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PRIMARY RESEARCH PAPER

Water quality at the end of the Mississippi River for 120 years: the agricultural imperative

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Abstract Archived water quality data collected between 1901 and 2019 were used to reconstruct annual averages of various forms of C, N, P, and silicate concentrations and alkalinity in the lower Mississippi River. During this interval the average annual nitrate concentrations doubled pre-dominantly from fertilizer applications and tiling, silicate concentrations decreased by half as diatom sedimentation increased as dams were built, and alkalinity increased 16%. Variances in silicate concentrations were proportional to river discharge before 1980 and concentrations have been stable since then. Average annual temperatures, discharge and alkalinity increased simultaneously around 1980; this suggests that there was greater weathering thereafter and is supported by the positive relationships between variations in alkalinity and variations in nitrate, phosphate, and silicate concentrations. The conversion of forests and grasslands into farmlands and improved drainage resulted in less evapotranspiration, a higher percent of precipitation going into streams and altered soil water bio-geo-chemistries. Field trials demonstrating soil health improvements resulting from more live roots and soil cover and greater biodiversity demonstrate water quality improvements and no effect on farm profitability. Lowering nitrate loading to the coastal waters will reduce summertime hypoxic waters formation offshore, but alkalinity in the river will increase further with climate warming.

Keywords Water quality · Alkalinity · Mississippi River · Soil carbon · Climate change

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> "In every respect, the valley rules the stream"
>
> Hynes (1960)

Introduction

Water quality impairments in the world's rivers noticeably declined in the last century with chemical and microbial contamination, and pH declines (Meybeck, 2003), including in the United States (US) where 200 years of colonization and population growth resulted in plowed fields replacing forests, impervious surfaces covering 6.4% of the land, and 90,000 dams being built (https://nid.sec.usace.army.mil/ords/f?p=105:22:4482115045565::NO; Turner & Rabalais, 2003; Stets & Striegl, 2012; Homer et al., 2015; Yin et al., 2023). Agricultural land uses influenced nitrate concentrations in the Mississippi River watershed by the early 1900s—a half century before the use of artificial fertilizer (Broussard & Turner, 2009) and waterways became both a recipient of waste and a drinking water source. The initial growth in farmed acreage in the contiguous states plateaued at 1.4–1.5 million km^2 between 1960 and 1980, fewer new dams were constructed thereafter, and the growth in nitrogen and phosphorus fertilizer use slowed (Fig. S1). The nitrogen and phosphorus sources in this watershed today are geographically centered in the US midwestern states (Alexander et al., 2008) where intense fertilization and drainage of corn and soybean fields are located (https://nassgeodata.gmu.edu/CropScape/; Jaynes & James, 2007; Figs. S2, S3, and S4).

Some water quality improvements occurred by the late 1900s as sewerage treatment expanded after the 1972 Clean Water Act and related legislation was implemented; bacterial densities and lead concentrations declined, oxygen saturation rose, and pH increased from a monthly low of 5.8 in 1965 to 8.2 in 2019 (Turner, 2021). However, the concentrations of other constituents increased and by the 1980s the nitrogen loading from the Mississippi River caused the formation of the largest hypoxic zone in the western Atlantic Ocean; its size in late July/early August is predicted by the May nitrogen loading from the Mississippi River (Turner et al., 2012; Scavia et al., 2017).

A clearer understanding of the relationships among land, water, atmosphere, climate and a people's history is coming into focus as this watershed has become dominated by human-centered enterprises. New and future water quality stressors include global scale changes affecting water availability, temperature, storm frequency and intensity, and flooding, etc., driven by rising concentrations of greenhouse gases (GHGs) in the atmosphere (IPCC, 2021). Increasing soil carbon this century is a seen as a significant modulator of global climate changes (Six et al., 2004; Bai & Cotrufo, 2022; Chabbi et al., 2022). The interplay of forces within and between ecosystems are becoming recognized more explicitly, sometimes addressed in parts, and now considered more often as existing within a panoply of conditions, including acknowledgment of unknowns.

Here I ask how water quality changed over the last one hundred and twenty years of agricultural intensification in the Mississippi River watershed and then focus on the last few decades of relatively stable land use and a changing climate. It is the largest watershed on the North American continent, drains 41% of the conterminous US, and brings 80% of the river water entering the Gulf of Mexico from the US, and 91% and 88% of the nitrogen and phosphorus, respectively (Dunn, 1996). The USGS estimate of land cover in the watershed in 2001 is based on land use/land cover classifications systems designed specifically for use with remotely sensed imagery (https://edna.usgs.gov/watersheds/ws_chars.php?title=Mississippi&name=mississippi). These data showed that landcover in the watershed in 2001 was approximately 36.2% cropland and pasture, 24.9% grassland and sedges, 21.9% forest, 6.8% shrubland, 5.3% urban, 4.5% water, and 0.3% barren (bare rock/sand/clay or quarries). The watershed has a robust water quality data base, a capable research community, and consequential economic and social capital. I use archived water quality data collected from 1901 to 2019 from Federal and State agencies, the New Orleans Sewerage and Water Board (NOSWB), and universities to reconstruct a 100+ year record of some indicators of water quality in the lower Mississippi River. The analytical focus is on the alkalinity, and the concentration of various forms of carbon, nitrogen, phosphorus, and silica. It concludes with a discussion of national policies and future possibilities for agriculture and climate change adaptations.

Methods

Water quality archival data

Water quality data are from five locations on the southern end of the Mississippi River at St. Francisville, Baton Rouge, two locations in New Orleans, and at Belle Chasse, LA, located 428, 370, 167, 153, and 122 km, respectively, upstream from the Head-of-Passes where the river divides into three main outlets to the Gulf of Mexico (Fig. 1). The two major metropolitan areas are Baton Rouge and New Orleans (ca. 830 thousand and 1270 thousand people in 2020, respectively). The Belle Chasse station is associated with a ferry crossing, and the New Orleans samples are from river water intake pipes at the Carrollton and Algiers water treatment plants bringing drinking water to the New Orleans area.

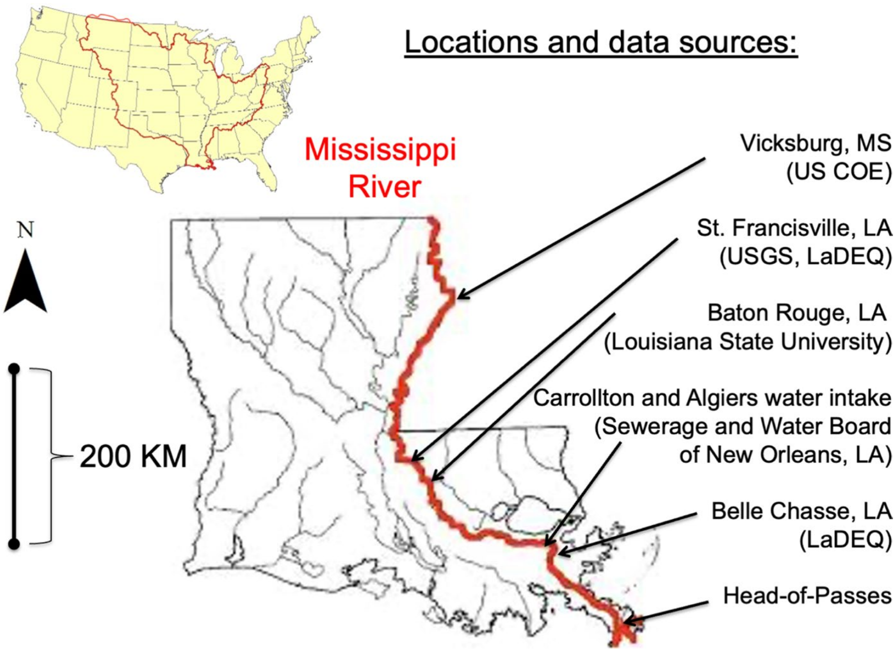

Fig. 1 Location map of sampling stations and data sources. The Mississippi River watershed is outlined in the map of the United States in the upper left. The Mississippi River sampling stations are at: (1) St. Francisville, LA [United States Geological Survey (USGS) and Louisiana Department of Environmental Quality (LaDEQ)]; (2) Baton Rouge, LA (this study); (3) New Orleans, LA (NOSWB sampling at Carrollton and Algiers water intakes); and, (4) Belle Chasse, LA (LaDEQ)

The Louisiana Department of Environmental Quality (LaDEQ) sampling occurred at two locations: St. Francisville (LaDEQ stations 9, 55, 318, and 4031), and Belle Chase (LaDEQ stations 51, 52, and 320). The LaDEQ stations were sampled from 1966 to the present.

