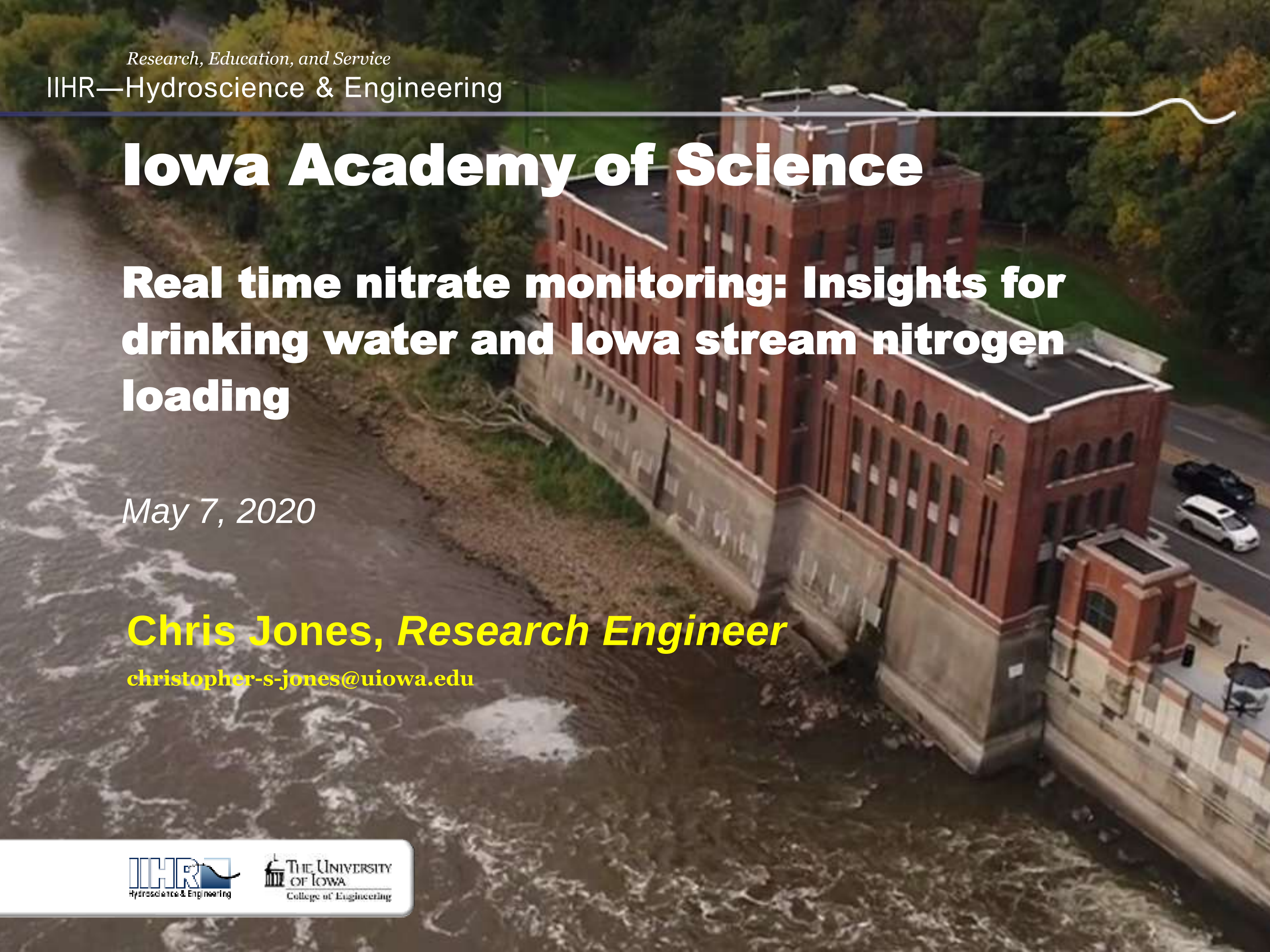


Research, Education, and Service

IIHR—Hydroscience & Engineering

Iowa Academy of Science

Real time nitrate monitoring: Insights for drinking water and Iowa stream nitrogen loading

