Recent trends and spatial patterns in nitrate loading from the Mississippi River to the Gulf of Mexico

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science for a changing world

USGS National Water Quality Assessment (NAWQA)

In 1991, Congress established the National Water-Quality Assessment (NAWQA) to address where, when, why, and how the Nation's water quality has changed, or is likely to change in the future, in response to human activities and natural factors.

Comprehensive national project to assess water quality in the U.S.

NAWQA concludes after Fiscal Year 2021, but most NAWQA activities are transitioning into new priorities for the USGS Water Mission Area.

One example priority is to shift towards holistic, integrated water availability assessments.

Stay tuned for details.

Groundwater Assessments

Surface Water Assessments

Watershed Modeling

New methods and analytical techniques

Regional stream quality assessments

USGS National Water Quality Assessment (NAWQA)

1. **Status**—What is the current quality of the Nation's surface water and groundwater?

2. **Trends**—Is water quality getting better or worse?

3. **Understanding**—What are the natural and human factors that control water quality?

USGS NAWQA Trend Analysis

- Largest-ever evaluation of trends in U.S. stream quality between 1972 and 2012
  - Over 20,000 trend results
  - 51 chemicals and 38 measures of aquatic life
  - 1,400 sites with at least one trend result
- Leverages the power of monitoring data collected by the USGS and 73 other monitoring organizations
- Results are the foundation for answering critical questions about the causes and effects of changes in stream quality

USGS NAWQA Trend Analysis

- Scope
  - Stream and river trends in nutrients, pesticides, sediment, carbon, salinity, fish, invertebrates, and algae
  - Four time periods: (1) 1972-2012, (2) 1982-2012, (3) 1992-2012, and (4) 2002-2012
- Data sources
  - NWIS, STORET, and other Federal, State, and local databases
  - 185 million water-quality records from 480,000 sites and over 600 organizations

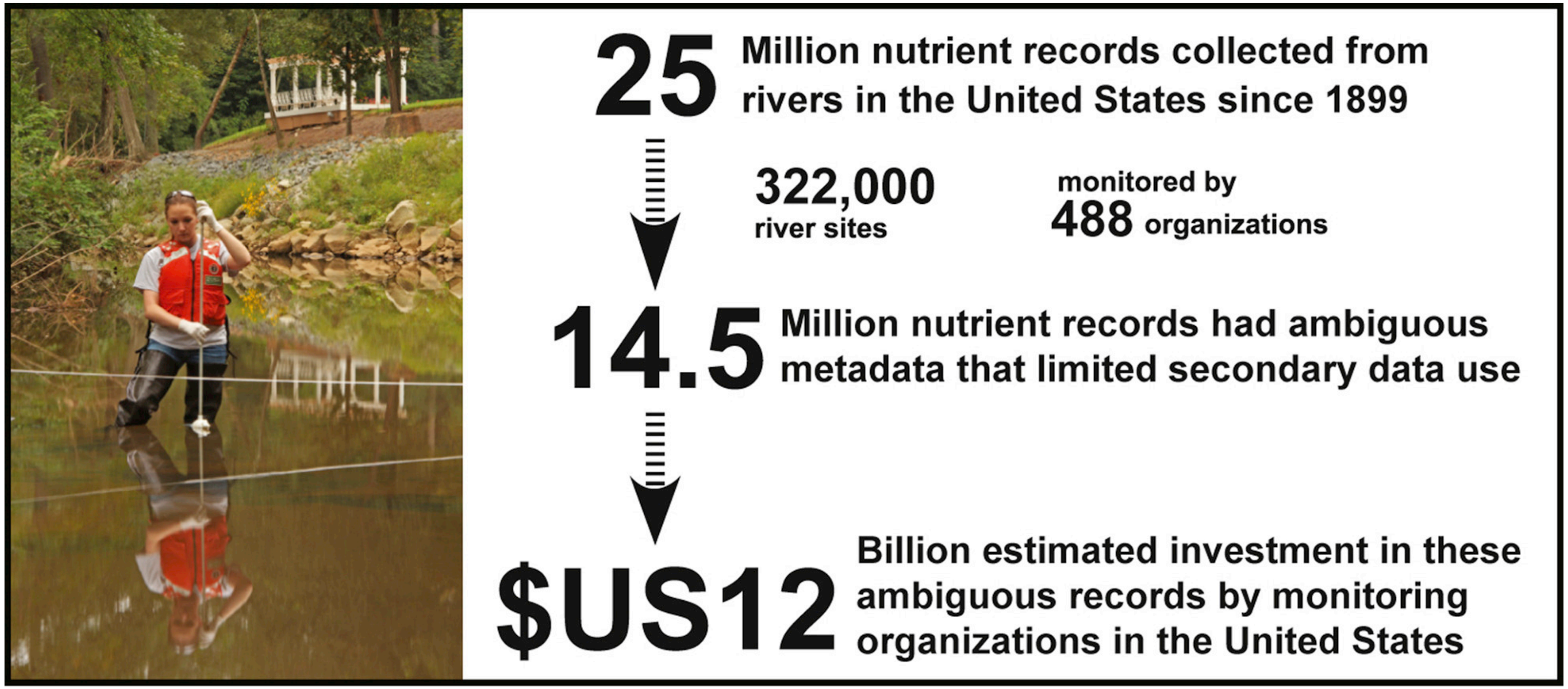
Data Processing and Screening for Trend Analysis

1. Harmonize data and address metadata gaps
2. Ensure adequate data coverage over the trend period
3. Obtain streamflow data

Original parameter name	Example
Nitrate plus nitrite, water, filtered, field, milligrams per liter as nitrogen	1
NO2+3 (mg/L)	2
NITROGEN, NITRITE (NO2) + NITRATE (NO3), Dissolved	3
Inorganic nitrogen (nitrate and nitrite)	4
Inorganic nitrogen, water, dissolved, calculated as NH3+NO2+NO3, milligrams per liter as nitrogen	5
Inorganic Nitrogen	6
Nitrogen, Inorganic||Nitrogen, inorganic, total (ug/L as N)	7
Nitrogen, Inorganic||Nitrogen, inorganic as N	8
Total NOX mg/L	9
Nitrogen, oxidized	10

Sprague et al. 2017

Samples with missing or incomplete metadata are costly!

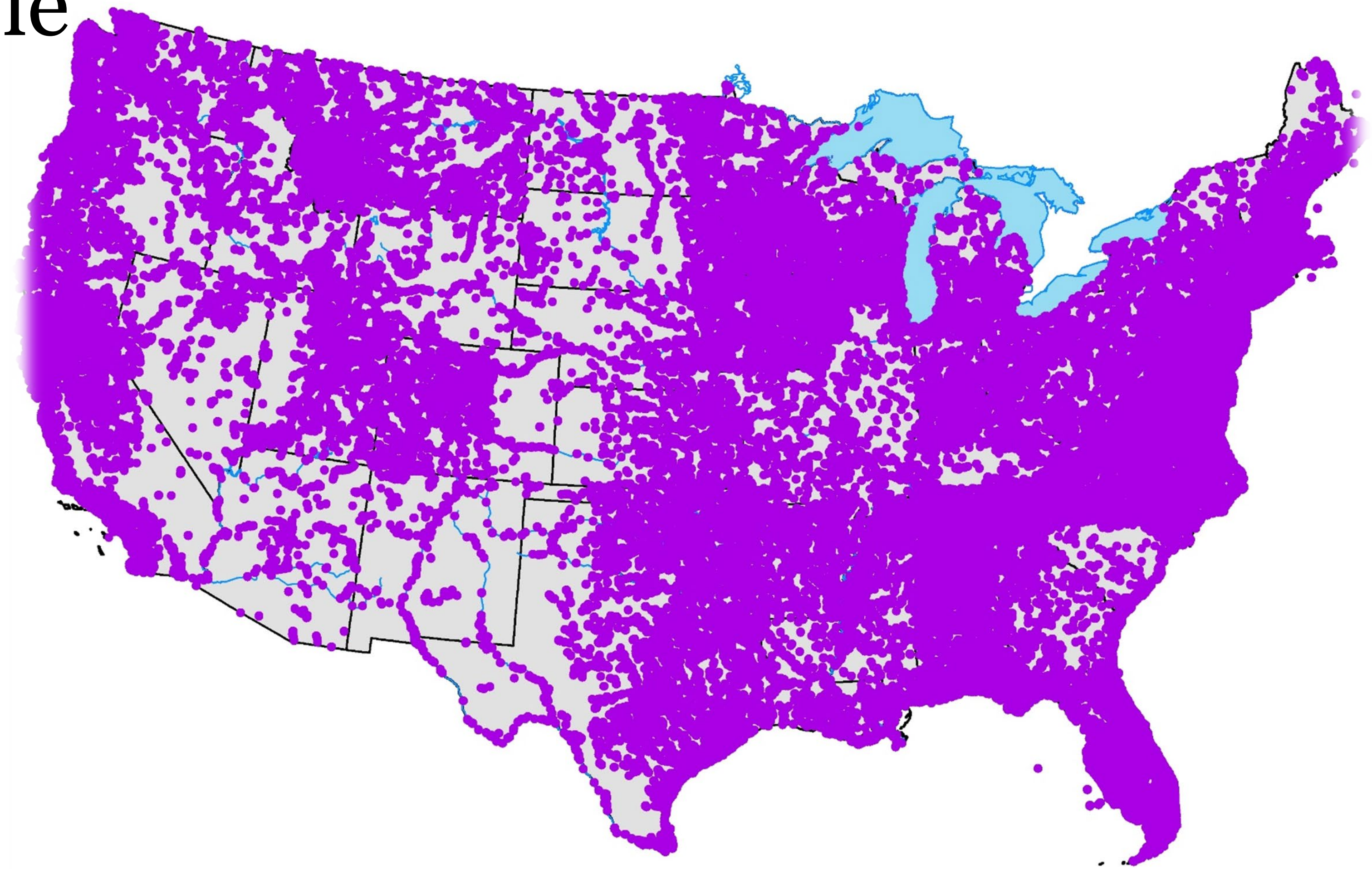


USGS

Sprague et al. 2017

Data Processing and Screening for Trend Analysis – Orthophosphate example

All sites with at least 1 sample and adequate metadata.