The United States Geological Survey (USGS) reported water quality data at St. Francisville, LA, in Water Supply Papers (WSP) from 1954 to 1998. These WSP data begin before the LaDEQ data collections started in 1968 and overlap with the LaDEQ data. The USGS provided a flow-averaged estimate of monthly loadings and concentrations for the Mississippi River from 1968 to 2015 using a Loadset formulation (Runkel et al., 2004); these data no longer exist on the web but are in a data repository (Table 1). The monthly estimates of loading in each calendar year were summed to calculate the annual load,

Table 1 Data sources used in the analysis

Year(s)	Data description	Data provider/location
1817–2019	Water discharge at Vicksburg, MS	https://doi.org/10.5061/dryad.1jwstqjzb
1901, 1909–2020	Alkalinity	New Orleans Sewerage and Water Board Annual Reports
1901	Nitrate and silicate	Sewerage & Water Board (1903)
1905–06	Nitrate and silicate	Dole (1909)
1915	Nitrate	McHargue & Peter (1921)
1930	Nitrate	Wiebe (1931)
1950–2007	Suspended sediments	Meade & Moody (2010)
1954–1998	Dissolved inorganics and total C, N, and P	USGS WATER SUPPLY PAPERS
1966–2019	Dissolved inorganics and total C, N, and P	Louisiana Department of Environmental Quality (https://waterdata.deq.louisiana.gov/)
1968–2018	Dissolved inorganics and total C, N, and P	USGS (http://toxics.usgs.gov/hypoxia/mississippi/flux_ests/delivery/index.html)
1996–2018	Dissolved inorganics and total C, N, and P	Turner (2021) (https://doi.org/10.5061/dryad.x95x69pkm)
1901–2020	Average annual temperatures in the contiguous states of the US	https://www.epa.gov/climate-indicators

and the concentration calculated by dividing loads by discharge. A newer interpretation of the same USGS data are for 1968 through 2021 using a flow-normalized concentration and loads described by Lee (2022; https://www.sciencebase.gov/catalog/item/629e0d14d34ec53d276f6960). This more recently developed flow-normalized method adjusts for variations of concentration with discharge among many years and infrequent sampling using weighted regressions on time, discharge, and season (WRTDS) with Kalman filtering (WRTDS–K) methods (Lee et al., 2017). These estimates use multiple years to compute discharge-concentrations relationships and so there is a reduction in the variation from 1 year to the next (Fig. S5). For this reason, the WRTDS flow-normalized data were not used when trends in the annual variations were being investigated, but were used in the discussion of reductions in nitrate loading to meet the goals of the Hypoxia Action Plan of 2001 (Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2001) because that model's output is used as a metric of success.

The water quality instruments, and analytical methods used for samples collected at Baton Rouge, LA, from 1996 to 2018, are described in Turner et al. (2019). Briefly, water samples were collected at least once monthly, and up to five times per month during spring and summer. Unfiltered water samples were frozen until determination of dissolved forms of nitrogen (N), phosphorus (P), and silicate (DSi) using either a Technicon Autoanalyzer II (USEPA Method 353.2 for ammonia and nitrate/nitrite (DIN), USEPA Method 365.2 for phosphate (DIP), and Technicon Method 186-72W/B for DSi) or a Lachat Quick-Chem 8000 Flow Injection Analyzer using the Lachat Methods approved by USEPA: method 31-107-06-1-B for ammonium, method 31-107-04-1-C for nitrate/nitrite, method 31-115-01-1-H for phosphate (DIP), and method 31-114-27-1-C for DSi. A 5-point standard curve was used and QC standards were analyzed before, during and after each set of samples analyzed. Total nitrogen (TN) and total phosphorus (TP) concentrations were measured using a Technicon Autoanalyzer II or LaChat Quick-Chem after persulfate wet oxidation digestion (Raimbault et al., 1999). The concentration of total carbon (TC) was measured using a Shimadzu® TOC-5000A Analyzer. Total organic carbon (TOC) was measured by acidifying samples with HCl and then sparging before analysis to remove the inorganic carbon (IC). The Coefficient of Determination for the standard curve was > 0.98 for all nutrient analyses. The data are at https://doi.org/10.5061/dryad.x95x69pkm.

Miscellaneous other water quality data used

There are four data sources for nitrate concentrations and one of silicate concentrations that were made in the early 1900s. McHargue & Peter (1921) measured nitrate in one sample from the Mississippi River at Baton Rouge in spring, 1915. Wiebe (1931) collected 15 surface water samples from the river at Baton Rouge in 1930. Wiebe reported minimum and maximum nitrate concentrations of 0.82 and 14.74 µmol l^{-1}, respectively, and the average value was used here (7.78 µmol l^{-1} nitrate). Dole (1909) report water quality measurements of dissolved silicate and nitrate concentrations for 1905 and 1906 at the New Orleans water intake pipe. The NOSWB (Sewerage and Water Board, 1903) made measurements of nitrate in 1901 at the same intake pipe.

Normalized values of silicate, nitrate, phosphate, and alkalinity

A 3-year running average of the concentrations for nitrate and silicate from the USGS data (1974–2015) was supplemented by samples collected in Baton Rouge from 2016 to 2018, inclusive. The alkalinity data were compared to a similar calculation for alkalinity using the NOSWB alkalinity data and LaDEQ data for 2006 to 2015. The values were then converted to a proportion of the average value over the entire record so that the normalization yielded an average value = 1.0. The monthly average bicarbonate concentration (mg C l^{-1}; µmol $l^{-1} \pm 1$ SE) was converted to carbon as described by Raymond et al. (2008). They calculated that the inorganic carbon represented in alkalinity titrations is mostly from bicarbonate, with little contribution from carbonate in the well buffered Mississippi River. Raymond et al. (2008) used temperature and pH measurements from the Mississippi River to estimate that on average ~ 93% of total dissolved inorganic carbon (CO_2, HCO_3^-, CO_3^{-2}) is in the form of HCO_3^-, with the remaining 7% being mostly CO_2. The bicarbonate flux, therefore, captures the majority of the fluvial export of DIC that is not evaded to the atmosphere.

River discharge

The annual discharges of the Mississippi River at Vicksburg, MS, from 1900 to 2019 are for daily measurements made by the United States Army Corps of Engineers (USACE) but are found in two different report series. I used two sources of the daily river discharge data that have overlapping data records with annual data. The annual discharge data at Vicksburg extends from 1817 to 2021 and are in the Mississippi River Commission (1955). These data were compared to the second dataset derived from the daily discharge records available at the USGS website (https://waterdata.usgs.gov) under the State tab for 'current conditions,' then 'daily discharges,' and then 'time series' tabs. The data are in Turner (2022; https://doi.org/10.5061/dryad.1jwstqjzb) and used to plot discharge versus silicate concentrations.

Suspended sediments

Meade & Moody (2010) report results from isokinetic point sampling at five depths along each of 5 to 8 verticals across the Mississippi River at Tarbert Landing that were paired with sediment-discharge values every 2 weeks from calendar year 1950 to 2007. Daily discharge values of suspended sediments were used to determine annual fluxes. The annual tons were normalized to the highest concentration year (1950). The data were used to test the hypothesis that impoundment influences silicate retention as a result of improvements in light conditions and longer residence time that favors phytoplankton that sink behind dams to sequester the silica in diatom frustrules (Humborg et al., 2000).

Annual temperatures

The United States Environmental Protection Agency website 'Climate Change Indicators' https://www.epa.gov/climate-indicators) has the average annual air temperatures in the 48 contiguous States and the deviations from the long-term average from 1901 to 2020 (anomalies). The source data is from weather station and updated in July 2022. Details about the data analysis are in USGCRP (2017).

Summary of data set sources

The data set (Table 1) includes alkalinity, inorganic nitrate, ortho-phosphate (phosphate), silicate (DSi), total phosphorus (TP), total nitrogen (TN), inorganic and organic carbon, suspended sediment, temperature, and discharge. Some samplings resulted in multiple data collections for each month and some months had only one sample. Multiple values for 1 month were combined and an average value for the 12 months made to determine an average and standard error for each year.

Statistics

I used Prism Version 10.0.0 (131), June 13, 2023 software for Mac (GraphPad Software, Boston, Massachusetts USA, www.graphpad.com for statistical analyses where significance $P = 0.05$ and to compute an annual average and standard error. Regression slopes for different intervals tested the null hypothesis that the slopes were identical (the lines are parallel) by comparing slopes to calculate a P value (two-tailed test) determining if the chance that randomly selected data points had slopes that were different. Log transforms were made for graphing purposes. Data were fit to a spline/Lowess analysis with three knots to identify the inflection point where the discharge rates went from a declining to an increasing rate.