May 7, 2020

Chris Jones, *Research Engineer*

christopher-s-jones@uiowa.edu

IIHR Hydroscience & Engineering

The University of Iowa College of Engineering

Slides Available at:

https://www.iihr.uiowa.edu/cjones/welcome/

Safe Drinking Water Act passed into law in 1974

Gave the federal government the authority to regulate drinking water quality and treatment in Public Water Supplies (CWS)

~20 regulated parameters initially, now >100

Nitrate was one of the original 20 (MCL=10 mg/L)

Public Water Supply Definition

EPA has defined three types of public water systems:

***Community Water System* (CWS):** A public water system that supplies water to the same population year-round.

***Non-Transient Non-Community Water System* (NTNCWS)**: A public water system that regularly supplies water to at least 25 of the same people at least six months per year. Some examples are schools, factories, office buildings, and hospitals which have their own water systems.

***Transient Non-Community Water System* (TNCWS)**: A public water system that provides water in a place such as a gas station or campground where people do not remain for long periods of time.

Iowa

880 Public Water Systems

- 30% are classified as "vulnerable" to nitrate contamination, i.e. finished water >5 mg/L at times
- ~60 are removing nitrate or blending to lower finished water levels

Private Wells

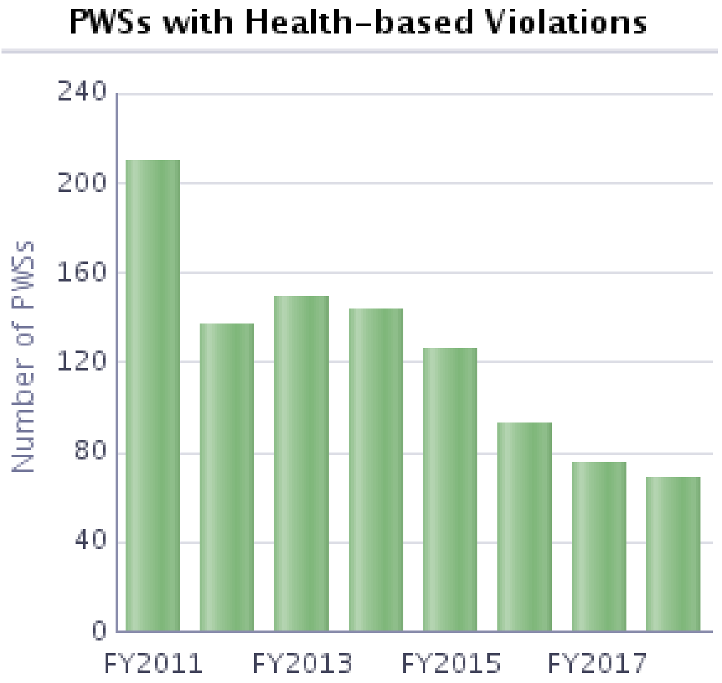
- 12% >10 mg/L

National Compliance: SDWA

TABLE 3: HEALTH-BASED VIOLATIONS OF THE SAFE DRINKING WATER ACT IN CALENDAR YEAR 2015 RANKED BY POPULATION SERVED[i]			
RULE NAME	POPULATION SERVED	NUMBER OF VIOLATIONS	NUMBER OF SYSTEMS
All Violations	27,412,987	12,137	5,009
Combined Disinfectants and Disinfection Byproducts Rules[ii]	12,584,936	4,591	1,552
Total Coliform Rule	10,118,586	2,574	1,909
Combined Surface, Ground Water, and Filter Backwash Rules[iii]	5,336,435	1,790	813
Nitrates and Nitrites Rule	1,364,494	459	192
Lead and Copper Rule	582,302	303	233
Radionuclides Rule	445,969	962	258
Arsenic Rule	358,323	1,135	352
Synthetic Organic Contaminants Rule	301,099	17	13
Inorganic Contaminants Rule	83,033	291	77
Volatile Organic Contaminants Rule	5,276	15	6

Slide courtesy Dave Cwiertny

Iowa's Drinking Water – Where do we struggle?