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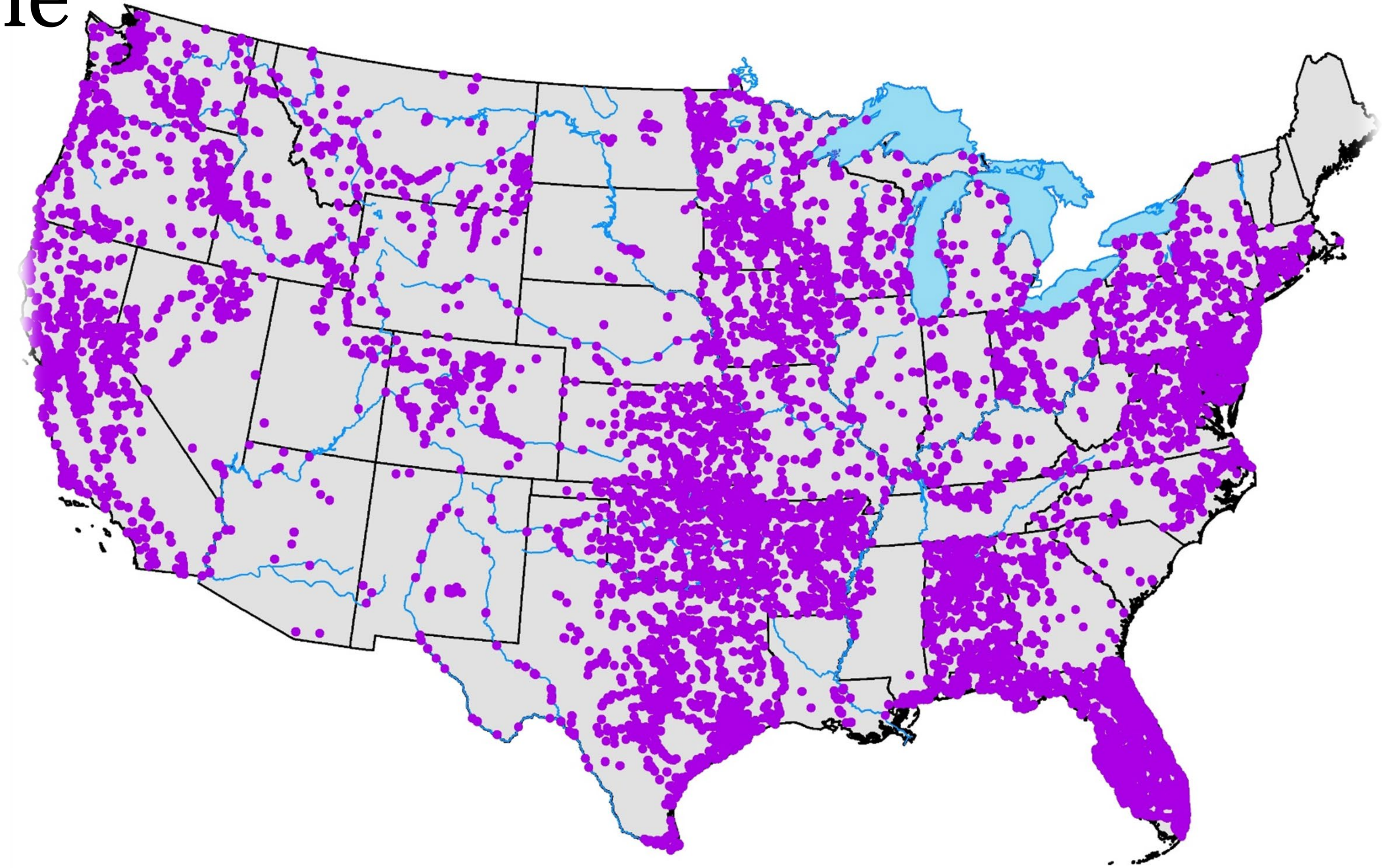
Data Processing and Screening for Trend Analysis – Orthophosphate example

Sites with data through 2011



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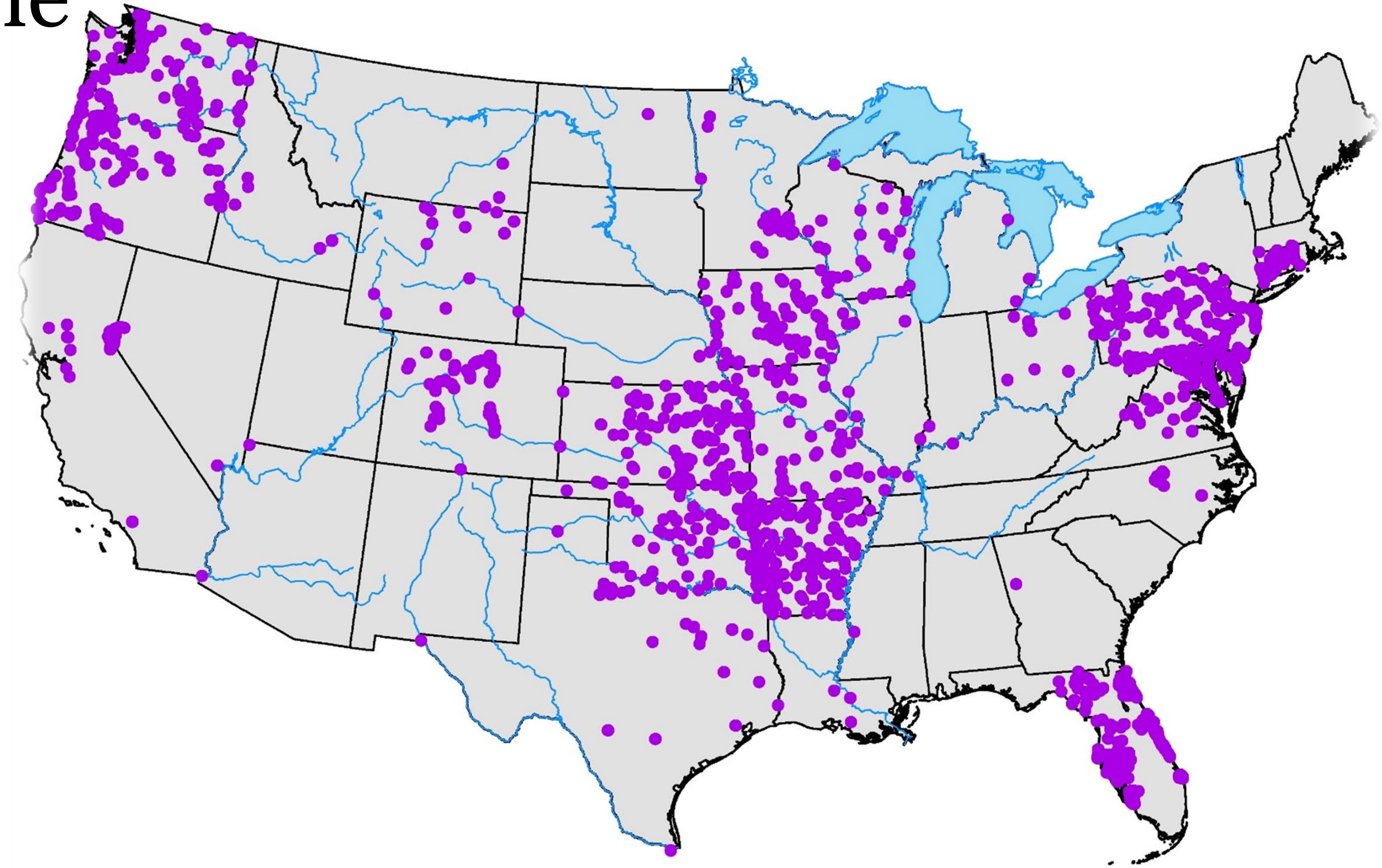
Data Processing and Screening for Trend Analysis – Orthophosphate example



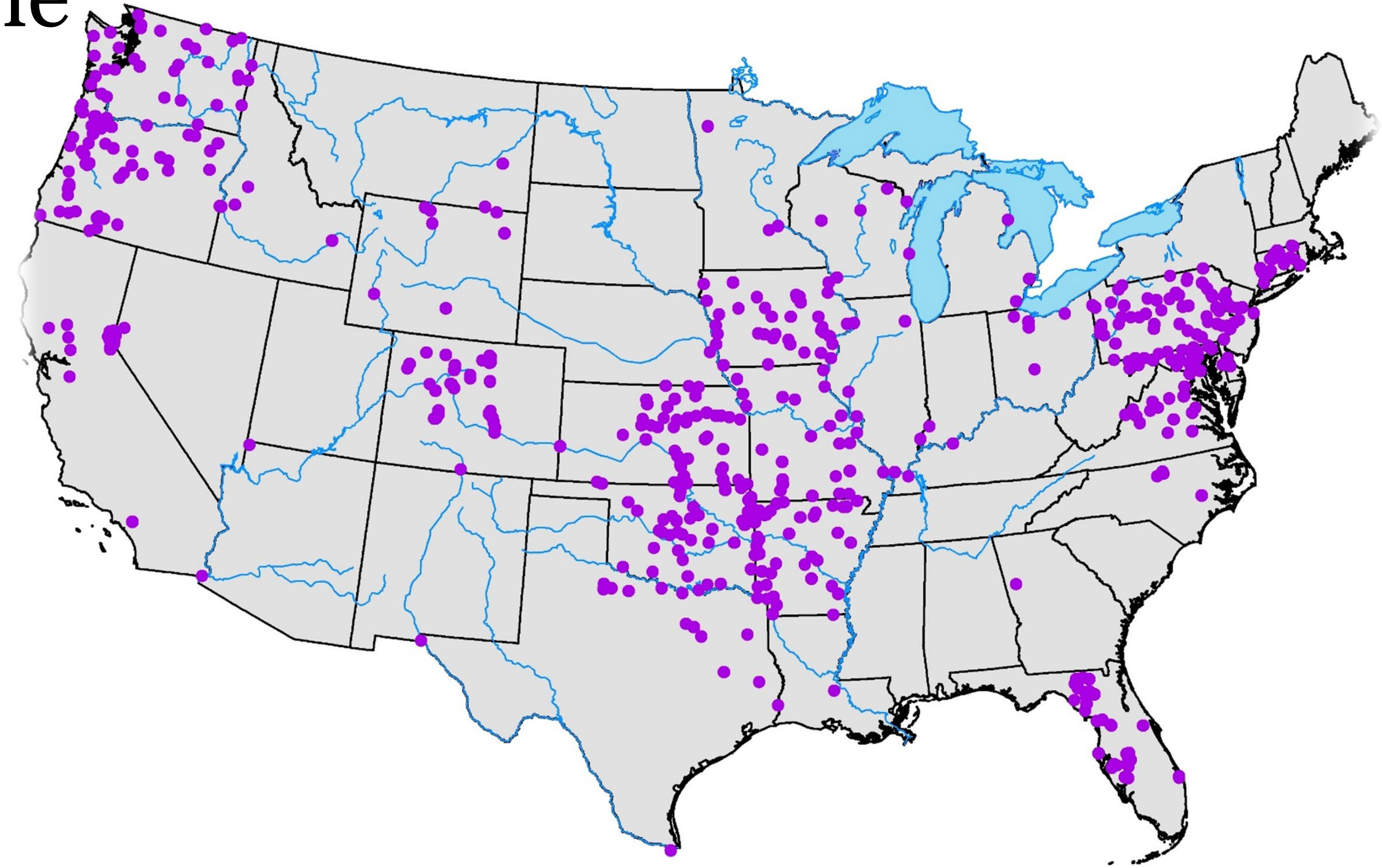
Sites with enough data to calculate a trend

(quarterly samples in first and last two years of trend period AND quarterly samples in 70% of all years)