Results

Discharge and alkalinity

The river discharge at Vicksburg, MS, was not correlated with year from 1900 to 1979 but significantly increased with year from 1980 to 2019 [Discharge (km^3 year^{-1}) = 4.07*Year − 7521 ($R^2 = 0.14$, $F = 5.98$, $P = 0.02$)]. The slopes for before and after 1980 were different (Fig. 2A; $F = 3.93$, DFn = 1, DFd = 116; $P = 0.0498$) (Fig. 2A).

The average annual temperature anomaly in the lower 48 States was not correlated with year from 1900 to 1979 but was significantly related with year from 1980 to 2019 [Anomaly (°C) = 0.0256*X − 50.71 ($R^2 = 0.33$, $F = 19.7$,

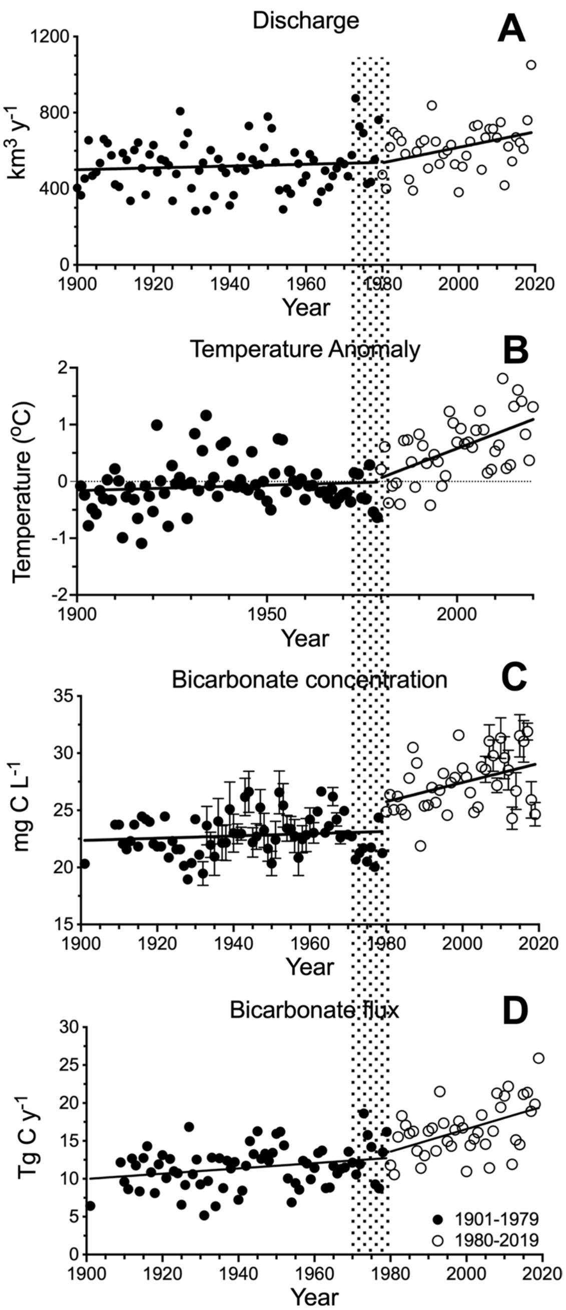

Fig. 2 River discharge, temperature anomaly, bicarbonate concentration, and bicarbonate flux in the lower Mississippi River from 1901 to 1979, and 1980 to 2020. **A** The average discharge for each year in the main stem of the Mississippi River below St. Francisville, LA (at Tarbert Landing, MS); **B** The average annual temperature in the 48 contiguous states; **C** The annual average bicarbonate concentration (mg C l^{-1}; μmol $l^{-1} \pm 1$ SE) at New Orleans, LA; **D** The annual bicarbonate flux (Tg C $year^{-1}$). The shaded vertical bar is the 1970 to 1980 interval

$P<0.001$)]. The slopes for before and after 1980 were different ($F=16, 5$, DFn = 1, DFd = 117; $P<0.001$) (Fig. 2B).

The simple linear regression of the bicarbonate C concentration (mg l^{-1}) versus year was also not significant for the years 1900 to 1979 but was from 1980 to 2020: Concentration = 0.0849–140.5 ($R^2=0.16$, $F=7.17$, $P=0.01$). The slopes for bicarbonate C concentration for before and after 1980 were different ($F=6.51$, DFn = 1, DFd = 108; $P=0.01$) (Fig. 2C). Alkalinity increased 16% from 1900 to 1920.

The annual bicarbonate flux (TgC $year^{-1}$) increased slightly from 1900 to 1979 ($Y=0.0346*year-55.8$; $F=5.36$, DFd = 70, $P=0.02$), and even more so after 1979 ($Y=0.1477*year-278.8$; $F=12.1$, DFd = 38; $P=0.02$) and there was a difference in the two slopes ($F=7.32$, DFn = 1, DFd = 108; $P<0.01$). The averaged bicarbonate C flux was 41% higher in 2019 than in 1980 (Fig. 2D).

Similarities among different observations

There is good agreement, in general, between the annual average annual concentrations of DSi, nitrate, and phosphate calculated from the different data sources for the same analyte when compared to the flow-normalized values calculated by the USGS (Fig. 3). The concentrations of nitrate and silicate (Fig. 3A, B), in particular, had an R^2 value of 0.99 and small intercept, but the $R^2=0.29$ for annual phosphate concentrations at Baton Rouge, LA. The silicate:nitrate ratios are in agreement with the USGS values, but there were two values from the NOSWB that appear as outliers (Fig. 3D). The annual total phosphate concentrations for samples collected at New Orleans by the LaDEQ and at St. Francisville by the USGS were not significantly related to concentrations calculated using the flow-normalized USGS estimates, whereas the concentrations at Baton Rouge were significantly related to the flow-normalized USGS estimates. The concentrations of total nitrogen at Baton Rouge were 11% lower than the concentrations determined using the flow-normalized USGS data (Fig. 3F).

The concentration of DSi increased slightly from 1901 to 1960, decreased after 1960 and became relatively stable by 1980 at about half of the concentration in the beginning of the 1900s (Fig. 4A). The nitrate concentration increased from the beginning