Iowa PWS Health-Based Violations (2017)

Radionuclides	79
Nitrates	39
Surface Water Treatment Rule	32
Revised Total Coliform Rule	21
Arsenic	19
Stage 2 DBP	14
Groundwater Rule	8
Volatile Organic Contaminants	7
Total Coliform Rule	6
Long-term 1 Enhanced Surface Water Treatment Rule	2
Other Inorganic Contaminant	1

https://echo.epa.gov/

1. Nitrate is regulated by the EPA in drinking water (at 10 mg/L or ppm)

Des Moines Register

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High nitrate levels plague 60 Iowa cities, data show

Donnelle Eller, deller@dmreg.com Published 9:48 p.m. CT July 4, 2015 | Updated 8:09 a.m. CT July 7, 2015

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(Photo: Michael Zamora/Register photos)

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More than 60 Iowa cities and towns have battled high nitrate levels in their drinking water over the past five years, evidence of a contamination problem that reaches across the state, state environmental data show.

Nitrate pollution affects Iowa's largest cities — Des Moines, Cedar Rapids, Cedar Falls and Waterloo — but also many of its smallest — Elliott, Griswold, Manchester and Woodbine.

The Iowa Department of Natural Resources data provide a snapshot of the cities reporting nitrate levels of 5 milligrams per liter or higher, a warning sign that nitrates are approaching harmful levels.

Nitrate regulation of 10 mg/L set for methemoglobinemia (blue-baby syndrome)

- Nitrate transforms to nitrite in body, reacts with hemoglobin, reduces ability of blood to carry oxygen
- Can lead to trouble breathing, vomiting, anoxia
- Rarely diagnosed in U.S.
- ~2000 cases diagnosed worldwide from 1945-1970
- Most recent Iowa case was in late 1970s / early 1980s

More recent concerns: Endogenous formation of carcinogenic *N*-nitroso compounds (NOC) from ingested nitrate and nitrite

Nitrate from drinking water

Dietary nitrite/nitrate

Nitrite +
Amines/amides (protein)

Endogenous formation of NOC in GI tract

-Catalyzed by heme iron (red meat)
-Inhibited by antioxidants (Vitamin C)

Is our MCL for nitrate strict enough?

International Journal of
Environmental Research and Public Health

MDPI

Review

Drinking Water Nitrate and Human Health: An Updated Review

Mary H. Ward [1,*], Rena R. Jones [1], Jean D. Brender [2], Theo M. de Kok [3], Peter J. Weyer [4], Bernard T. Nolan [5], Cristina M. Villanueva [6,7,8,9] and Simone G. van Breda [3]

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Abstract: Nitrate levels in our water resources have increased in many areas of the world largely due to applications of inorganic fertilizer and animal manure in agricultural areas. The regulatory limit for nitrate in public drinking water supplies was set to protect against infant methemoglobinemia, but other health effects were not considered. Risk of specific cancers and birth defects may be increased when nitrate is ingested under conditions that increase formation of *N*-nitroso compounds. We previously reviewed epidemiologic studies before 2005 of nitrate intake from drinking water and cancer, adverse reproductive outcomes and other health effects. Since that review, more than 30 epidemiologic studies have evaluated drinking water nitrate and these outcomes. The most common endpoints studied were colorectal cancer, bladder, and breast cancer (three studies each), and thyroid disease (four studies). Considering all studies, the strongest evidence for a relationship between drinking water nitrate ingestion and adverse health outcomes (besides methemoglobinemia) is for colorectal cancer, thyroid disease, and neural tube defects. Many studies observed increased risk with ingestion of water nitrate levels that were below regulatory limits. Future studies of these and other health outcomes should include improved exposure assessment and accurate characterization of individual factors that affect endogenous nitrosation.

Is 10 mg/L low enough?