Data Processing and Screening for Trend Analysis – Orthophosphate example

Sites with adequate flow records

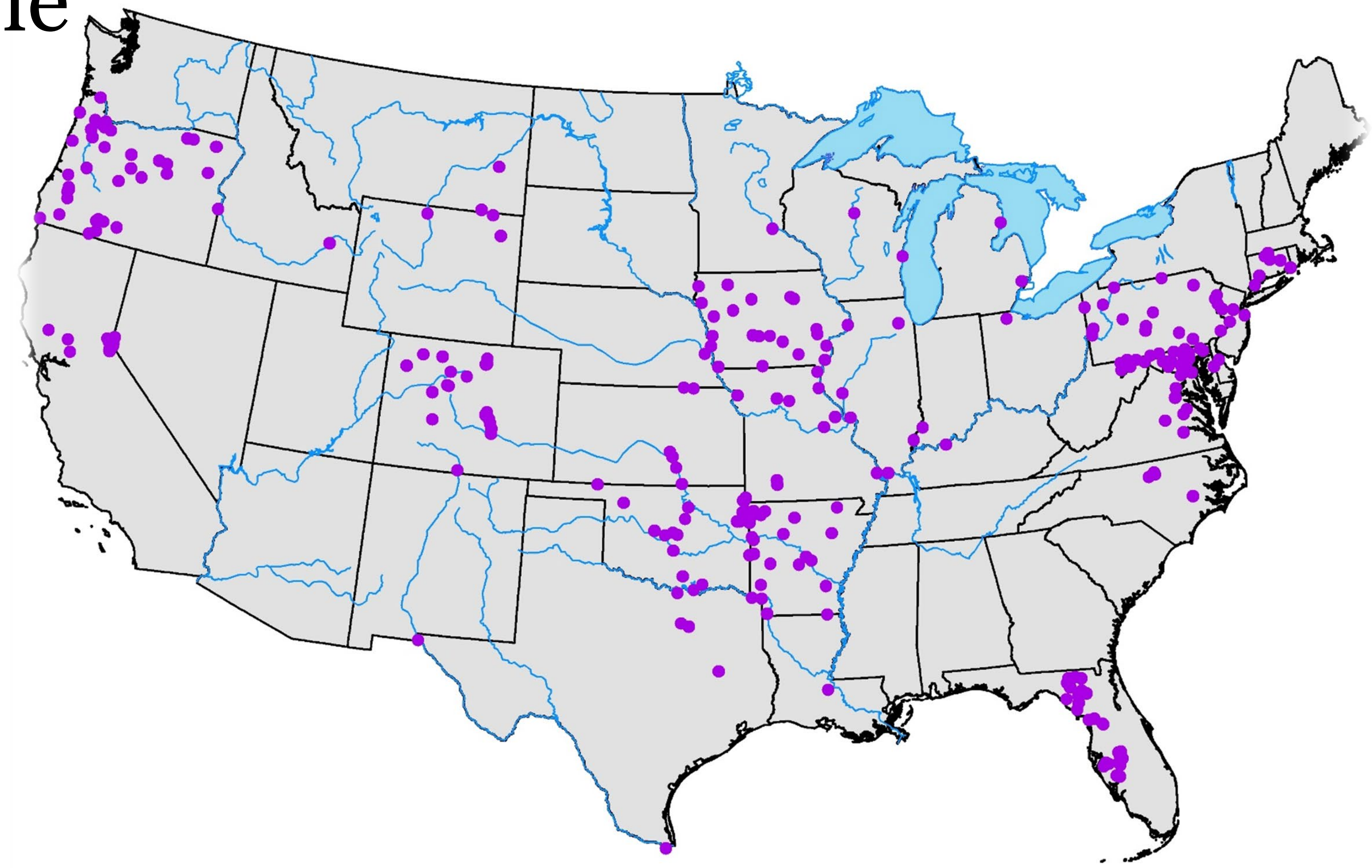
(daily average discharge over the trend period)



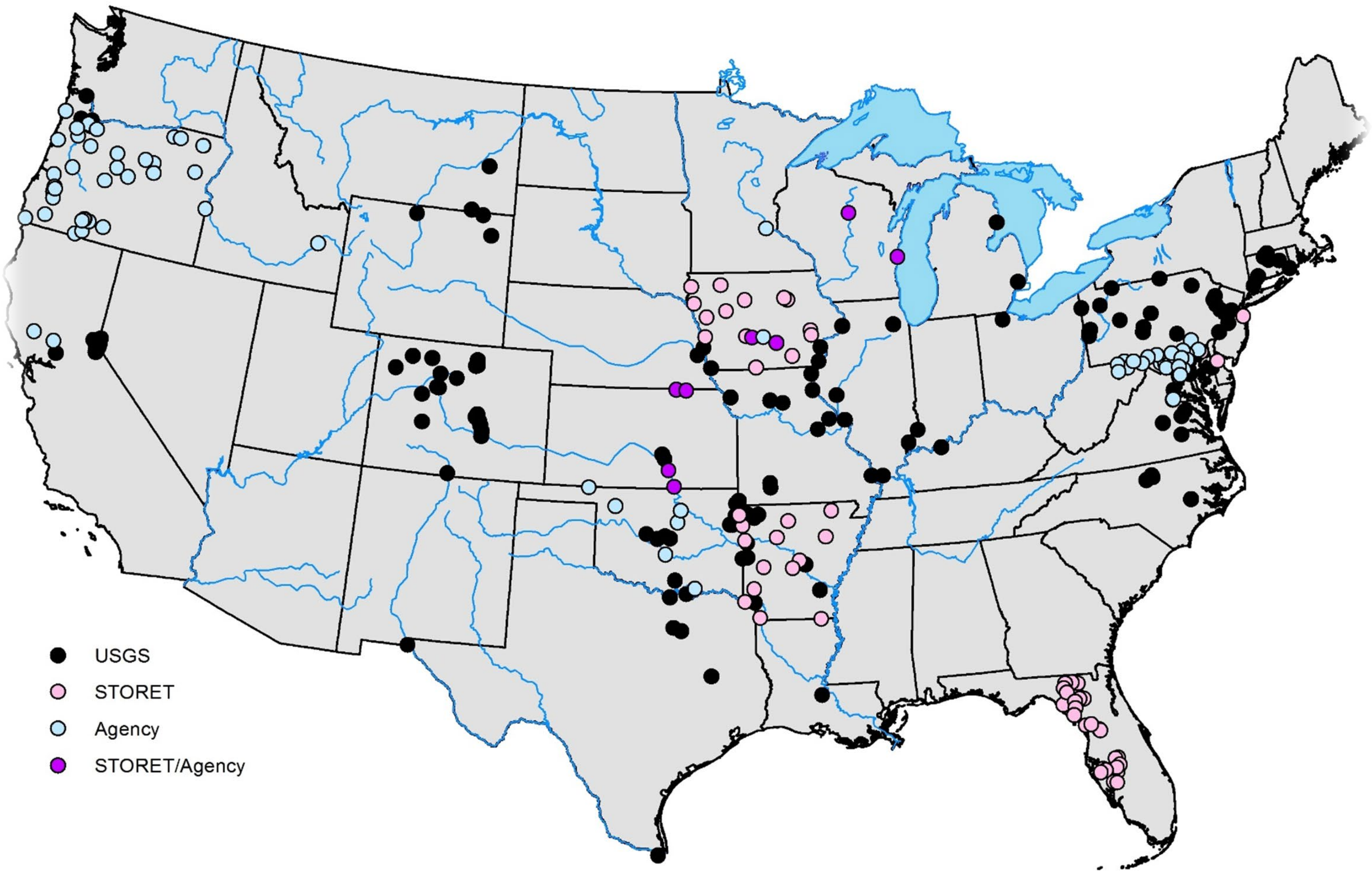
USGS

Data Processing and Screening for Trend Analysis – Orthophosphate example

Sites with adequate sampling during high-flow events.



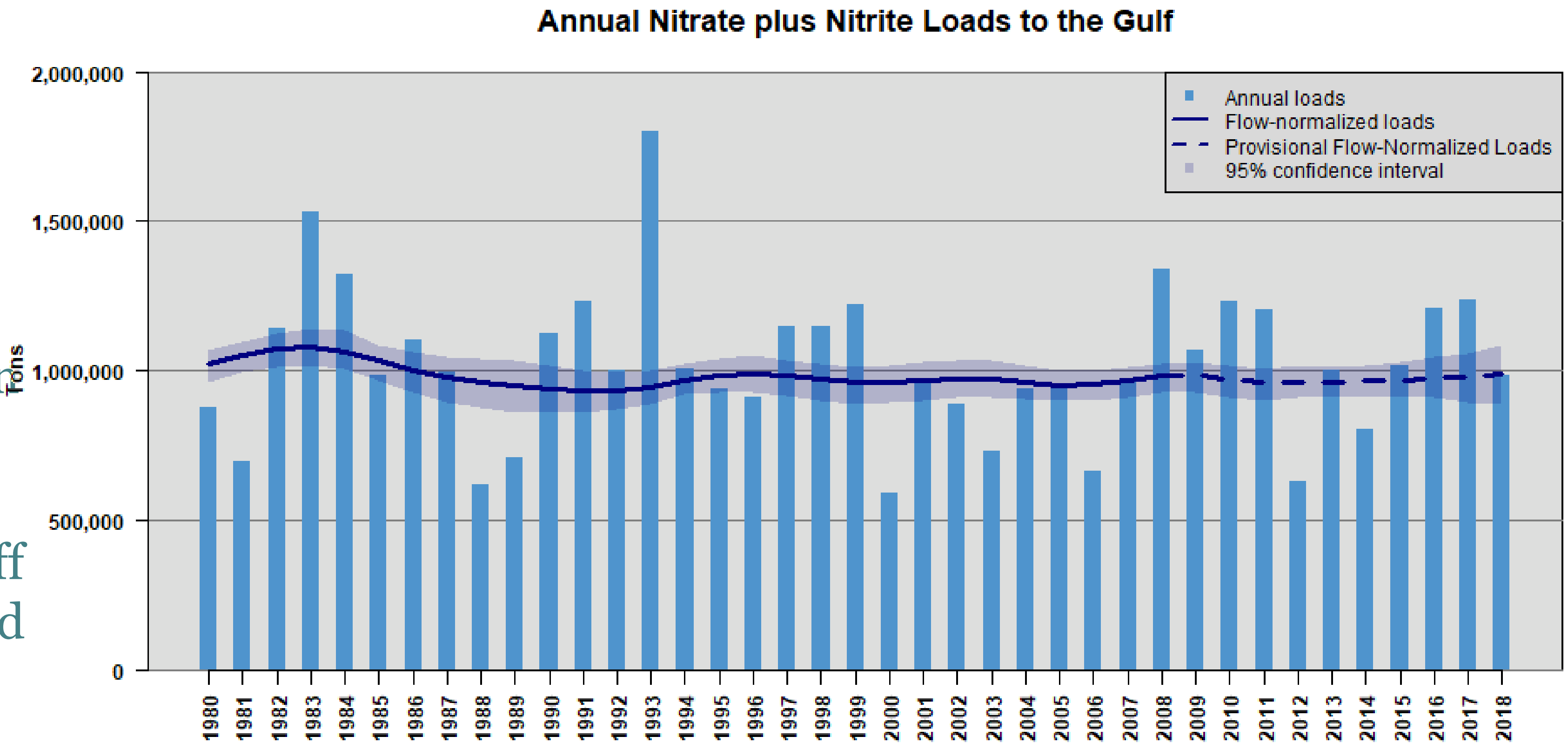
Final list of sites for orthophosphate



USGS

Nitrate loading to the Gulf of Mexico

- Hypoxia Task Force target
  - 45 % reduction in nitrogen loading to Gulf of Mexico by 2035
  - Interim goal of 20 % reduction by 2025.
  - Additionally recognized that nitrogen loading in high runoff years will need to be addressed consistently.
- Nutrient flux has remained relatively constant in recent years



