to 2012 and also reported a decline in yield from the basins that initially had the largest yields, but they did not incorporate land cover and trends components in their analysis as they were only considering the stationary flow normalized data, that corresponds to the nutrient supply component of our analysis. We found that, although basins with the largest 2000 concentration and yield values experienced the largest reductions in the nutrient supply component for yield trends ( $r=-0.6$  and  $-0.77$ , respectively), these basins also had the largest increases in the streamflow trend component ( $r=0.71$  and  $0.7$ , respectively) (Figure 6). Increases on the streamflow component were buffered by the magnitude of the nutrient supply component decreases, producing a total decreasing effect.

FN concentrations and yields in 2000 were positively correlated ( $r = 0.67$  and  $0.70$ , respectively) with the percentage of cropland land cover in 2001. Changes in total nitrate yield, nutrient supply component and streamflow component from 2000 to 2020 were statistically ( $p<0.05$ ) correlated ( $r = -0.39$  and  $-0.61$ , and  $+0.57$ , respectively) with cultivated cropland cover in 2001 (Figure 6). The basin area feature had no significant correlations other than a weak correlation



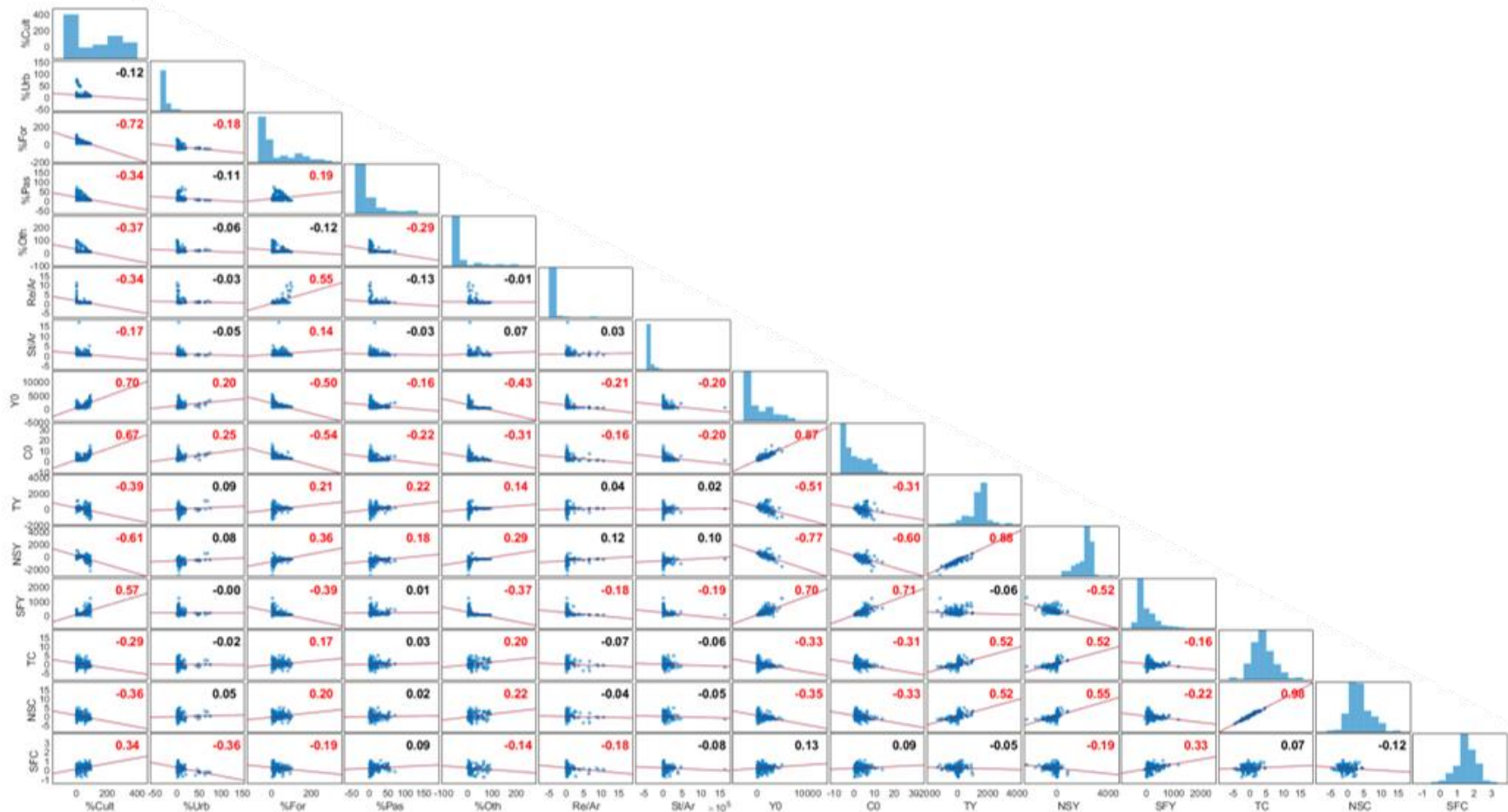


Figure 6. Pearson correlation matrix for watershed features (Table A- 1) and changes on TP concentration (relative) and yield (absolute). Coefficient values in red are statistically significant ( $p < 0.05$ ).

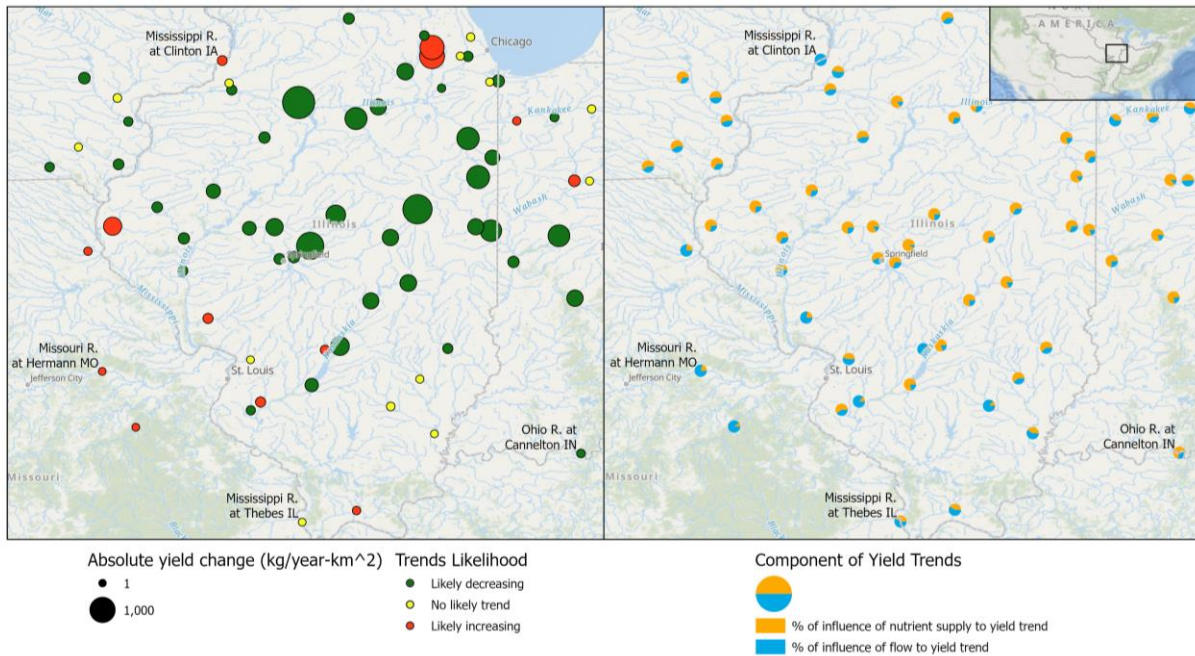
## 5.5. Mississippi River and Major Tributaries