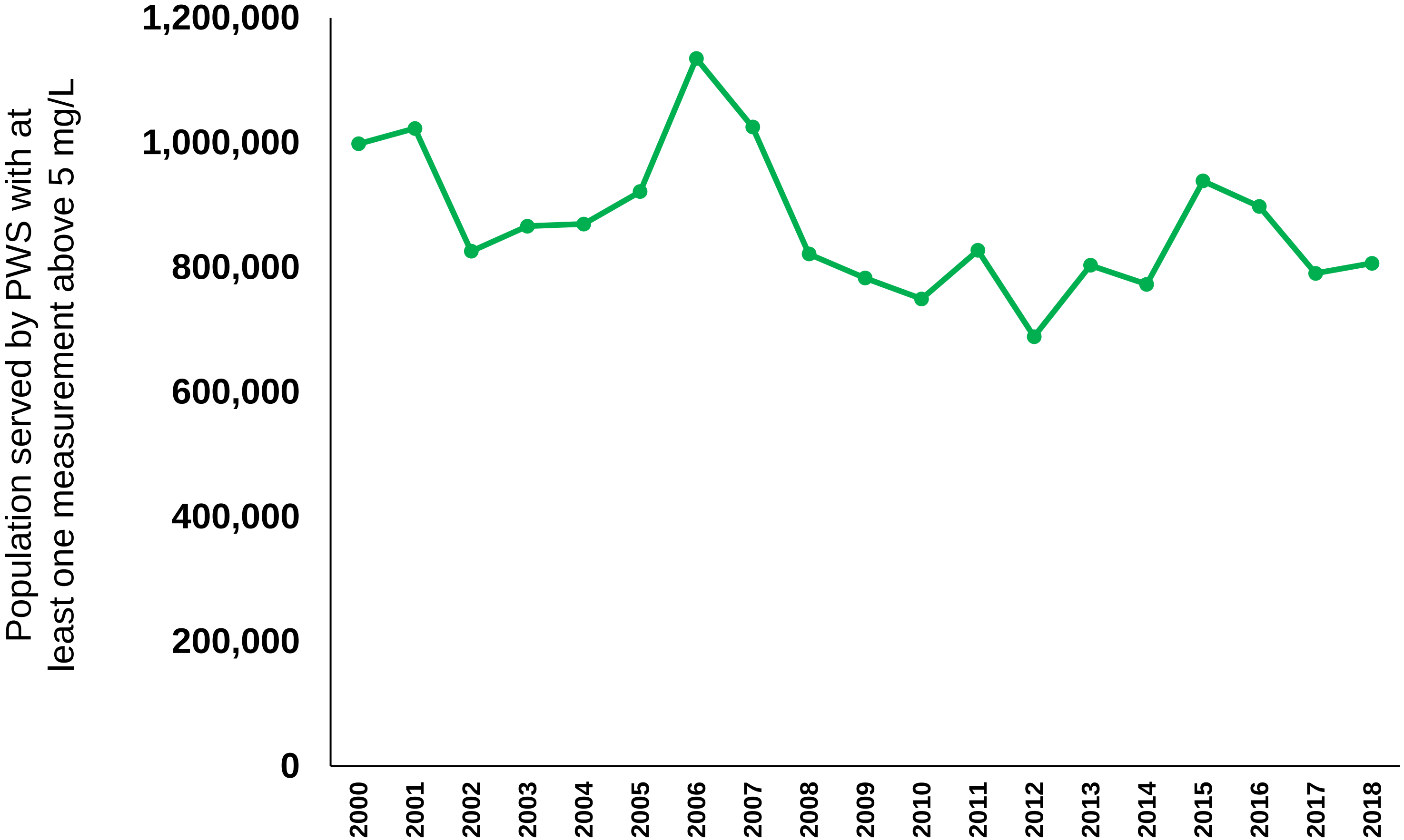
Cancer Risks (Iowa Women's Health Study)

- Bladder cancer
  - 1.6× risk at **>5 mg/L** for ≥4 years (Jones 2016)
- Ovarian cancer
  - 2.0× risk at **>3.0 mg/L** for ≥11 years (Inoue-Choi 2015)
- Thyroid cancer
  - 2.6× risk at **>5 mg/L** for ≥5 years (Ward 2010)

Reproductive Health (National Birth Defects Prevention Study)

- Iowa-Texas Study results (Brender 2013)
  - Spina bifida: 2× more likely to ingest **≥ 5 mg** of nitrate daily from drinking water than control mothers
  - Limb deficiencies: 1.8× more likely to ingest **≥ 5.42** mg of nitrate daily
  - Cleft palate: 1.9× more likely to ingest **≥ 5.42 mg** of nitrate daily

Who in Iowa is drinking water above 5 mg/L?