Nitrate loading to the Gulf of Mexico

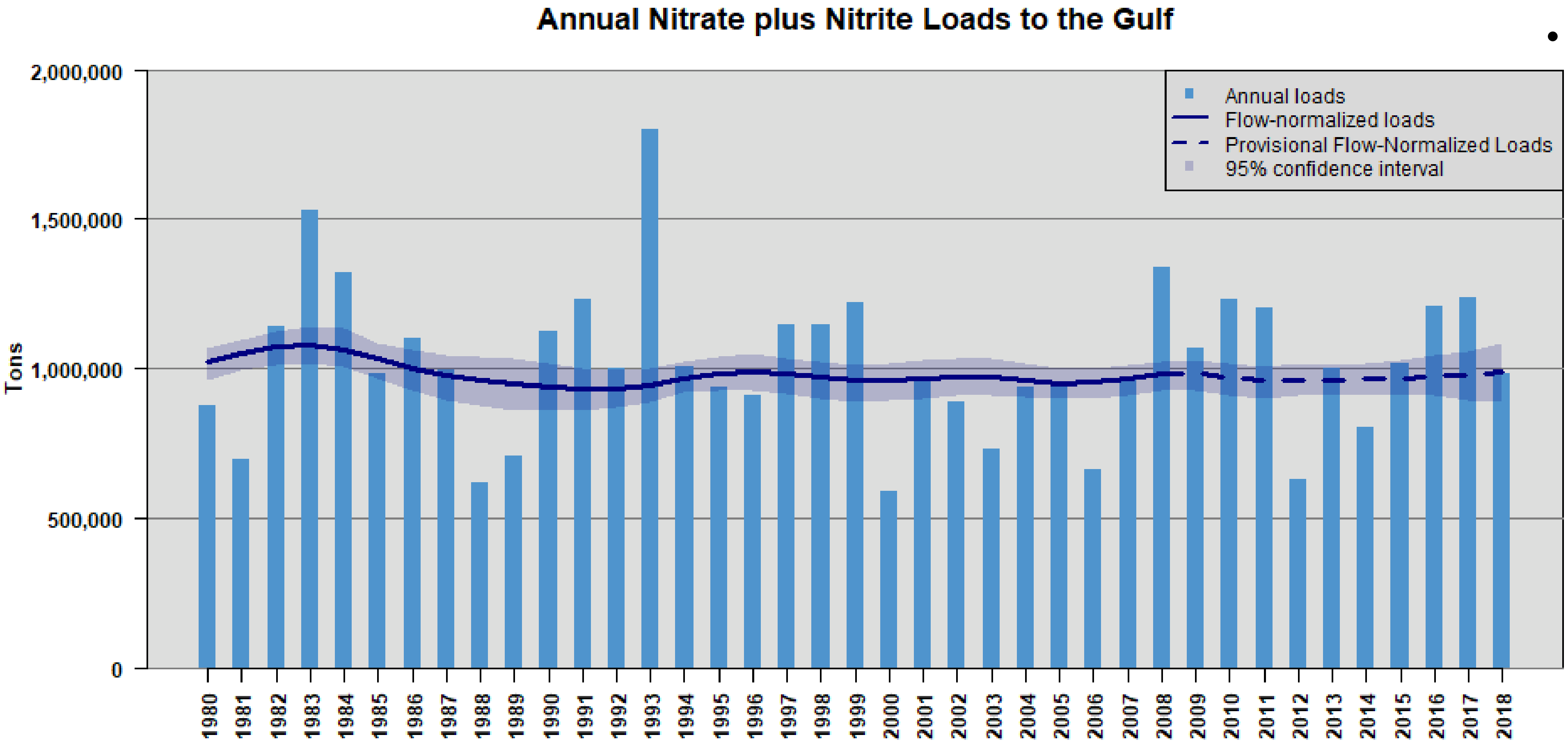
- What is the spatial pattern of nitrate loading trends in the basin?
- Where have improvements been made? What information is missing?
- What can be done to better understand interannual variation in nitrate loading in the Mississippi River Basin?

Load and trend analysis – Weighted Regression on Time, Discharge, and Season (WRTDS)

- Regression-based water quality model
- Requires concentration (c) data and daily discharge (Q) data.
- Allows flexible concentration-discharge relationships to be developed and applied over the time series

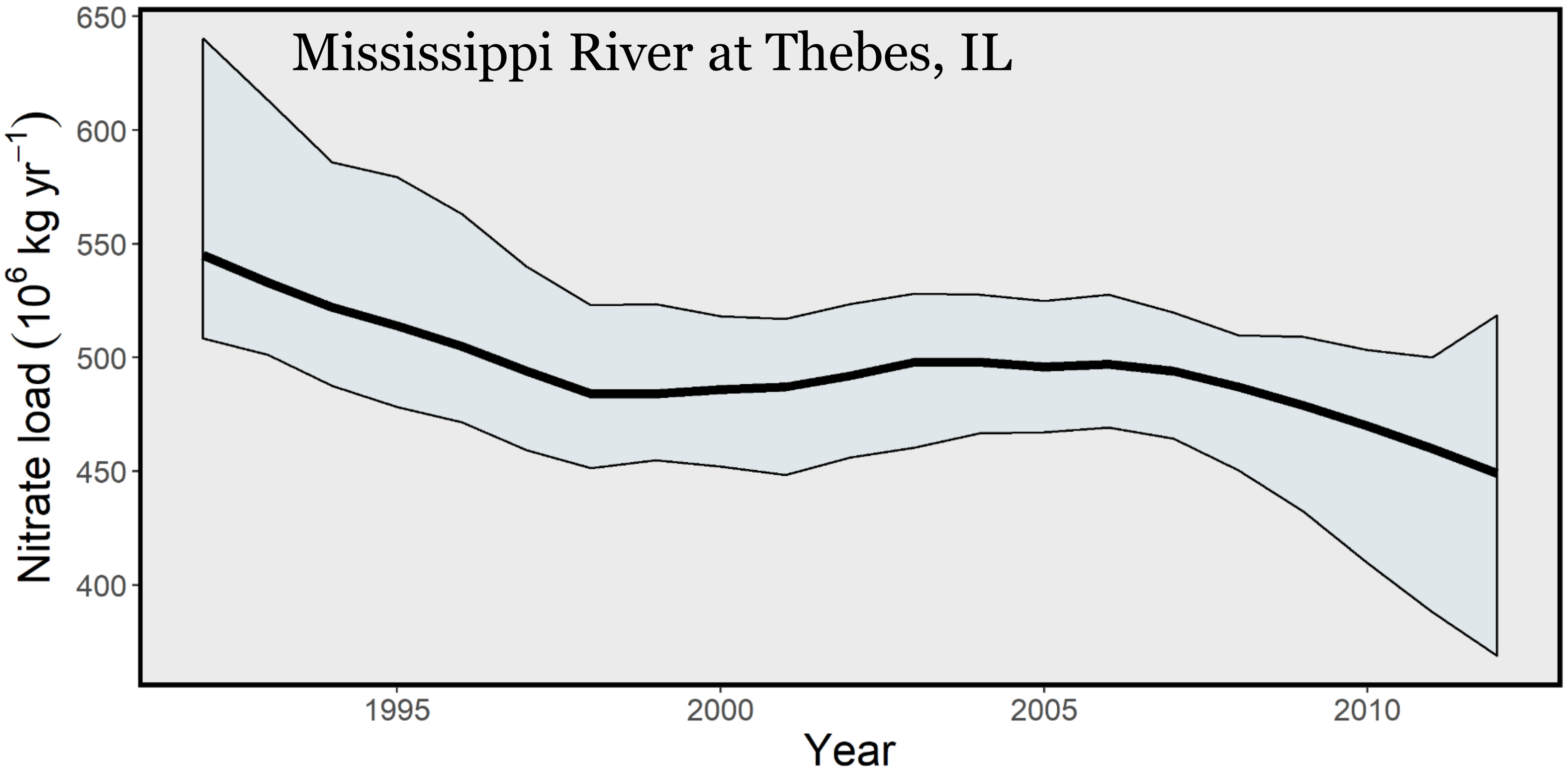
$$\ln(c) = \beta_0 + \underset{\text{Temporal trend}}{\beta_1 t} + \underbrace{\beta_2 \ln(Q)}_{\text{Discharge}} + \underbrace{\beta_3 \sin(2\pi t) + \beta_4 \cos(2\pi t)}_{\text{Seasonality}} + \varepsilon$$

Load and trend analysis – Weighted Regression on Time, Discharge, and Season (WRTDS)



- *Flow normalization* is meant to remove variability due to random variation in streamflow.
- Trend detection accomplished by bootstrapping time series and using likelihood analysis.

Trends detected using bootstrapping and likelihood analysis



- Confidence intervals were calculated by sub-sampling model calibration data.
- Trends were determined based on the number of model runs showing an *increase* or *decrease* over the trend period.
- Likelihood definitions:

>85 % *increase* or *decrease*	"Trend likely"
70% to 85% *increase* or *decrease*	"Trend somewhat likely"
<70 % *increase* or *decrease*	"Trend about as likely as not"

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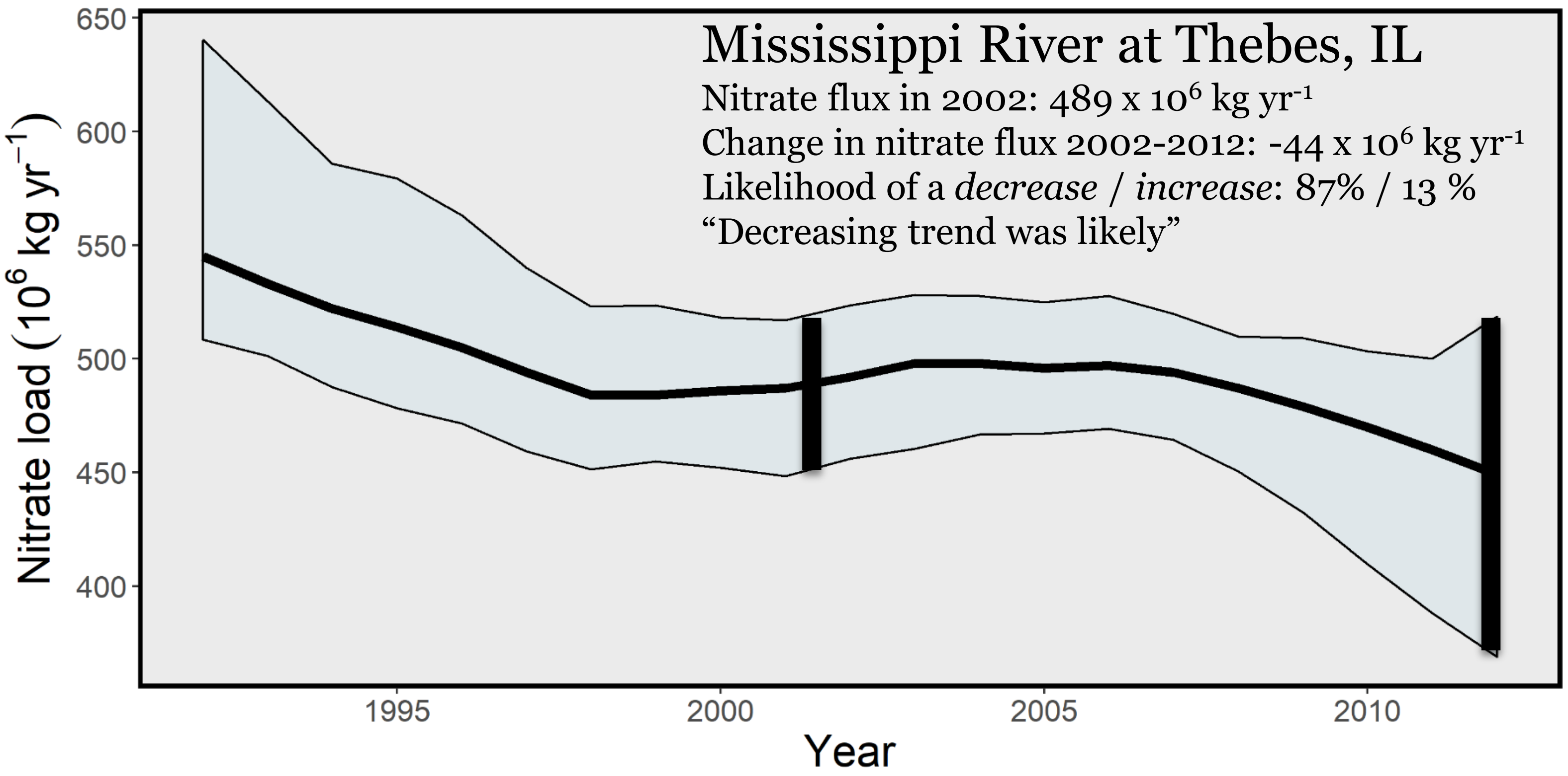