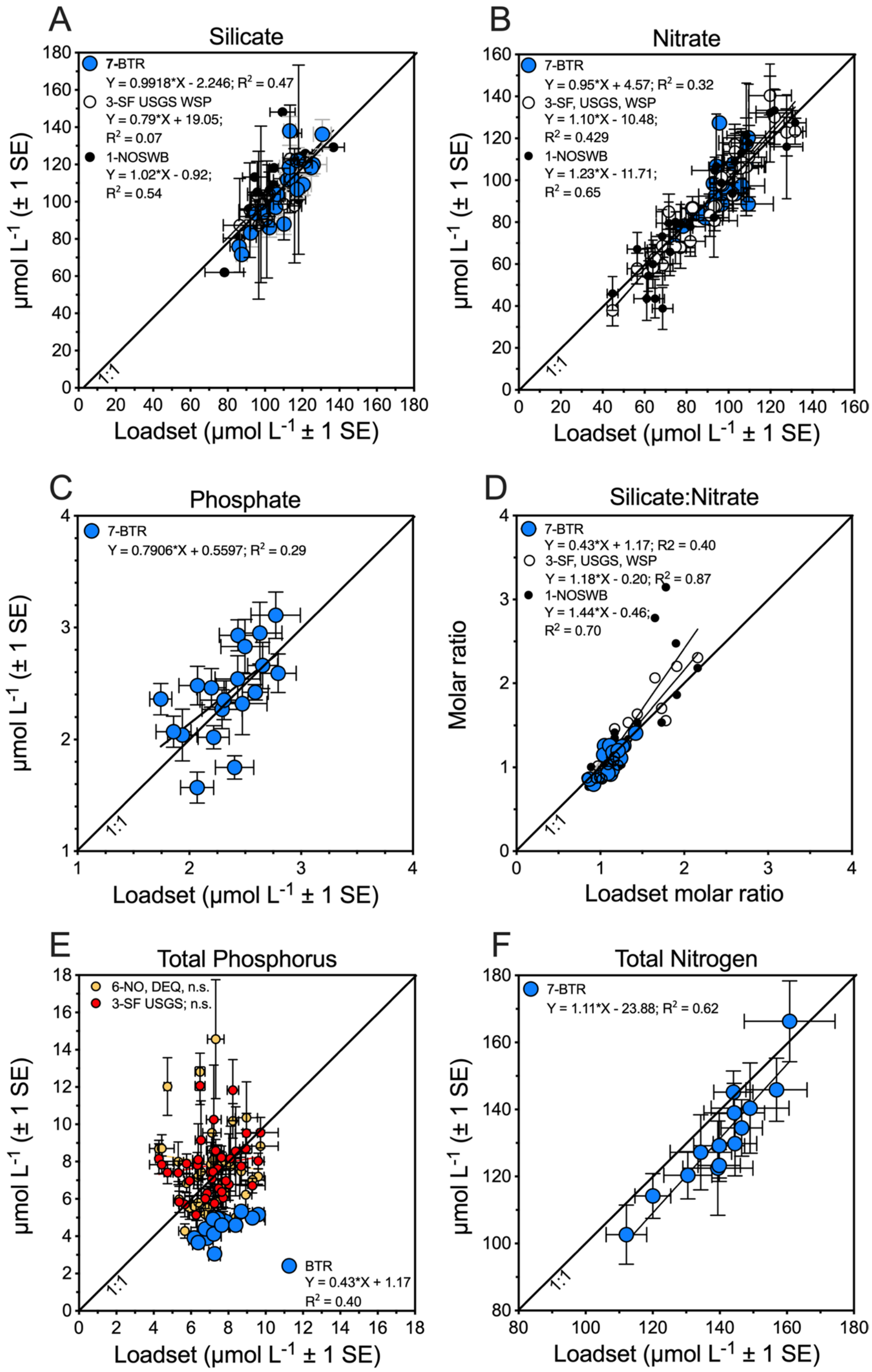

Fig. 3 The annual concentrations (μmol $l^{-1} \pm 1$ SE) of inorganics, total N, total P, and the silicate:nitrate molar ratio in the lower Mississippi River compared to the annual flow-normalized USGS values at St. Francisville, LA. **A** silicate, **B** nitrate, **C** phosphate, and **D** silicate:nitrate molar ratio, **E** total phosphorus, and **F** total nitrogen. The numberings for data sources are: 1 = NOSWB sampling at the Carrollton and Algiers water intakes; 3 = USGS at St. Francisville, Louisiana; 6 = Louisiana Department of Environmental Quality at New Orleans; 7 = Baton Rouge, Louisiana (BTR)

of the twentieth century until the late 1950s, but then declined (Fig. 4B) before rising to a value from 2009 to 2018 that was 9 times greater than the 1901 value at New Orleans. There were no data on phosphate before the 1980s (Fig. 4C). By the late 1980s the phosphate concentration dropped to one third of the value in 1980, and then rose slightly between 1998 and 2019. The ratio of DSi:nitrate changed from 14:1 to 1:1 over the last 100 years and the

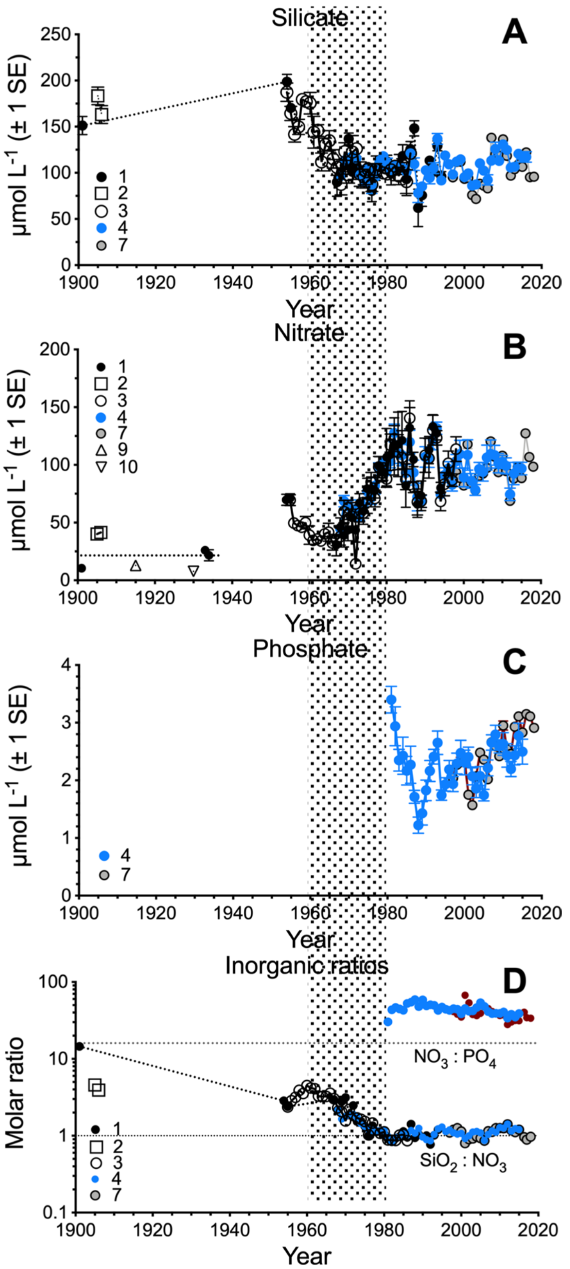

Fig. 4 The annual concentration (μmol $l^{-1} \pm 1$ SE) of inorganic nutrients in the lower Mississippi River and their molar ratios. **A** silicate, **B** nitrate, **C** phosphate, and **D** inorganic ratios for annual averages. The dotted lines in D are the 16:1 and 1:1 molar ratios. The numberings for data sources are: 1 = NOSWB sampling at the Carrollton and Algiers water intakes; 2 = NOSWB sampling at the Carrollton water intake, reported in Dole 1909; 3 = USGS Water Supply Papers; 4 = USGS LOADSET flow-normalized data; 7 = Baton Rouge; 9 = McHargue & Peter, (1921); 10 = Wiebe, (1931). The shaded vertically aligned box is the interval of the rapid increase in industrial-scale corn-soybean farming

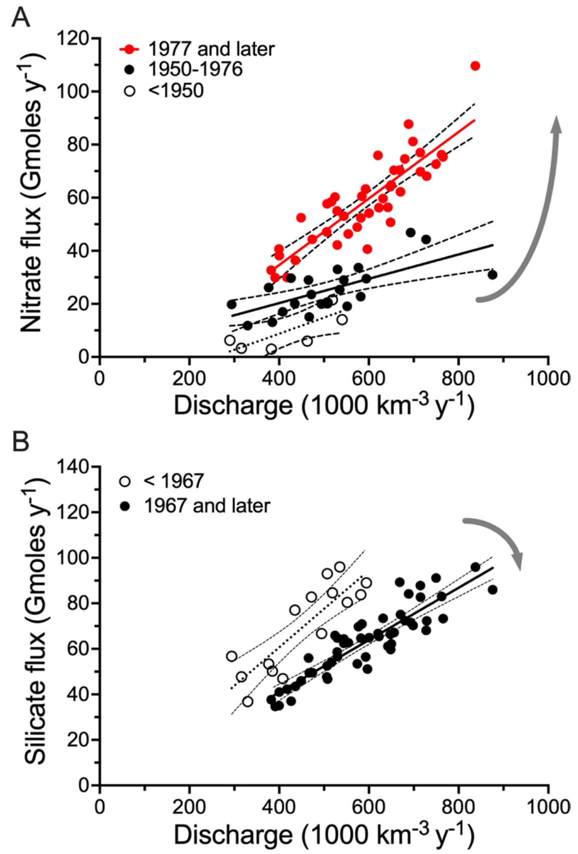

Fig. 5 River discharge vs flux for nitrate (**A**) and silicate (**B**) over different intervals for data shown in Fig. 4

dissolved nitrate:phosphate molar ratio was above 30:1 in the last decade (Fig. 4D).

The fluxes of nitrate and silicate were proportional to discharge over different intervals (Fig. 5). There were fewer data points for before 1950 than later, but the distinctions are evident. The slope of the nitrate flux versus discharge rose from before 1950, from 1950 to 1979, and then again after 1980 with significant differences between slopes ($P = 0.001$, $F = 12.4$; Fig. 5A). The equations for each are: before 1950, $Y = 0.061*\text{discharge} - 15.46$ ($F = 7.53$, DFd = 5; $P < 0.05$); from 1950 to 1980, $Y = 0.066*\text{discharge} - 5.54$ ($F = 16.7$, DFd = 23; $P \leq 0.001$); after 1980, $Y = 0.125*\text{discharge} - 15.5$ ($F = 123$, DFd = 40; $P < 0.001$). The slope of the silicate flux versus discharge fell from before 1967 to after 1967 from 0.17 to 0.11 Gmoles year^{-1}, respectively, with significant differences between them ($P = 0.02$, $F = 5.6$; Fig. 5B). The equations for each are: before 1967,

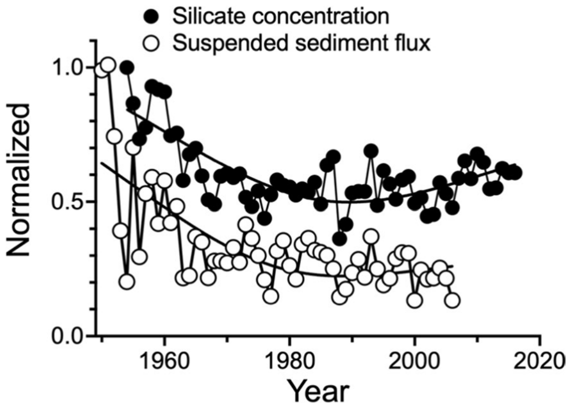

Fig. 6 The changing relative silicate concentrations normalized to the concentration in 1954 and the suspended sediment flux normalized to the 1950 value (the beginning of the data records)

$Y = 0.169$*discharge $- 6.86$ ($F = 34.7$, DFd $= 13$; $P < 0.0001$); after 1967, $Y = 0.115$*discharge $- 4.97$ ($F = 209$, DFd $= 50$; $P < 0.001$).