Research | Open Access | Published: 17 January 2019

Environmental justice and drinking water quality: are there socioeconomic disparities in nitrate levels in U.S. drinking water?

Laurel A. Schaider, Lucien Swetschinski, Christopher Campbell & Ruthann A. Rudel

Environmental Health **18**, Article number: 3 (2019) | Cite this article

24k Accesses | **20** Citations | **188** Altmetric | Metrics

5.6 million Americans drink water with Nitrate-N >5 mg/L

800,000 are Iowans

1% of the U.S. population

14% of Americans drinking water >5 mg/L are Iowans.

Treatment Mitigation

Ion Exchange

Pros:

- Low energy
- Doesn’t alter hardness or alkalinity

Cons:

- Wastes water
- Salt Purchases
- Increases Na Content of finished water
- Produces salty discharge

Reverse Osmosis

Pros:

- Waste is more benign than IX
- Good for small systems

Cons:

- Wastes water
- High Energy
- Reduces hardness alkalinity

Blending

Pros:

- No waste stream
- Doesn’t waste water
- Low Energy

Cons:

- Reduces finished water quality
- Capacity problems

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Monitoring

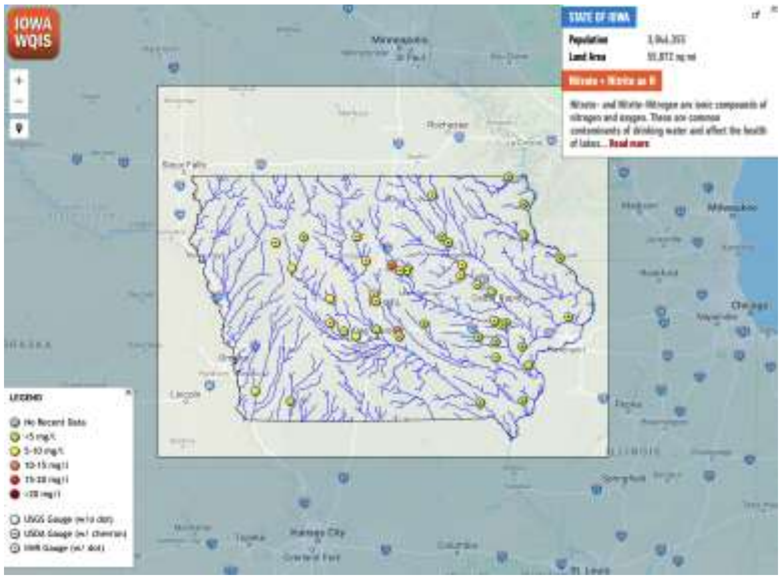
Compliance Monitoring governed by PWS permit (IDNR)

- Annual, Monthly, Daily lab monitoring depending upon source water nitrate and available treatment. **(Is compliance monitoring adequate to protect public health?)**
- Methods: Ion Chromatography, Automated colorimetry (Lachat), ion selective electrode **(How applicable is continuous monitoring to compliance).**

Real Time Sensors for Nitrate

Nitrate absorbs UV at 210 nm


IIHR Water Quality
Sensor Setup



Use of real-time sensors for compliance monitoring of nitrate in finished drinking water

Christopher S. Jones, Tianyi Li, Alex Sukalski, Darrin A. Thompson and David M. Cwiertny