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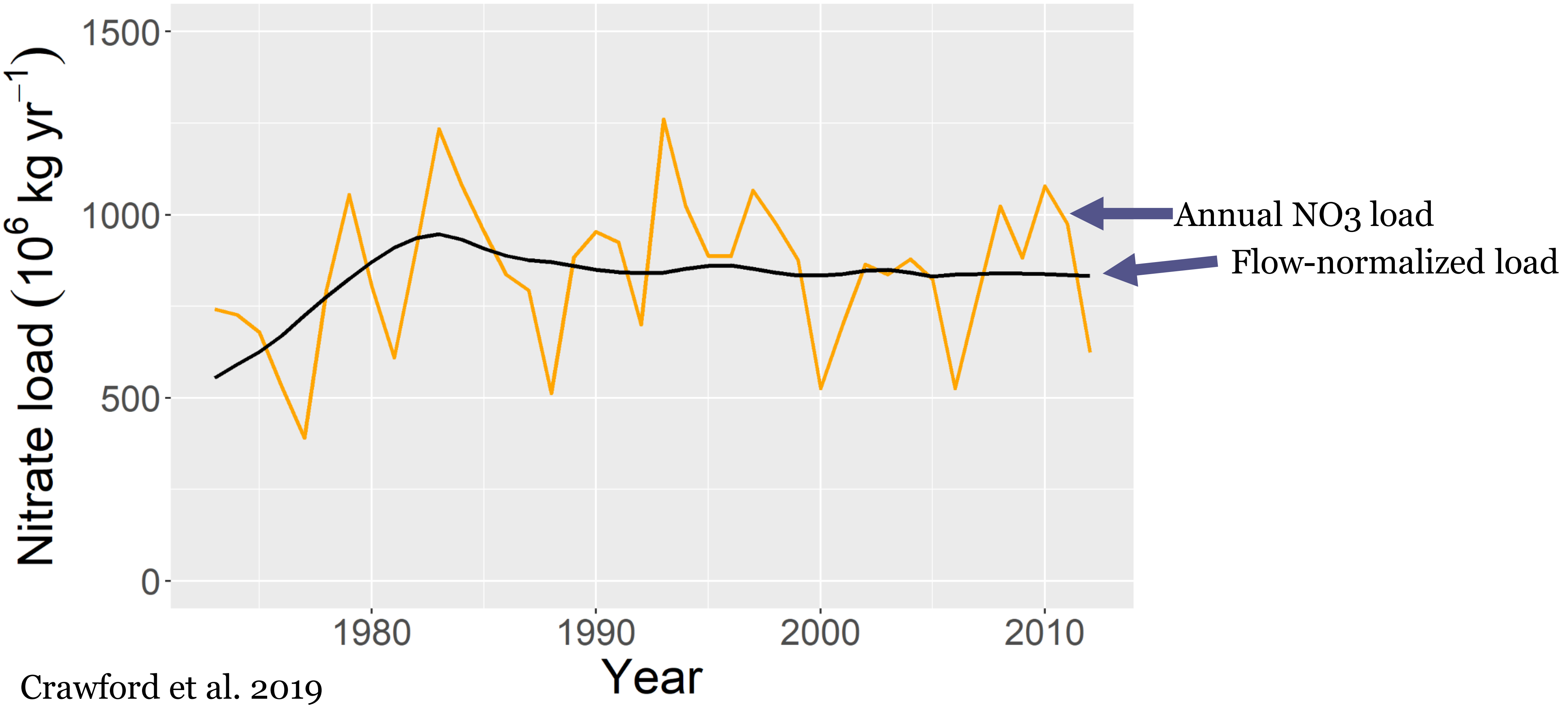
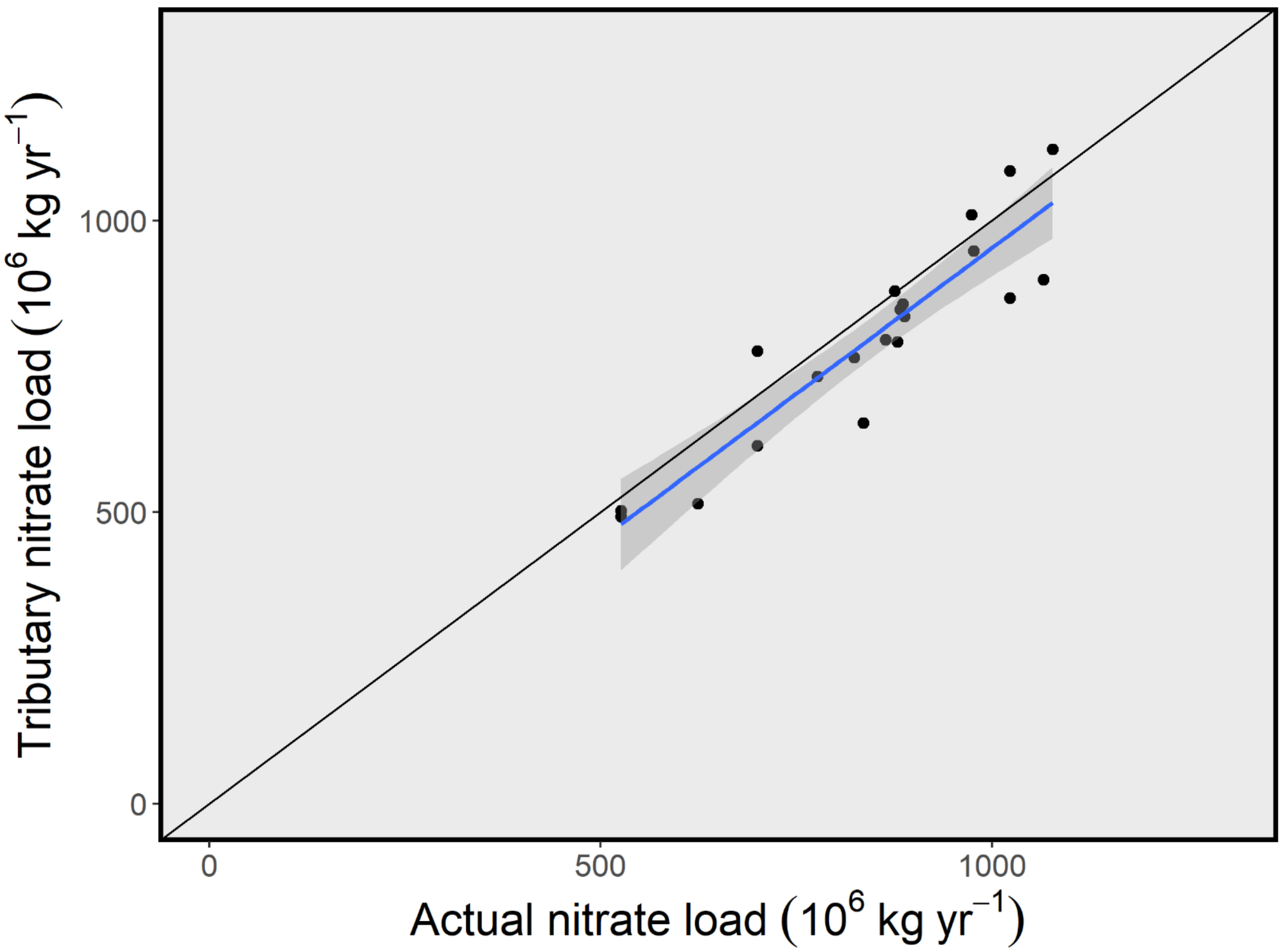
Lack of nitrogen trends in the Mississippi River Basin

Mississippi River, St. Francisville



Crawford et al. 2019

Nitrate loads from the major tributaries approximates nitrogen load at outlet of the Mississippi River



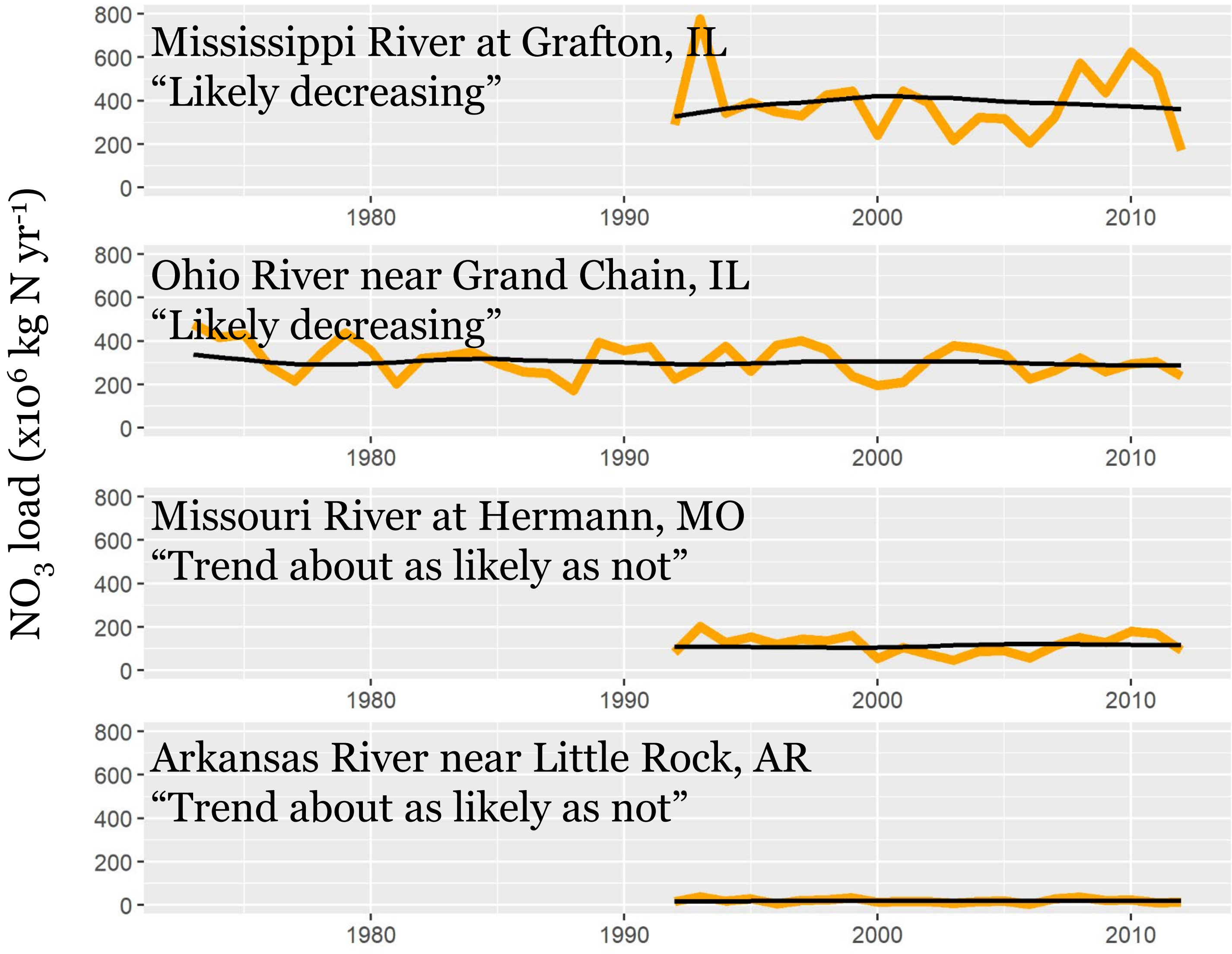
Major tributaries:

- Upper Mississippi (Grafton, IL)
- Ohio River (near Grand Chain, IL)
- Missouri River (Hermann, MO)
- Arkansas River (Little Rock, AR)

Sum of tributary nitrate load –

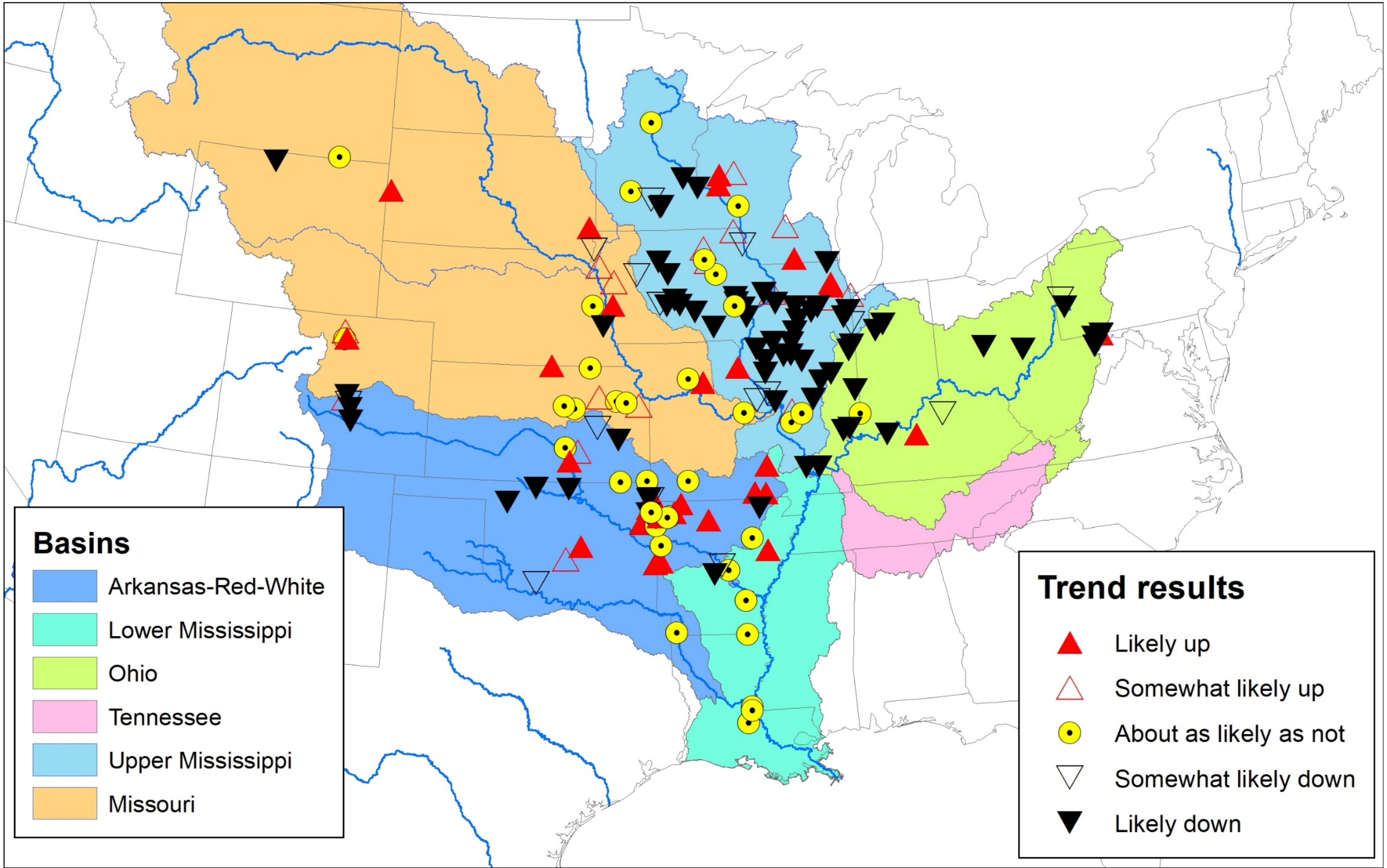
Average 95 % of nitrate load at St Francisville, MS

Nitrate flux from major tributaries of the Mississippi River

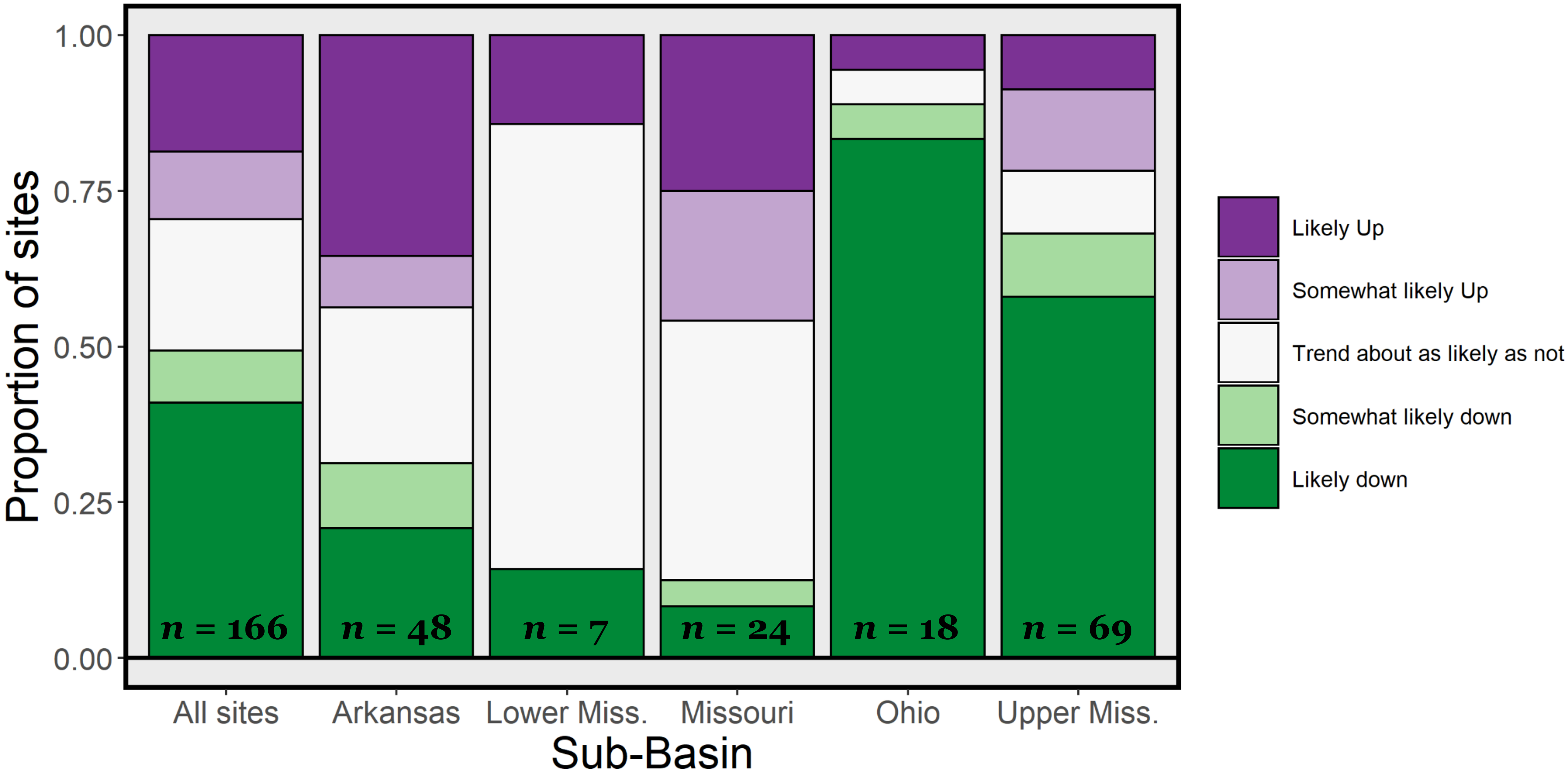


Load 2002 $\times 10^6$ kg N yr^{-1}	Load 2012 $\times 10^6$ kg N yr^{-1}	Net change $\times 10^6$ kg N yr^{-1}
415 (403-447)	351 (321-403)	-54 (-126 - -14)
305 (290-315)	286 (266-309)	-19 (-46 - 11)
112 (104-124)	115 (84-135)	3.5 (-38 - 25)
19 (18-23)	19 (17-22)	+0.1 (-2.5 – 3.6)