The sediment flux before and after 1967 is coincidental with the changes in silicate concentration (Fig. 6). Furthermore, the minimum values for the spline-modeled curves were similar for both—between 1987–1990 and 1989 for suspended sediment flux and silicate concentrations, respectively.

Alkalinity tends to increase each year, but there is also variance around this general upward trend. The normalized values of this variance in alkalinity changes with the normalized values of nitrate, silicate, and phosphate concentration (Fig. 7), but only after 1994, not before 1994. The slope of the normalized values for nitrate vs. alkalinity and silicate

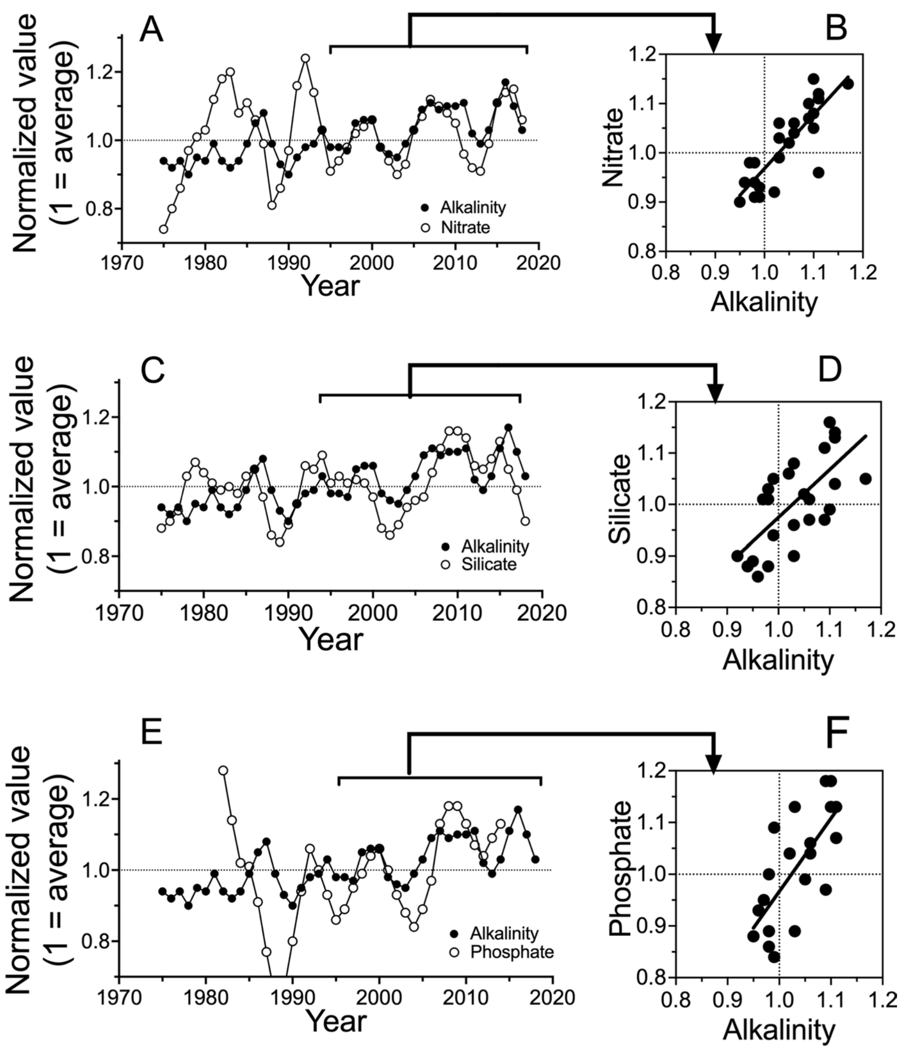

Fig. 7 The normalized relationships (1 = average) of: **A** alkalinity and nitrate versus year for 1974 to 2019, **C** alkalinity vs nitrate for 1974 to 2019, and **E** alkalinity and phosphate versus year for or 1981 to 2015. A linear regression of the alkalinity versus nitrate, silicate, and phosphate is in **B**, **D**, and **F**, respectively. The data are a 3-year running average

vs. alkalinity from 1995 to 2019 were significant (Fig. 7B, $F = 50.9$, DFd = 22, $P < 0.01$, $R^2 = 0.70$; Fig. 7D, $F = 20.4$, DFd = 22, $P < 0.01$, $R^2 = 0.46$; Fig. 7F = (Fig. 6F, $F = 18.8$, DFd = 18, $P < 0.01$, $R^2 = 0.51$). The coefficient of determination (R^2) between the normalized values for nitrate and silicate was 0.24 ($F = 11.6$, $P < 0.01$; not shown).

Total C, N, P

The concentrations of total nitrogen (Fig. 8A) and total phosphorus (Fig. 8B) were relatively constant after 1990. Before 1990 the TN concentration rose but the concentration of TP did not. The same yearly trend in TN was exhibited by nitrate; a simple linear regression had an R^2 of 0.72 ($P < 0.001$; $F = 519$; not shown), indicating a common driver of the variance. The average TN concentration from 2003 to 2015 at Baton Rouge was 132 ± 4.9 µmols l^{-1} N and 4.6 ± 0.2 µmol l^{-1} P (molar ratio = N:P::28.7:1). The data for the concentration of total carbon (TC) and both inorganic carbon and total organic carbon (TOC) for the same interval indicate, in contrast, increases over the time series (Fig. 8C). The average annual concentration of inorganic carbon (2.39 mmol l^{-1}) was 86.7% of the TC (2.75 mmol l^{-1}) from 2003 to 2015. The average concentration of TOC over the same interval (0.37 mmol l^{-1}) was 13.5% of the TC and increased at a faster rate than the TC concentration at 0.039 mmol l^{-1} $year^{-1}$ from 2003 to 2015 ($Y = 0.0385 * year - 74.4$; $F = 196.4$, DFd = 531; $P < 0.0001$). The molar ratios of the total amounts for this interval was 524:29:1::C:N:P.

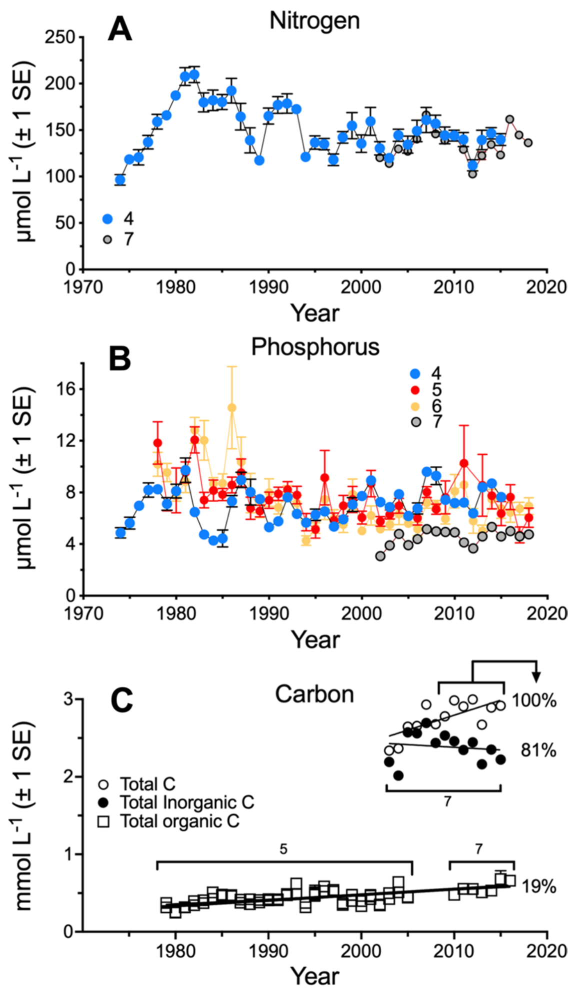

Fig. 8 The variations in the annual concentration of: **A** Total nitrogen (µmol l^{-1} ± 1 SE); **B** Total phosphorus (µmol l^{-1} ± 1 SE); **C** Total carbon (mmol l^{-1} ± 1 SE). The total carbon is subdivided into the total inorganic carbon fraction and the total organic carbon. The percent of the total amount in each of the three categories is for 2010 to 2018. A linear regression is fit to the carbon data. The numberings for data sources are: 4 = USGS, flow-normalized data at St. Francisville, LA; 5 = LaDEQ at St. Francisville, LA; 6 = LaDEQ at Belle Chasse, LA; 7 = Baton Rouge, LA