ABSTRACT

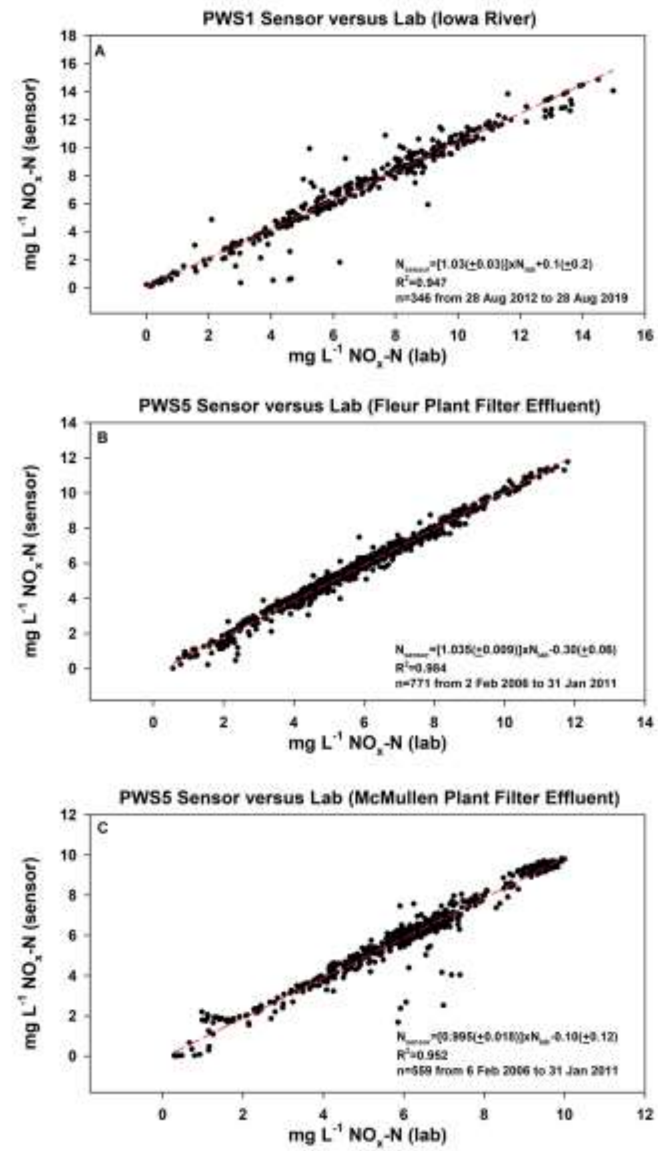
Across the Midwestern United States, Public Water Systems (PWSs) struggle with high levels of nitrate in source waters from intense agricultural activity. Leveraging a sensor network deployed across Iowa surface waters, we evaluated the potential of the Hach Nitratax SC Plus, which uses UV-light absorption to quantify dissolved nitrate-nitrite (NO_x-N) down to 0.1 mg-N L^{-1}, for real-time monitoring of NO_x-N in drinking water. For six different PWSs over multiple years, we compare NO_x-N levels in source waters (surface and groundwater under surface influence) to those measured via traditional methods (e.g., ion chromatography (IC)) for US EPA compliance monitoring. At one large PWS, we also evaluated sensor performance when applied to near-finished drinking water (filter effluent). We find good agreement between traditional analytical methods and *in situ* sensors. For example, for 771 filter effluent samples from 2006–2011, IC analysis averaged NO_x-N of 5.8 mg L^{-1} while corresponding sensor measurements averaged 5.7 mg L^{-1} with a mean absolute error of 0.23 (5.6%). We identify several benefits of using real-time sensors in PWSs, including improved frequency to capture elevated NO_x-N levels and as decision-support tools for NO_x-N management.