Nitrate loading trends at 166 sites

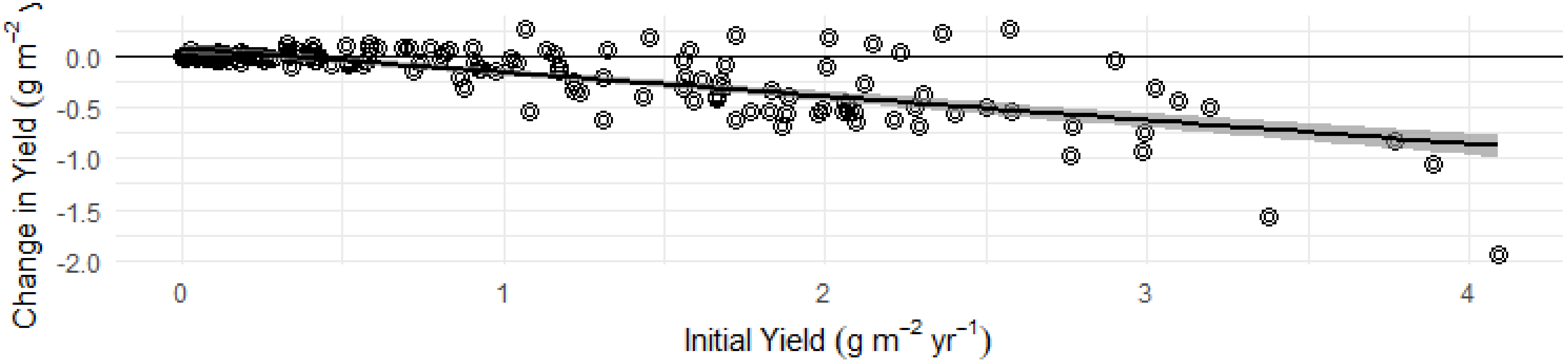


Trend result summary by sub-basin

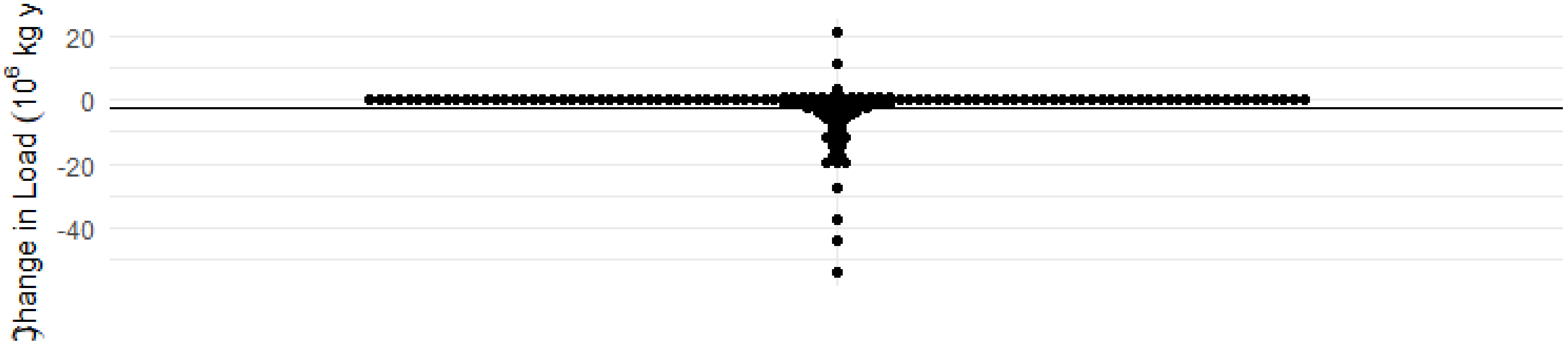


Lack of nitrogen trends in the Mississippi River Basin

yield = Load / drainage area

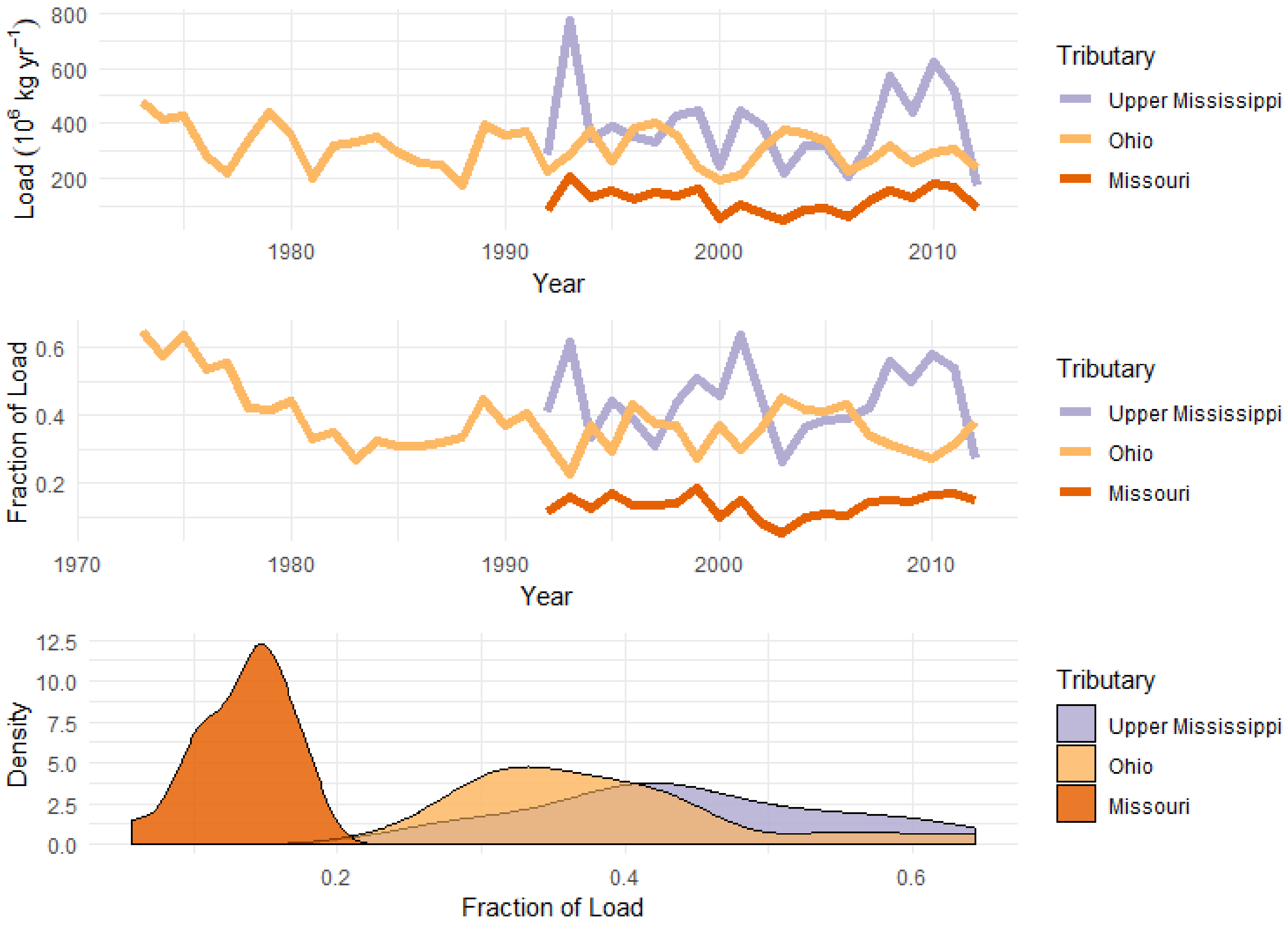


Largest improvements occurred at the most degraded sites



However, most trends were small and off-setting

Interannual variability of nitrate flux is much higher from Upper Mississippi than other tributaries



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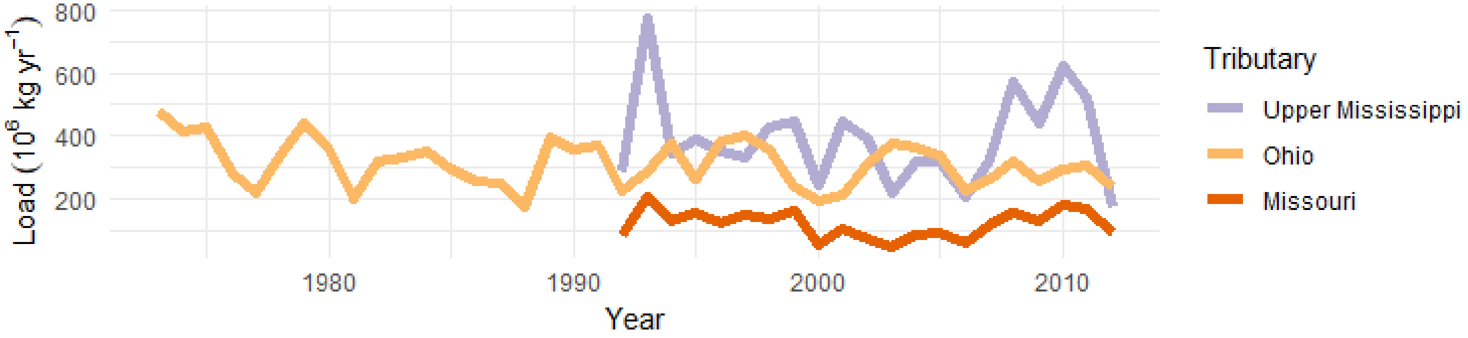
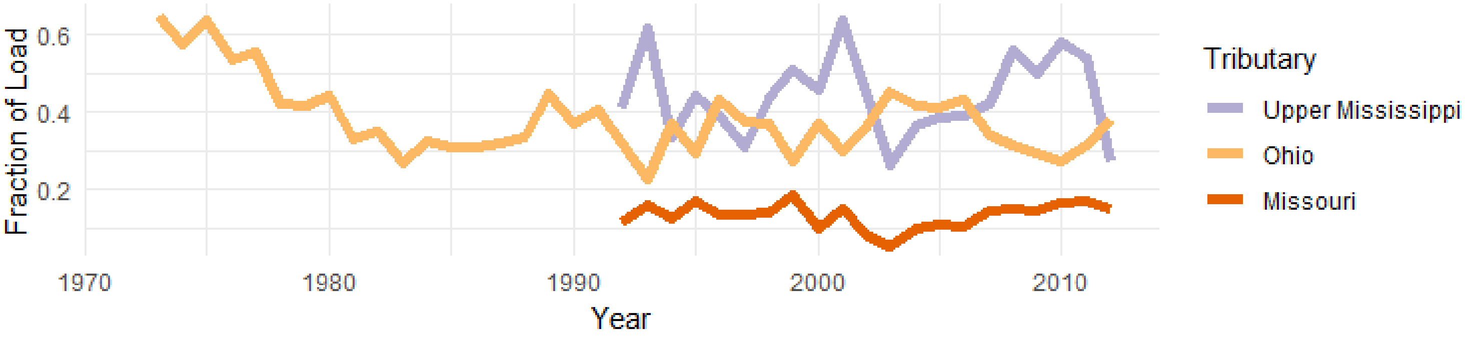
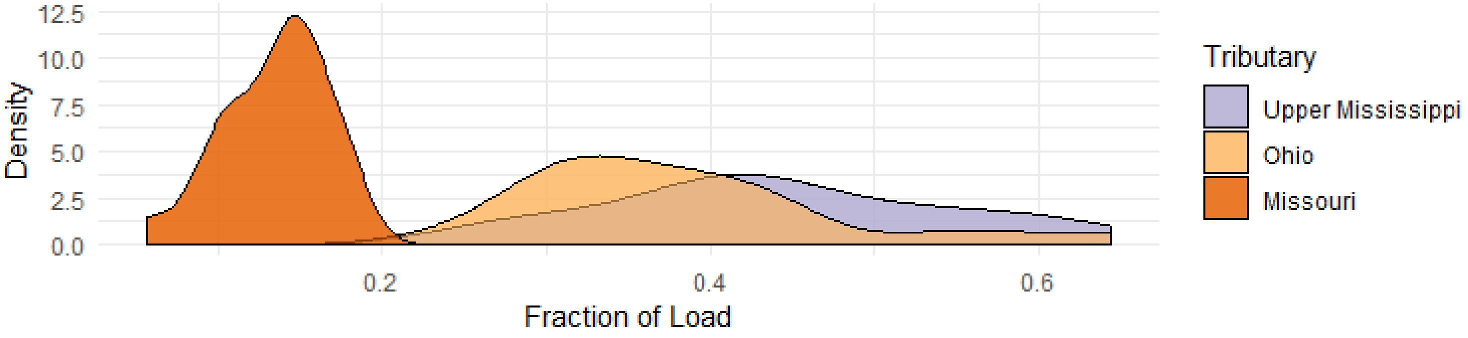






Variance ratio test –

"How much of the variance in NO3 flux from the outlet of the Mississippi River is contributed by each major tributary?"