Discussion

The water quality measurements discussed here are from the lower end of the largest river in North America; they are the summed consequences of varying loadings and processing within different channel sizes that have varying relationships within a heterogenous landscape, including lagged responses (Murphy et al., 2014). The channel sizes have changed over the last 100 years with wetland losses, deforestation, urbanization, flood control levee growth, and tiling, etc. (Paul & Meyer, 2001; Allan, 2004; Julian et al., 2015). As a result, the water quality at New Orleans does not represent a homogenous water quality found throughout the basin now or 100 years ago. Compared to large channels, for example, headwater streams have greater total channel length contact with the landscape (Wollheim et al., 2022), greater heterotrophy, and are shaded and shallow (Gardner & Doyle, 2018) so that the benthic to water column dominance is larger than in downstream channels (Reisinger et al., 2015). Water is retained within wetlands that release dissolved organic matter (DOM) and denitrify nitrogen that decreases rapidly with channel size (Alexander et al., 2000; Alvarez-Cobelas et al., 2008). Also, downstream channels have higher DOM concentrations than upstream, but phosphorus and silica concentrations are reduced by up to 50% downstream compared to in headwaters (Finlay et al., 2011). Climate change will increase the number of rarer but large precipitation events that are a significant source of terrestrial DOM to riverine systems (Raymond et al., 2016). The result is that land use, hydrologic alterations, drainage improvements and climate change from the headwaters to the Gulf of Mexico have changed water quality at the lower end of the River but have had different spatial and temporal effects within the watershed.

Discharge

The discharge of the lower end of the Mississippi River varied with changes in global weather patterns from 1826 to 1969, but not afterward when it appears that drainage improvements and climate change are the dominating drivers (Turner, 2022). Schilling & Libra (2003) provide an example of these effects by examining changing stream discharges in eleven HUC8 watersheds in Iowa. They found that converting habitats to agricultural fields replaces deeply rooted perennial plants with shallow-rooted annuals, (principally corn and soybeans today) which reduces evapotranspiration and shunts more water into streams that then increases the total amount of water discharge and the percentage of runoff as baseflow (Schilling & Libra, 2003; Schilling et al., 2008). These have such a significant effect that Xu et al. (2013) concluded that land use change contributed twice as much as climate change to stream discharge increases in 55 unregulated streams in the Midwest from the 1930s to 2010. The reason for the inflection point in discharge around 1980 is coincidental with the acceleration in temperature, but drainage improvements could also have been a factor, as well as an increase in precipitation (Peterson et al., 2013). The records for tiling fields, unfortunately, do not record the drainage intensity or diverse equipment. A recent survey, perhaps the most comprehensive one, showed that 63% of the counties in Iowa had drainage improvements amounting to between 20 and 60% between 1969 and 2017 (Edwards & Thurman, 2022). But the time between estimates are too long to determine if tiling activities distinctively increased around 1980. Data demonstrating that there was a dramatic change in drainage improvements around 1980 is lacking and seems improbable given how slowly drainage improvement policies are implemented (Jaynes & James, 2007).

Alkalinity

Alkalinity is the acid-neutralizing capacity of water and primarily a result of mineral weathering dependent on exposure to carbonic, sulfuric, and nitric acids, and nitric and sulfur oxides (Raymond & Hamilton, 2018). Because the conversion of one mole of ammonium to nitrite and then nitrate produces two moles of H^+, an ammonium-based fertilizer becomes a weathering agent for carbonate and silicate minerals when the pH is >6.5, which it was in the river after 1969 (Turner, 2021). The nitrogen in ammonium fertilizer applied in the US has been comprised of about 90% ammonium since the 1990s (Lu et al., 2018). A rise in alkalinity, therefore, may be accompanied with proportional increases in the concentration of nitrates (Jarvie et al., 1997). Other sources of HCO_3^- will be added when weatherable soils are exposed a higher pH as a result of the oxidation of sulfur in newly drained soils. Lime is sometimes added to raise soil pH and may dissolve, particularly when nitrogen additions of fertilizer and manure are added, also causing an increase in the concentration of dissolved inorganic carbon (DIC) (Barnes & Raymond, 2009). Respiration of soil organic matter can be stimulated by nutrient additions and will also contribute to alkalinity. The weathered minerals release silicates and nitrates as a result and are an explanation for why variations in alkalinity are directly related to nitrate, phosphate, and silicate concentrations over the last few decades. The flux of bicarbonate C since 1980 now represents about 81% of the total carbon in the river. The increased bicarbonate flux becomes a sink for atmospheric carbon when it dissociates into carbonate and silicate deposition in the ocean. The eventual dissolution of carbonates will take thousands of years, and silicate weathering will take millions of years (Berner et al., 1983), making carbonate and silicate deposition a temporary, but long-lasting carbon sink.

The rise in alkalinity in the Mississippi River over the last 120 years, first described by Raymond & Cole

(2003) and Raymond et al. (2008), has since been shown to occur elsewhere. Tank et al. (2012), for example, showed that thawing of ancient permafrost deposits raises HCO_3^- fluxes as the weathering zone is exposed. Small temperate northeastern US streams (49 to 1492 km^2) draining agricultural lands contained 3.3 more dissolved inorganic carbon than in forest-draining streams (Barnes & Raymond, 2009). Raymond et al. (2008) estimated that about 60% of the rise in downstream alkalinity flux in the Mississippi River watershed at the 1980 inflection point was due to tile drainage but not river discharge, which is similar to the 75% that Stets & Striegl (2012) found for the eastern seaboard watersheds. The remaining 40% was due to either precipitation or other factors. The 9% increase in discharge that is not balanced by precipitation is ascribed to drainage improvements (Raymond et al., 2012). The coincidental inflection points of alkalinity and temperature around 1980 are consistent with the observation of an inverse relationship between average annual silicate concentration and latitude in the world's rivers (Turner et al., 2003).

Organic carbon

The total carbon (TC) delivered by the Mississippi River to the Gulf of Mexico in 2019 was about 20.1 TgC year^{-1} and the organic carbon was about 4.2 TgC year^{-1} (20% of the total). Much of the carbon going into the river is not present at the mouth because a significant amount of CO_2 gas is evaded from river to atmosphere. Dubois et al. (2010), for example, estimated that CO_2 evasion was 130% of the DIC flux in the Mississippi River (samples mostly from 2000 to 2001) when they used a gas diffusion coefficient determined by Wanninkhof (1992) but was 63% higher if they used the gas diffusion coefficient from Raymond & Cole (2003). Butman & Raymond (2011) used a longer water quality record of alkalinity and pH from mostly 1965 to 2000 data to estimate that 26.7 TgC year^{-1} is emitted as CO_2 from the lower Mississippi River. Dubois et al. (2010) used isotopic composition data in the lower Mississippi River to indicate that the respired carbon source in the CO_2 going into the atmosphere was from carbonate dissolution in soils. Butman & Raymond (2011) point out that some of the evasion of recently fixed CO_2 in the Mississippi River's streams and rivers may represent carbon that has been shunted into hydrologic networks. CO_2 losses from streams and rivers through evasion, therefore, apparently equal or even exceed the annual discharge of total carbon in the lower Mississippi River. This suggests that the evasion of CO_2 from the watershed to the atmosphere is greater than the delivery of DIC by the river to the sea.