There was a high likelihood of increased ( $\sigma \geq 0.9$ ) FN nitrate yield at the Mississippi River at Clinton, Iowa (Table 5). Several of the smaller sites upstream of Clinton also had increasing nitrate yield trends. The cluster of sites in the north central portion of the MARB that had decreased FN nitrate yield trend mostly contributed flow and load downstream of Clinton and upstream of Thebes, as does the Missouri River at Herman, MO, which had a likely increased yield trend. The increased loads at Clinton, IA and Herman, MO and perhaps some smaller tributaries appeared to offset the reduced loads from the north central cluster so that there was not a detectable trend at Thebes, IL. A similar phenomenon was reported by Crawford et al. (2019) for the 2002-2012 nutrient trends analysis at the MARB, in which load reductions at the Upper Mississippi and Ohio Rivers were offset by increasing loads and other parts of the basin, resulting in a near zero net change downstream.

There was a highly likely downward ( $\sigma \leq 0.1$ ) trend in the Ohio River at Cannelton, IN a tributary that joins the Mississippi River downstream of Thebes, IL (Figure 7). For all four of these sites, the nutrient supply component was zero or less, while the streamflow component was greater than zero (Table 5). Only at Ohio R. at Cannelton, IN, these decreases in the nutrient supply component contributed to a highly likely reduction in the total Nitrate-N yield trend, where the percent influence of the nutrient supply component was larger than the streamflow component (Figure 7).

**Table 5. Nitrate-N yield trend results for two Mississippi River mainstem sites and two major tributaries.**

<i>Location</i>	<i>Yield trend</i>			
	<i>Total trend (kg N/yr km<sup>2</sup>)</i>	<i>Likelihood</i>	<i>Nutrient supply component (kg N/yr km<sup>2</sup>)</i>	<i>Streamflow component (kg N/yr km<sup>2</sup>)</i>
<i>Mississippi R. at Clinton IA</i>	126.3	High+	0.00	126.30
<i>Missouri R. at Hermann MO</i>	12.56	Likely+	-4.36	16.92
<i>Mississippi R. at Thebes IL</i>	17.87	Unlikely	-46.02	63.88
<i>Ohio R. at Cannelton IN</i>	-75.63	High-	-127.37	51.75



**Figure 7. Location of Mississippi River mainstem and two major tributary sites.**

## 6. Uncertainties and limitations

Flow normalized concentrations and yields are estimates of values that are hypothetically expected to occur under “normal” flow conditions based on past statistical probabilities, not on mechanistic modeling of the interactions of concentration and flow. Since flows are rarely “normal” (however normal is defined), FN concentrations and loads may differ substantially from actual concentrations and loads in a given year, which are causes of eutrophication and are the targets of nutrient reduction efforts. Flow normalization can be useful in estimating relative impacts of changes in hydrology versus other factors, but these estimates should be understood as estimates of hypothetically “normal” conditions.

Trend period selection can impact the trends magnitude and direction, since trends are estimated as the difference in concentration and yield between initial and final years. The identification of long-term flow variations and their impacts in the trends results might be

impacted if the trends period is not long enough to discern random variations from non-stationary flow variability, especially at sites with extreme flow events.

Analysis of factors influencing riverine nutrient trends is limited by available data and resources. Data such as fertilizer and manure applications and crop nutrient uptake are undergoing a process of updating and refinement that is expected to be completed in 2025. These updated data should be incorporated into future studies of factors influencing riverine nutrient trends.

## 7. Summary and Conclusions

Screening and harmonization of nitrate concentration and associated streamflow data in the MARB resulted in 217 sites where annual FN concentrations and yields were calculated and 2000-2020 trends evaluated. Most of the watersheds dominated by cultivated cropland presented evidence of high concentrations and yields in 2000 and likely downward trends in concentration and yields over the subsequent 20 years. Many of these sites were located in the north-central portion of the basin. These reductions appear to have been offset by increased nitrate yields from the Mississippi River drainage area upstream of Clinton, Iowa and the Missouri River above Herman, MO, and other tributaries resulting in no detectable change in nitrate yield at the Mississippi River at Thebes, IL. There was a highly likely decline in nitrate yield from the Ohio River upstream of Cannelton, IN. Nitrate-N yield reductions from cropland watersheds may have been due to improved N fertilizer use efficiency, although this deserves further investigation. Causes for the increased nitrate yields upstream of Clinton, IA and in the Missouri River, basin also deserve further investigation.