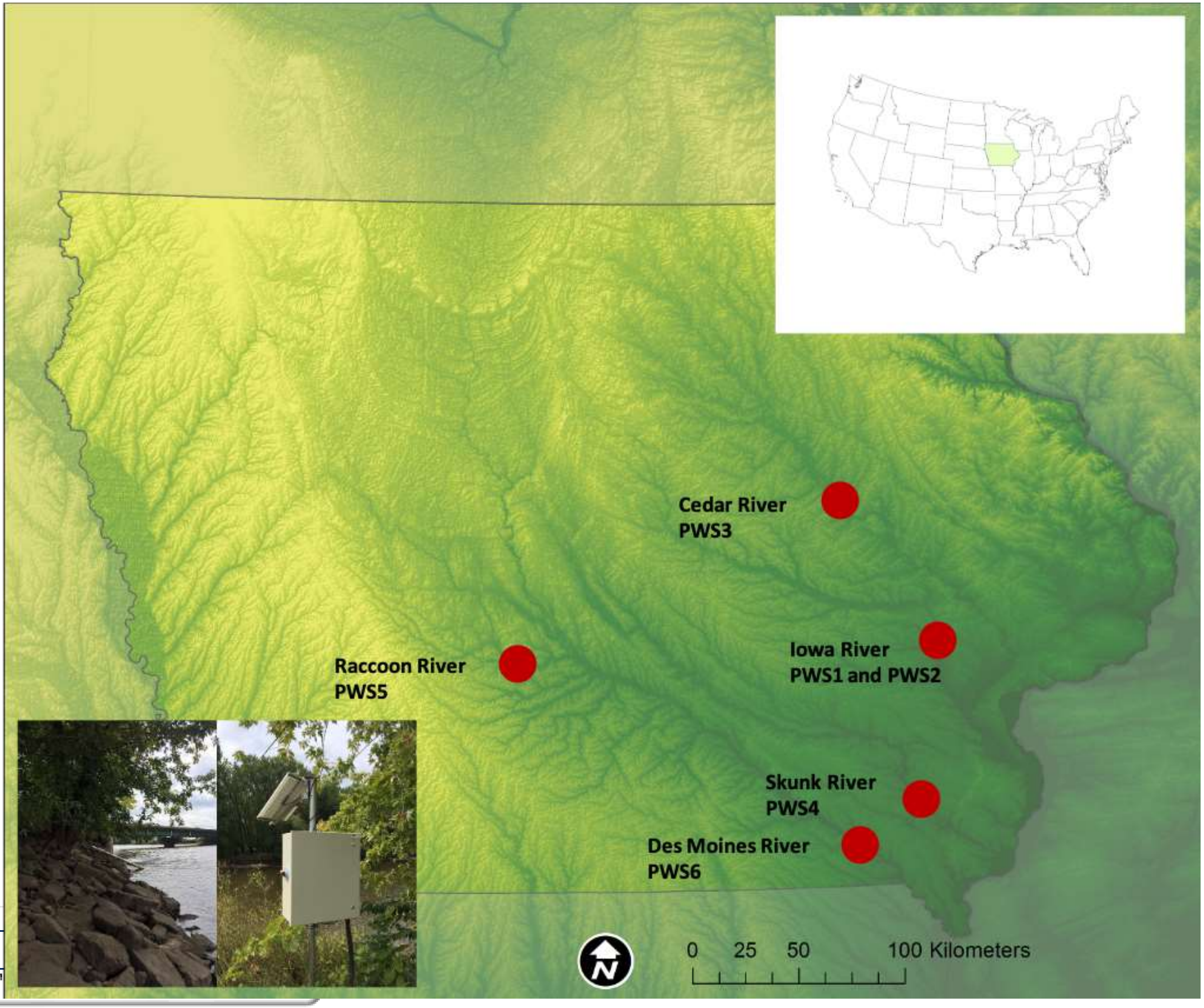
Key words | compliance, drinking water, monitoring, nitrate, regulation, sensor

HIGHLIGHTS

- Monitoring of drinking water nitrate using *in situ* sensors at six community water systems is evaluated.
- Sensors placed in source and finished water agree well with more traditional nitrate analyses.
- Sensors provide accurate, high frequency monitoring data responsive to temporal dynamics in agricultural watersheds.
- Automated nitrate sensors can improve monitoring for better compliance with health-based regulations.
- Sensors can also be used as decision-support tools to guide nitrate management strategies.