The 4.2 TgC year^{-1} of total organic carbon entering the Gulf of Mexico at the river's end increased 19% over the last 4 decades but is a minor part of changes in soil stocks of carbon. The carbon losses over the last 100 years are indicative of soil losses, but not a significant quantity relative to carbon losses in soils worldwide. Sanderman et al. (2017), for example, estimated that the carbon in the upper 2 m of global soils decreased by 8.1% compared to the historical stocks in 10,000 BC, primarily as a result from grazing and cropland agriculture (133 PgC). They estimated that 28% of the carbon in the soil's upper 1 m was lost when it converted from grasslands to croplands. Soil carbon stocks in watersheds of the midwestern United States lost even more, perhaps equaling 25 to 50% of the soil organic matter present before cultivation (West et al., 2010). The conversion of grassland to arable land reduces soil organic matter and releases mineral N (Whitmore et al., 1992). Lu et al. (2018) modeled the contribution of intensive and extensive farming to crop production in the five midwestern states known as the 'western cornbelt' (ND, SD, NB, MN, and IA). These states produced 47% and 41% of the US corn and soybean harvest, respectively, from 2005 to 2017 (Lu et al., 2018). They found that between 2006 and 2016 that every kilogram of additional grain yield led to a soil carbon loss of 2.3 kg. The large carbon cost per kg gain production achieved by cropland expansion and rotation in the past decade was about 390 times higher than that by crop technology improvement. Lu et al. (2018) also found that 45% of carbon loss occurred in what had been grasslands, followed by 31% in former wetlands, 13% in former cropland converted to other land cover types, and 9% in previously forested lands, while over 59% of carbon gain was found in cropland due to its expansion. Although 14% of the newly expanded cropland was converted from wetlands, it contributed to ~ one third of carbon loss due to the high soil carbon density in wetlands. The rising concentration of organic carbon in the river over the last four decades (19% of the total) indicates that these soil carbon losses will continue.

Nitrogen

The rise in nitrate concentration and decline in silicate concentration occurring in the two decades after the 1960s has become relatively stable over the last 40 years. The average annual nitrate concentration at St. Francisville, LA, for example, has been about the same from 1992 to 2015. The variability of nitrate and silicate concentrations is now moving coincidentally with variations with alkalinity. The rising nitrate concentrations are often ascribed to changing temporal and spatial applications of fertilizers. This is because fertilization increases loading rates to the land and converting forests to agricultural land and improving drainage, especially by installing subsurface tiles, increases the percent of the applied nitrogen that goes into drainage channels (Randall & Gross, 2001). The N fertilizer application rate increased almost three orders of magnitude from 1950 to 2015: from less than 0.01 gN m^{-2} $year^{-1}$ in 1850 to 9.04 g N m^{-2} $year^{-1}$ in 2015 (Cao et al., 2018) as fertilizer use climbed from 1.5 to 8.1 TgN $year^{-1}$ from 1960 to 2014 (Tian et al., 2020). After then use stabilized (Fig. S1). Nitrogen fertilizer use in the Mississippi River basin now accounts for ~ 65% of the total fertilizer application in the continental United States (Tian et al., 2020).

David et al. (2010) investigated how much drainage improvements affected nitrogen yield compared to fertilizer applications by conducting a whole basin analysis of 153 watersheds using county-level data for N inputs and land use. They found that fertilizer inputs were tightly coupled with the fraction of land in row crops, just as Crumpton et al. (2006; Fig. 11) did in Iowa, Hatfield et al. (2009) did in the Raccoon watershed, Iowa, and Broussard & Turner (2009) discovered in their analysis of nitrate yields in farmlands in the northern Mississippi River watershed from 1906 to 1912. Raymond et al. (2012) estimated that 34% of the applied nitrogen in the Mississippi River water is exported and Booth & Johnson (2007) suggested that fertilizer runoff was 59% of loading, and that 10% of the area contributed 75% of the input. Howarth et al. (2012) estimated that 25% of the nitrogen applied in 154 watersheds in Europe and the US was exported to rivers and streams where the nitrogen applied was greater than 1.07 kg N km^{-2} $year^{-1}$. Turner & Rabalais (1991) calculated that the nitrate concentration (at that time) could have come from 22% of the fertilizer applied. The increased P loading into P-limited systems would make diatom production more likely (especially in a nitrogen replete environment) as Downing et al. (2016) demonstrated to occur in agricultural fields, but not in reservoirs.

Much of the total nitrogen yield in the basin is a consequence of structural changes in the landscape from building swales and tiling, not from solely (or simply) the nitrogen fertilizer application rates (e.g., Kaspar et al., 2003; Tomer et al., 2003; McIsaac & Hu, 2004; Nangia et al., 2008; Randall & Gross, 2001). Land drainage dries soils, as intended, but reduces denitrification, and moves the leached nitrate to waterways that reduces the potential sediment trapping and denitrification in riparian zones (Burt & Pinay, 2005). Randall & Gross (2001) showed that there was a close correspondence between tile drain water yield and nitrate yield, which is visually apparent when maps of the county-level nitrogen yield and drainage are compared (Fig. S4). This is why McIsaac & Hu (2004) found that the 1945–1961 riverine nitrate flux in an extensively tile drained region in Illinois averaged 6.6 kg N ha^{-1} $year^{-1}$, compared to 1.3 to 3.1 kg N ha^{-1} $year^{-1}$ for the non-tile drained region, even though the nitrogen application was greater in the non-tile drained region. Arenas Amado et al. (2017) found that tiles "delivered up to 80% of the stream N load while providing only 15–43% of the water" in the 122 km^2 Otter Creek watershed in Iowa. Ikenberry et al., (2014) estimated that 97% of the nitrate flow occurred during 50% of the highest flows in a 5-year study of the 5132 ha Walnut Creek watershed in Iowa. They reported that two-thirds of row crop land in Central Iowa and the Minnesota Till Prairies Major Land Resources Area had subsurface tile drainage. Measurements of inorganic C concentrations in the intensively farmed Raccoon River, IA, by Jones & Schilling (2013) are another example of the consequence of drainage on nitrate concentrations. The alkalinity there doubled from 2000 to 2011 compared to in 1931 to 1944 (Jones & Schilling, 2013), during which there was an increase in drainage and nitrate concentrations, but not fertilizer applications (Hatfield et al., 2009).

Research done at the local scale suggests that tile depth and spacing are important factors for water quality restoration. Nangia et al. (2008), for example, used 14 years of field data from the Raccoon River watershed in Iowa to determine what controls variations in the nitrate yields for similar fields under different drainage. They found that a simple rearrangement of the fertilizer application (no reduction in total fertilizer application) resulted in a 21% reduction in nitrate yield. Hofmann et al. (2004) found that subsurface tile drainage spaced 20 m apart optimized corn crop yields.

In summary, Nitrogen yields from field to streams is generally dominated by fertilizer application which has increased in the 1960 and stabilized in the last decades. More nitrate escapes farm fields when tiled and so drainage improvements are a significant multiplier of these loadings.

Silicate and suspended sediment

The silicate concentrations are directly related to discharge, but there is less silicate per discharge now than earlier in the twentieth century. Fortner et al. (2012) also showed a direct relationship of Dsi yield and discharge. Silicate concentrations decreased from the 1900s to 1960s as alkalinity and nitrate concentrations rose, but after 1994 the nitrate and silicate concentrations are directly related to alkalinity concentrations. The Dsi:nitrate molar ratio in the river now is about 1:1, compared to 4:1 in the early 1900s.

Several hypotheses explain changes in the silicate concentration in riverine ecosystems which are distinct from why nitrogen concentrations have increased. Humborg et al. (2000) argued that damming created longer residence times and improved light conditions favoring algal growth, including diatoms that sequester the silica in their frustules. This was observed in the Danube River when silicate concentrations were reduced from 79 to 20 μmol l^{-1} after the construction of the Iron Gate I dams, and the decline was not a step-function but linear over 17 years (Cociasu et al., 1996). Data in a recent review (Ma et al., 2017) supports this interpretation because their data show a higher percent silicate removal in reservoirs as residence times increase (Fig. S6). The decline in silicate concentrations, coincidental with decreased suspended sediment concentrations, can be ascribed to be primarily due to a longer water turnover time as a result of dam construction. The 50% decline in suspended sediment flux after the early 1950s was when dam construction expanded rapidly to increase hydrologic storage behind them (Meade & Moody, 2010). Other concurrent activities such as channel straightening, dikes, revetments, and soil erosion controls also affected sediment storage in various ways (Belt, 1975; Meade & Moody, 2010). The Missouri-Mississippi River sediment supply separated into two periods in 1967 which Meade and Moody (2010) describe as the going from a transport-limited system to a supply-limited system. The silicate concentrations stabilized about 10 years earlier than the peak in nitrate concentration.

Vegetative cover

Vegetative cover and land use is also important. Struyf et al. (2010) and Fortner et al. (2012), for example, demonstrated that agriculture development led to a 50% reduction of silicate delivery. Struyf et al. (2010) suggested that the initial land disturbance raised Si releases, which later was lowered as crop removal had an effect. Crop harvesting removes a large enough amount of silica to significantly change terrestrial silica cycling (Vandevenne et al., 2012) because the return of silica is greatly reduced; also, the “absence of deep-rooting to shallow-rooted crops prevents vegetation-stimulated mineral weathering” (Schaller et al., 2021). DSI export, therefore, is also partially the result of a dynamic balance between weathering of lithosphere and vegetation, and how vegetation influences weathered products (Cornelis & Delvaux, 2016). The accumulation of Si in plants ranges over two orders of magnitude (Hodson et al., 2005) and mineral weathering increases at higher temperatures and with greater hydrologic throughput. Further, Si is bound in different forms of unequal dissolution potentials. The vegetative influences include plant type, pH, vegetative uptake through rhizo-fungal interactions, phytolith production and uptake by diatoms and sponges.