For the majority of sites, the nutrient supply component was more dominant than the stream flow component for both yield and concentration. Most sites having likely decreasing concentration or yield trends had a dominance of the nutrient supply component. Some sites where the flow component was dominant, declining FN concentration (8 sites) may be the result

of dilution from increased streamflow and the depletion of a limited N supply. Only 2 sites with flow dominance had a likely decrease on yield trends, while 51 sites had a likely increasing trend.

## 8. Data Availability

Sites information and detailed results of FN concentration and loads will be made available at the Great Lakes to Gulf Virtual Observatory web site (<https://greatlakestogulf.org/nutrient-trends>).

## 9. Acknowledgments

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## 10. Annexes

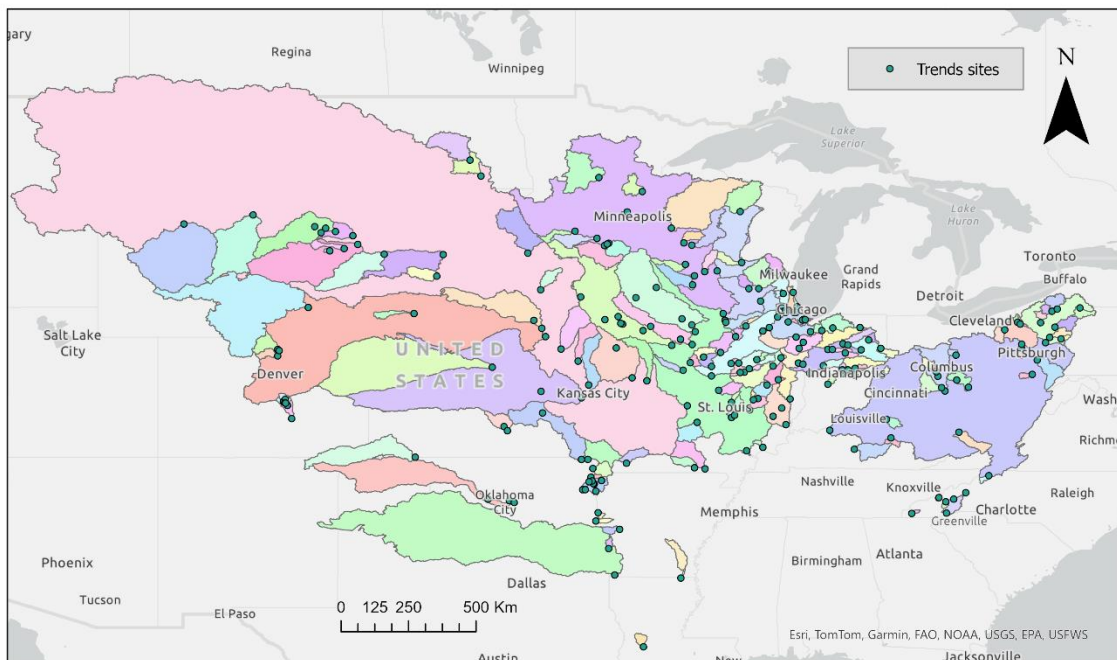
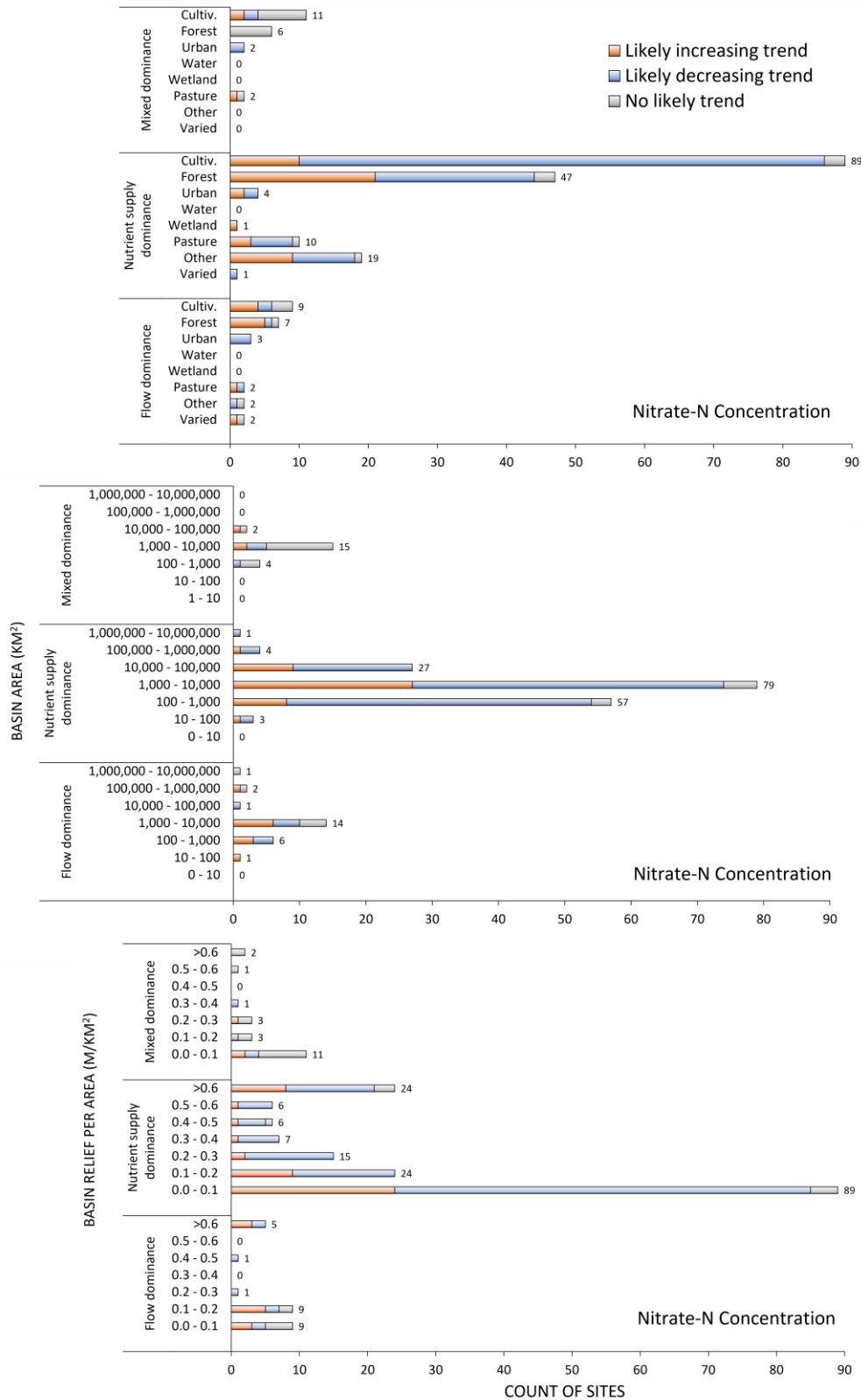
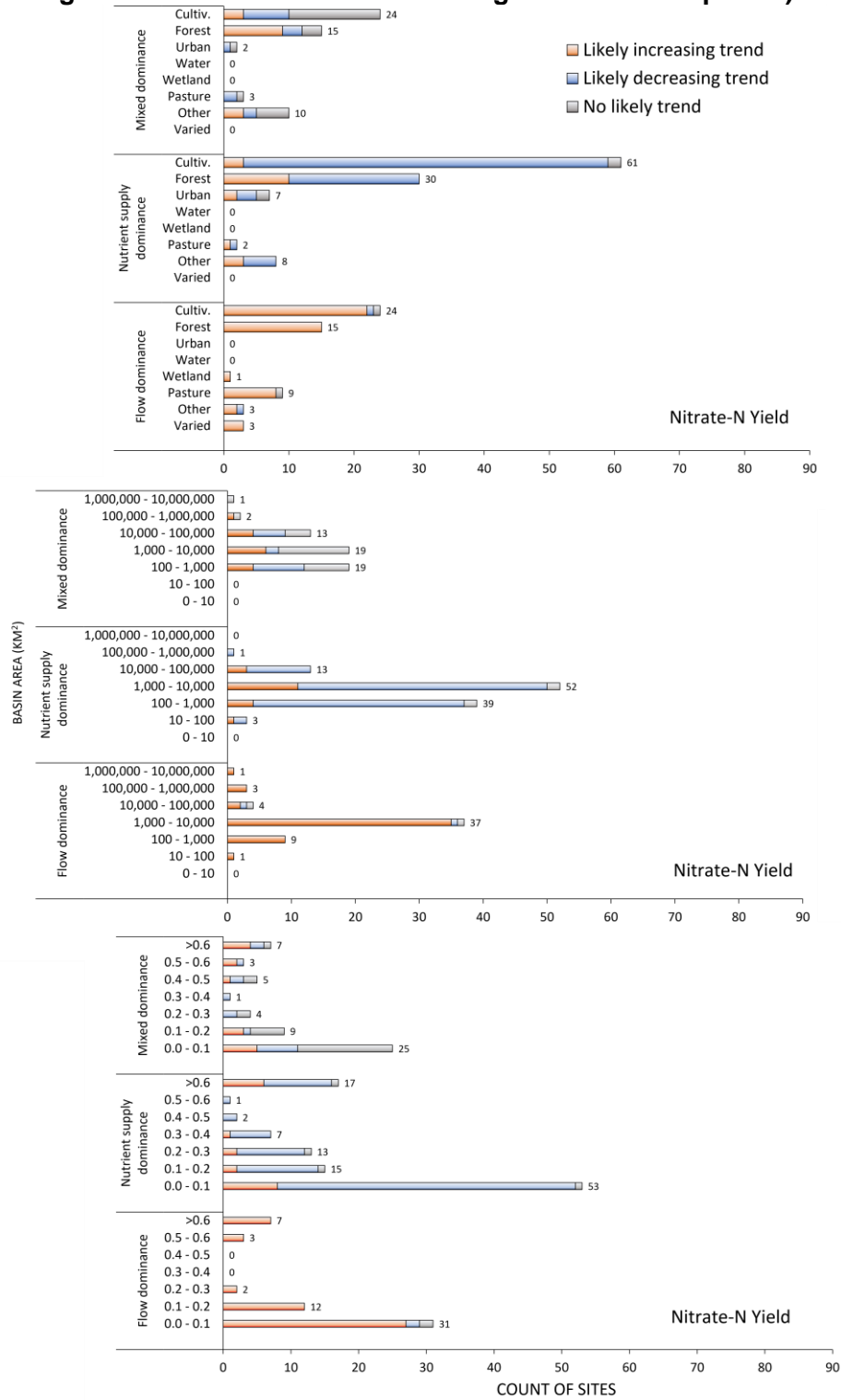