$$VR = \frac{s^2_{Tributary}}{s^2_{Miss-Tarbert}}$$

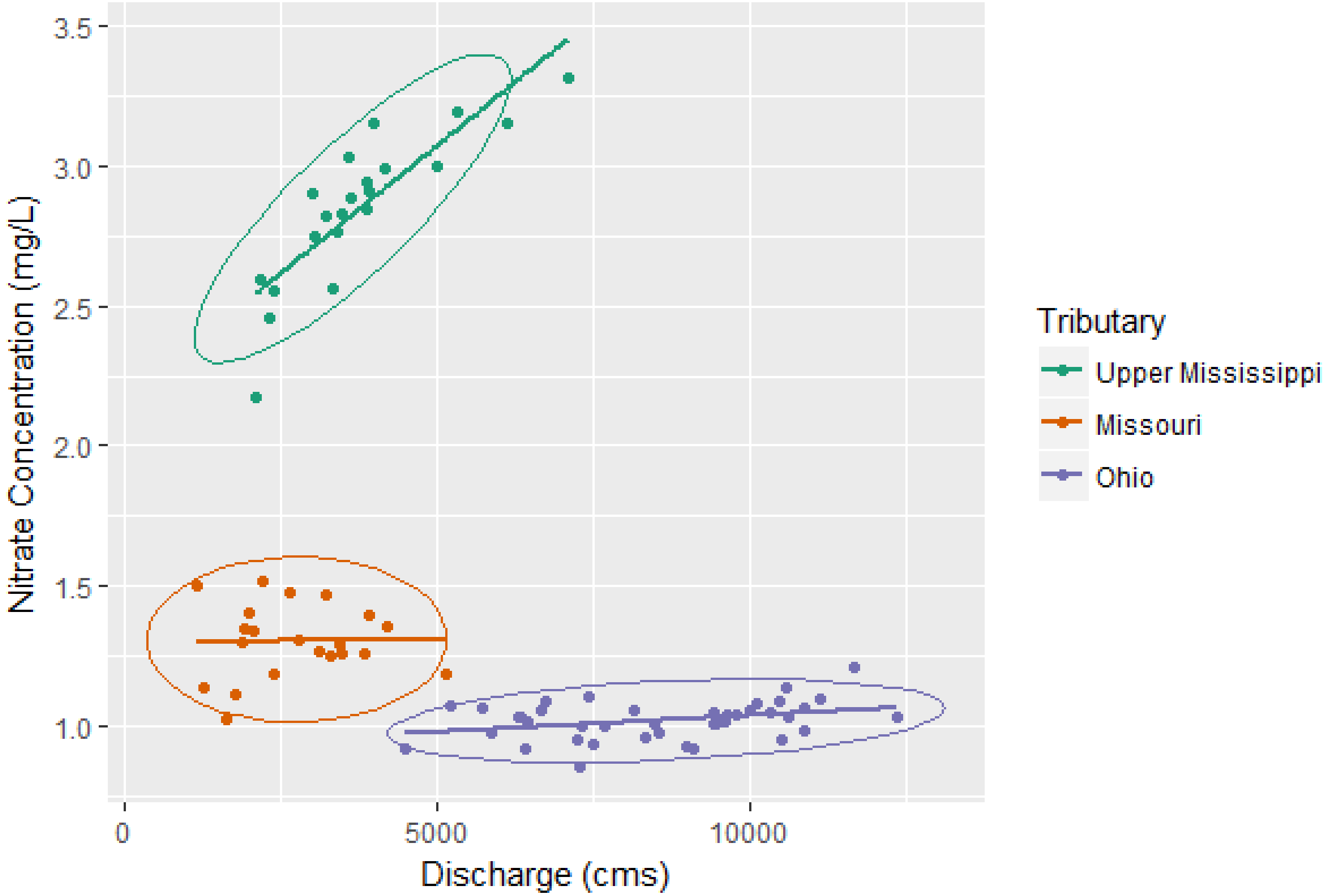
Comparison	**VR**	***p-value***
UMR vs Outlet	0.9	0.84
Ohio vs Outlet	0.1	0.002

Why do nitrate fluxes from the Upper Mississippi River exhibit such high variability?

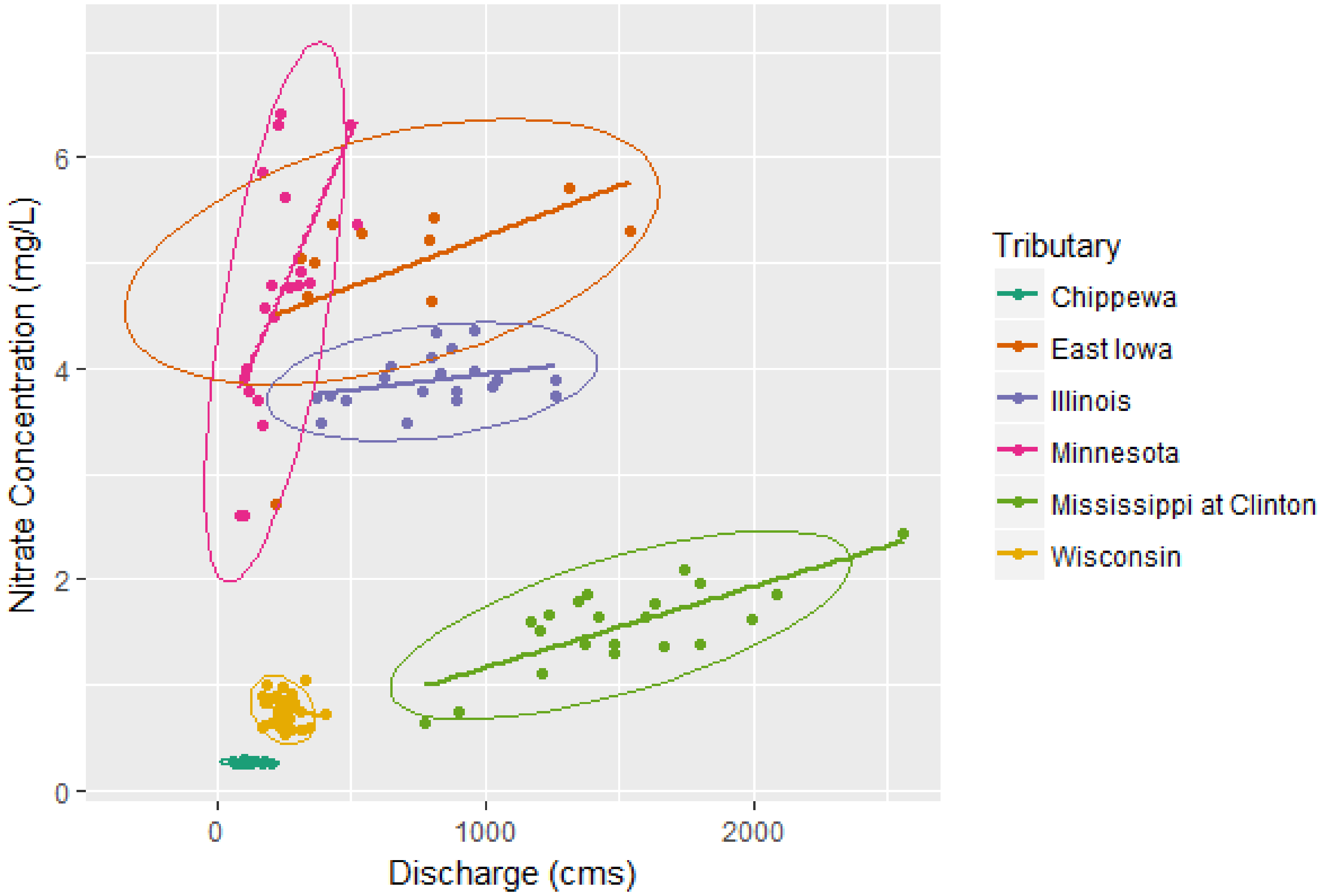
I. Flow variation

Tributary	Mean discharge	Std. dev.	CV (SD/Mean)
Upper Miss.	3780	1262	33 %
Ohio	8589	1947	23 %
Missouri	2748	1043	38 %

II. Concentration-discharge relationships



Upper Mississippi River nitrate load dynamics



Summary

- Nitrate fluxes from the Mississippi River to the Gulf of Mexico decreased slightly during the period 2002-2012:

  -1.58%

  Trend about as likely as not
- Nitrate flux trends differed by major tributary and by sub-basin.
- Sites with the highest initial nitrate yield had the strongest and most consistent decreases.
- Flux trends throughout the basin were approximately equal magnitude of increases and decreases.
- Despite documented decreases in some areas, especially those with highest initial nitrate yields, the improvements were not large enough nor widespread enough to cause a substantial decrease at St Francisville.
- Substantial geographic differences were found in the contribution of major tributaries to variability in nitrate loading at St. Francisville.

Further resources on Surface Water Status and Trends

Published manuscripts

Crawford, J.T., E.G. Stets, and L.A. Sprague. 2019. Network controls on mean and variance of nitrate loads from the Mississippi River to the Gulf of Mexico. Journal of Environmental Quality. doi:10.2134/jeq2018.12.0435.

Oelsner, G.P. and E.G. Stets. 2019. Recent trends in nutrient and sediment loading to coastal areas of the conterminous U.S.: Insights and global context. Science of The Total Environment 654: 1225-1240. doi:https://doi.org/10.1016/j.scitotenv.2018.10.437.

Sprague, L.A., R.M. Mitchell, A.I. Pollard, and J.A. Falcone. 2019. Assessing water-quality changes in US rivers at multiple geographic scales using results from probabilistic and targeted monitoring. Environmental Monitoring and Assessment. doi: https://doi.org/10.1007/s10661-019-7481-5.

Sprague, L.A., G.P. Oelsner and D.M. Argue. 2017. Challenges with secondary use of multi-source water-quality data in the United States. Water Research 110: 252-261. doi:https://doi.org/10.1016/j.watres.2016.12.024.

Stets, E.G., C.J. Lee, D.A. Lytle and M.R. Schock. 2017. Increasing chloride in rivers of the conterminous U.S. and linkages to potential corrosivity and lead action level exceedances in drinking water. Science of The Total Environment. doi:http://dx.doi.org/10.1016/j.scitotenv.2017.07.119.

Stackpoole, S.M., E.G. Stets and L.A. Sprague. 2019. Variable impacts of contemporary versus legacy agricultural phosphorus on US river water quality. Proceedings of the National Academy of Sciences: 201903226. doi:10.1073/pnas.1903226116.

Methodology and datasets
Oelsner, G.P., L.A. Sprague, J.C. Murphy, R.E. Zuellig, H.M. Johnson, K.R. Ryberg, et al. 2017. Water-quality trends in the nation's rivers and streams, 1972–2012—Data preparation, statistical methods, and trend results. Scientific Investigations Report. Reston, VA. p. 158.

WRTDS
Hirsch, R.M., D.L. Moyer and S.A. Archfield. 2010. Weighted Regressions on Time, Discharge, and Season (WRTDS), with an Application to Chesapeake Bay River Inputs1. JAWRA Journal of the American Water Resources Association 46: 857-880. doi:10.1111/j.1752-1688.2010.00482.x.

Hirsch, R.M., S.A. Archfield and L.A. De Cicco. 2015. A bootstrap method for estimating uncertainty of water quality trends. Environmental Modelling & Software 73: 148-166. doi:http://dx.doi.org/10.1016/j.envsoft.2015.07.017.

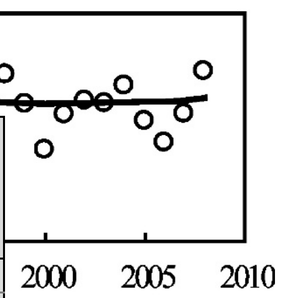
Online resources
EGRET R package: https://cran.r-project.org/web/packages/EGRET/index.html

Trends mapper: https://nawqatrends.wim.usgs.gov/swtrends/

Team updates: https://www.usgs.gov/mission-areas/water-resources/science/water-quality-nation-s-streams-and-rivers-current-conditions

Nitrate loading to the Gulf of Mexico

Nitrate flux at Mississippi River above Old River Outflow



prague et al. 2011

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