Phosphate

The records of phosphate concentrations in the river don’t begin until after the major changes in fertilization, dam construction, and discharge increases. We reasonably might expect that soil disturbance from fertilizer additions, agricultural expansion and forest clearance resulted in more phosphorus runoff. The phosphorus in soil is bound to clay particles but there is no direct relationship between suspended sediment and phosphate concentrations in these samples.

Furthermore, phosphorus has long been known to accumulate in soils (Bennett et al., 2001), and water treatment expansion after the Clean Water Act (Turner, 2021) makes hindsight predictions of cause-and-effects unreliable.

Summary of major influences on river constituents

A brief summary of the prominent drivers of variations in Mississippi River discharge and the concentration of five inorganic constituents over the last 120 years is in Table 2. Climate change and land use is exerting a strong enough effect on discharge rates to confound the pre-1980 relationship with the NAO. The land use changes include vegetative as well as hydrologic features, principally drainage improvements, that affect alkalinity. The variations in alkalinity have a knock-on effect on soil weathering that releases silicate, nitrate, and phosphate concentrations in riverwater for the last few decades when fertilizer applications and water impoundment construction stabilized. Suspended sediment concentrations declined before 1970 and with proportionality to silicate concentrations that a demonstrably higher trapping efficiency with greater hydrologic storage. The low in silicate concentrations from trapping behind impoundments preceded by about 10 years the dramatic rise in nitrate concentrations which were driven by fertilizer applications and drainage improvements. Before 1950, the changes in alkalinity appear to be driven by less intensive agricultural expansion than after 1950. The temporally sparse record of dissolved organic carbon is consistent with the various observations of soil carbon losses throughout the watershed.

Restoration/resilience

Because soil quality affects riverine carbon sources and sinks, there is interest in restoring soil organic matter to reduce the $11.2 \pm 0.4\%$ of the total global emissions of CO_2, N_2O, and CH_4 that are from agriculture (Tubiello et al., 2015; Rumpel et al., 2018). Current global soil stocks contain 2 to 3 times more carbon than the atmosphere (Le Quéré et al., 2018),

Table 2 Summary of the prominent factors controlling river discharge and inorganic concentrations in the Mississippi River watershed within three time periods

	Interval I	Interval II	Interval III
Discharge	1817–1950 (0)	1950–1980 (0)	1980–2019 (++)
	Land use (Drainage/vegetation)	Land use (drainage/vegetation)	Land use (drainage/vegetation) increased warming and precipitation)
Suspended sediments	1850–1950 (++)	1950–1967 (--)	1967–2019 (-)
	Soil disturbance (land clearance/farming)	Sediment retention behind small/large impoundments (transported-limited)	Revetments and dikes (supply-limited)
Alkalinity	1900–1950 (+)	1950–1980 (+)	1980–2019 (++)
	Land use drainage/vegetation	Land use drainage/vegetation	Land use drainage/vegetation/warming
SOC	1900–1950 (+)	1950–1980 (+)	1980–2019 (++)
	Vegetation/farming	Farming	Farming
Silicate	1900–1950 (0)	1950–1970 (--)	1980–2019 (0)
	Small changes discharge	Diatom retention behind small and large impoundments discharge	Alkalinity temperature discharge
Nitrate	1900–1950 (+)	1960–1980 (++)	1980–2019 (0)
	Land use	Fertilizers/drainage	Alkalinity
Phosphate	1900–1950	1960–1980	1980–2019 (0)
	No data	No data	Alkalinity

An estimate of the directional change for the three intervals is: much lower (--), lower (-), largely unchanged (0), higher (+) and much higher (++)

and grasslands contain about one third of it, almost entirely as roots and organic matter (Bai & Cotrufo, 2022). Sanderman et al. (2017) suggested that perhaps 10 to 30% of the historic loss could be restored, which is more than 75 years of the current global fossil fuel emissions. Fargione et al. (2018) estimated that as much as 21% of the current annual CO_2 emissions in the US might be captured each year by restoring soil carbon. The Mississippi's annual total carbon and organic carbon was 6.8 and 1.4%, respectively, of that amount. The path to restoring soil carbon will be through re-invigorating belowground plant production and storage.

Shifting to more diverse plant rotations will be needed to have a major effect on carbon losses and to sustain soil fertility and farming enterprises. Achieving this restoration does mean that it will result in negative consequences for farmers or consumers. Soil carbon restoration has many benefits important to sustaining agriculture because organic material holds water, minerals, nutrients and organisms giving it soil structure, resistance to erosion and increased soil fertility (Chambers et al., 2016; Jackson et al., 2017). Improving soil health will provide public benefits of improved water quality, flood reduction, enhanced wildlife habitat, reduced air pollutants, and reduced global warming potential (Boody et al., 2005; Jordan et al., 2007; Ryan et al., 2018). Plant rotations will include cover crops, especially deep-rooted perennials (Poeplau & Don, 2015; Jungers et al., 2019; Paustian et al., 2019). Land under tile drainage can be a part of these efforts (Randall & Mulla, 2001; Dinnes et al., 2002). Tile drainage can enter buffer strips before reaching streams, drain into wetlands, or even not be used if row cropped fields are converted to perennials. Planting only shallow-rooted annuals leaves the ground without plant cover for more than half the year and results in more soil erosion (Heathcote et al., 2013). Replacement of annuals with deep-rooted perennials provides continuous living cover and reduces soil erosion (Song et al., 2014). Water quality has improved in some sub-watershed streams of the Mississippi watershed because of soil conservation (Rabotyagov et al., 2014; McIsaac et al., 2016; García et al., 2016).

A signature example of alternative management of perennial grains is provided by Davis et al. (2012), Liebman et al. (2013), and Tomer and Liebmann (2014) who conducted a 7-year field trial of different cropping systems for corn-soybean rotations. Some key findings were that, by using cover crops for 4 years, there was a 50% or more reduction in fossil fuel use, a doubling of employment, and not loss of profits. The diversification of crop coverage with small grains and legumes had a 91% reduction in fertilizer use, 97% reduction in herbicide use, and increased carbon storage. There is much work remaining—half of the US stream and river miles violate water pollution standards (Keiser & Shapiro, 2019). Whole system analyses of land use alternatives for the small and large farms are needed to include not only GHG emissions, but also energy expenditures, wildlife, water quality, and social factors. Boody et al. (2005) found that alternative land management schemes using the same resources could create "improved water quality, healthier fish, increased carbon sequestration, and decreased greenhouse gas emissions, while economic benefits include social capital formation, greater farm profitability, and avoided costs." On-the-ground experiments at a watershed scale that include social governance (Meyfroidt et al., 2022) are recommended.

Restoring water quality within the watershed means, in part, reducing nitrate and phosphorous runoff that contributes to the hypoxic zone on the continental shelf of the northern Gulf of Mexico. A Hypoxia Action Plan of 2001 (HAP; Mississippi River/Gulf of Mexico Watershed Nutrient Task Force, 2001) established a goal of reducing the size of the hypoxic zone to less than an average of 5000 km^2 over 5 years by 2035. The identified mechanism to do this at the time was to reduce nitrate loading in the river which Scavia et al. (2017) estimated to be a 59% reduction in nutrient loading to meet the 5000 km^2 goal. But the nitrate loading in the river declined by only 4% since the 2001 agreement (Fig. S5). Clearly the results so far are insufficient, slow to develop and will result from changes in land use, primarily in the agricultural sector.

Conclusion

The relationships between alkalinity, nitrogen, phosphorus, and silica are interwoven so tightly today that it is difficult to conceive of modifying one without affecting the other. Fertilizer applications in the watershed are not always directly proportional to nutrient loading in the Mississippi River; their influence is modified by tile drainage, climate variation, plant choices, and farm management. Conversion of natural habitat to agricultural fields with improved drainage reduces plant cover (and hence evapotranspiration) and more water is shunted into streams. This, in turn, changes the rate of soil accumulation and denitrification as well as alkalinity and the concentrations of alkalinity, nitrate, phosphate, and silicate. The integrated culmination of these land use changes across the watershed over the last 100 years reduced water residence time and nutrient processing in soil but increased concentrations in water bodies; the percent of nitrate exported from soils to water becomes higher as a result. Today agricultural lands are hemorrhaging the carbon needed to build and sustain healthy soils and a significant carbon sink is not being realized. Examples of accommodations for simultaneous water quality improvements while building soil health exist, but more on-the-ground examples are needed to integrate both the biogeochemical factors and practical socio-political-economic aspects of farming.

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