Figure A- 1. Basins and monitoring locations of the 217 n sites analyzed in this study.





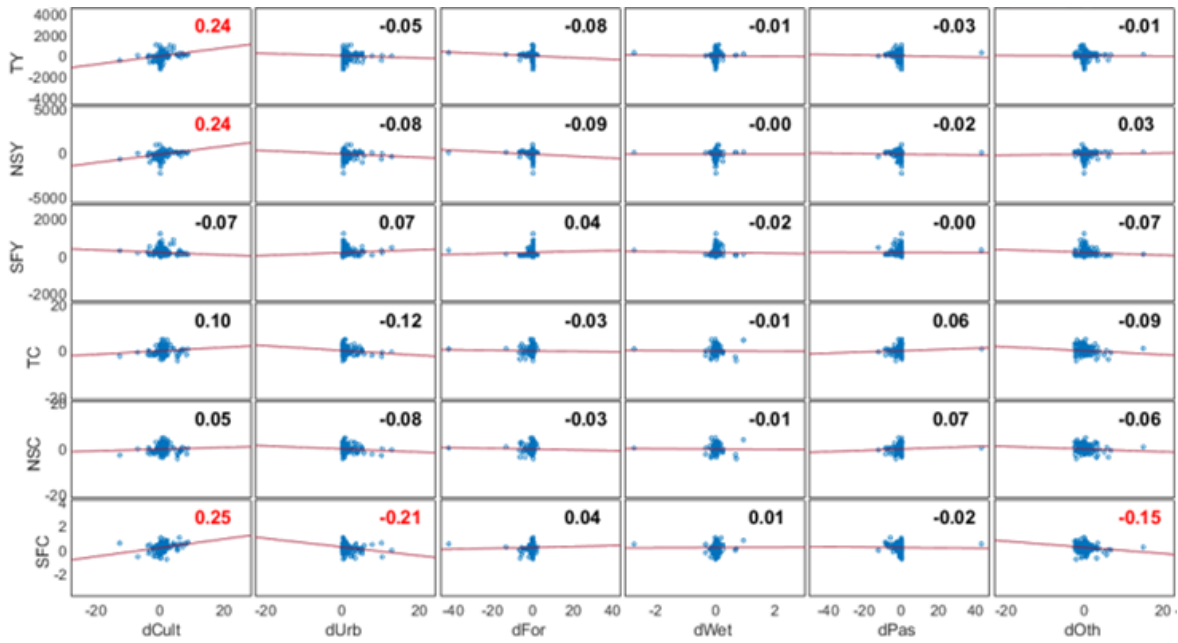
**Figure A- 2. Number of trends sites per dominant concentration trend component and dominant land use, basin area and relief per area ranges. (*Varied* land use indicates a change of the dominant land use during the 2000-2020 period).**



**Figure A- 3. Number of trends sites per dominant yield trend component and dominant land use, basin area and relief per area ranges. (*Varied* land use indicates a change of the dominant land use during the 2000-2020 period).**

**Table A- 1. Abbreviations used in correlation matrices.**

<i>Variable</i>	<i>Abbreviation correlation matrix</i>
<i>dif2001-2019Cult. (%)</i>	dCult
<i>dif2001-2019Urban (%)</i>	dUrb
<i>dif2001-2019Forest (%)</i>	dFor
<i>dif2001-2019Wetland (%)</i>	dWet
<i>dif2001-2019Pasture (%)</i>	dPas
<i>dif2001-2019Other (%)</i>	dOth
<i>PercCu2001 (%)</i>	%Cult
<i>PercUr2001 (%)</i>	%Urb
<i>PercFo2001 (%)</i>	%For
<i>PercPa2001 (%)</i>	%Pas
<i>PercOth2001 (%)</i>	%Oth
<i>Area (Km<sup>2</sup>)</i>	Ar
<i>Relief per area unit (m/Km<sup>2</sup>)</i>	Re/Ar
<i>Upst. dam storage&lt;2013/trend site drainage area (m<sup>3</sup>/Km<sup>2</sup>)</i>	St/Ar
<i>2000 FN Yield (kg/km<sup>2</sup>*yr)</i>	Y0
<i>2000 FN Conc (mg/L)</i>	C0
<i>abs. change/year Total trend Yield (kg/km<sup>2</sup>*yr)</i>	TY
<i>abs. change/year NS trend comp. Yield (kg/km<sup>2</sup>*yr)</i>	NSY
<i>abs. change/year SF trend comp. Yield (kg/km<sup>2</sup>*yr)</i>	SFY
<i>% change/year Total trend concent. (%/year)</i>	TC
<i>% change/year NS trend comp. concent (%/year)</i>	NSC
<i>% change/year SF trend comp.concent. (%/year)</i>	SFC



**Figure A- 4. Pearson correlation matrix of percent change of land use area (Table A- 1) vs. changes in yield (absolute) and concentration (relative to 2000 values) for the 2000-20 period. Coefficient values in red are statistically significant ( $p < 0.05$ )**

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