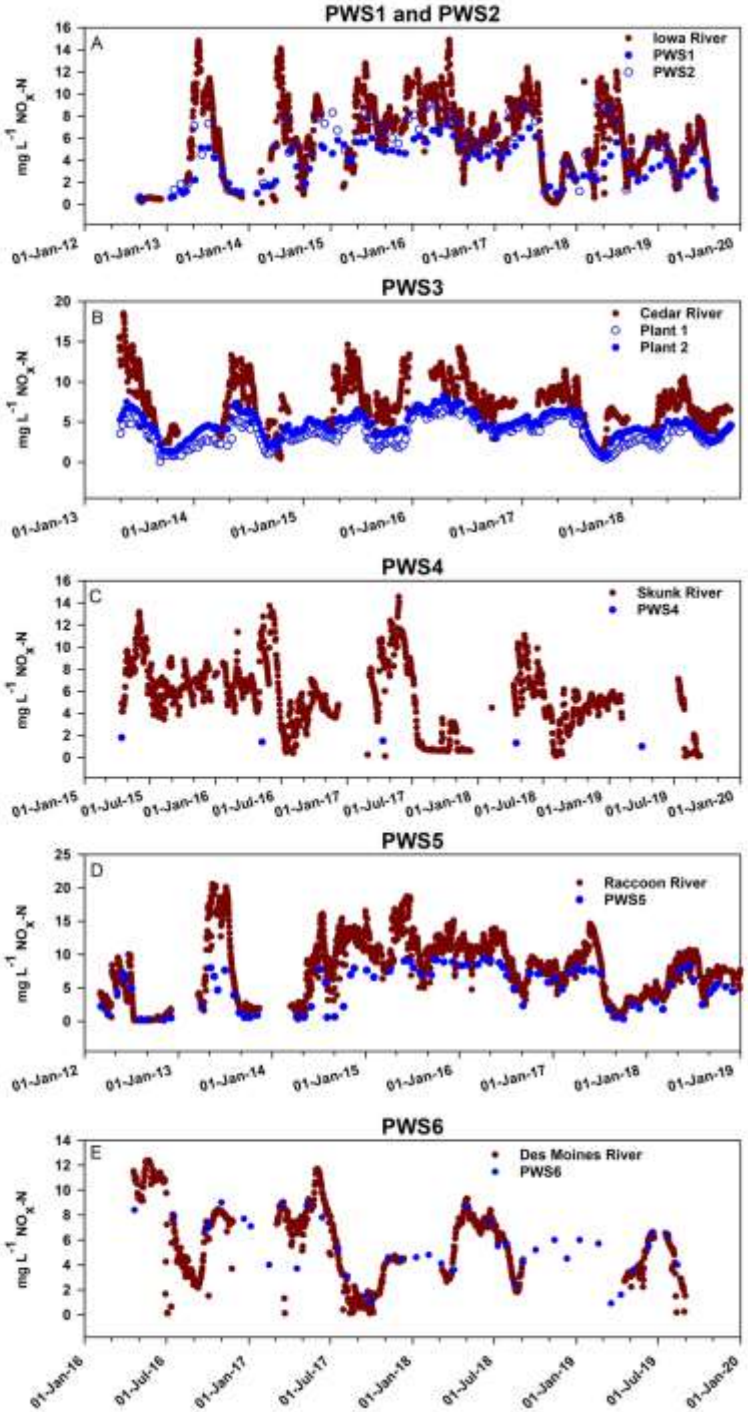
Establish accuracy and precision of sensor relative to lab analysis




Cedar River
PWS3
Iowa River
PWS1 and PWS2
Raccoon River
PWS5
Skunk River
PWS4
Des Moines River
PWS6
N
0 25 50 100 Kilometers

Utilities

Utility	Population Served	Water source	Nitrate Mitigation Strategy
PWS1	63,265	GWUDI	Blending with emergency sources
PWS2	26,684	Surface	Reverse Osmosis, blending
PWS3	133,499	GWUDI	Blending
PWS4	12,700	GWUDI	Blending
PWS5	523,098	Surface, GWUDI	Ion Exchange, blending
PWS6	25,594	Surface	Blending with emergency sources



Time series Sensor vs finished water data

River	n (days)	Average NO_x-N (mg L^{-1})	Maximum NO_x-N (mg L^{-1})	% of days > 10 mg L^{-1}
Iowa	2106	5.9	14.9	11.4
Raccoon	2426	7.7	20.5	31.1
Cedar	1607	7.3	18.5	17.1
Skunk	1227	5.4	14.5	8.5

Utility	PWS 1	PWS 2	PWS3 Plant 1	PWS3 Plant 2	PWS 4	PWS5 McMullen	PWS 6
Ratio of finished/sensor NO_x-N	0.66	0.97	0.51	0.62	0.26	0.68	0.93
Sensor NO_x-N that would generate 10 mg L^{-1} in finished water	15.1	10.3	19.7	16.1	38.5	14.8	10.8

Potential MCL violations

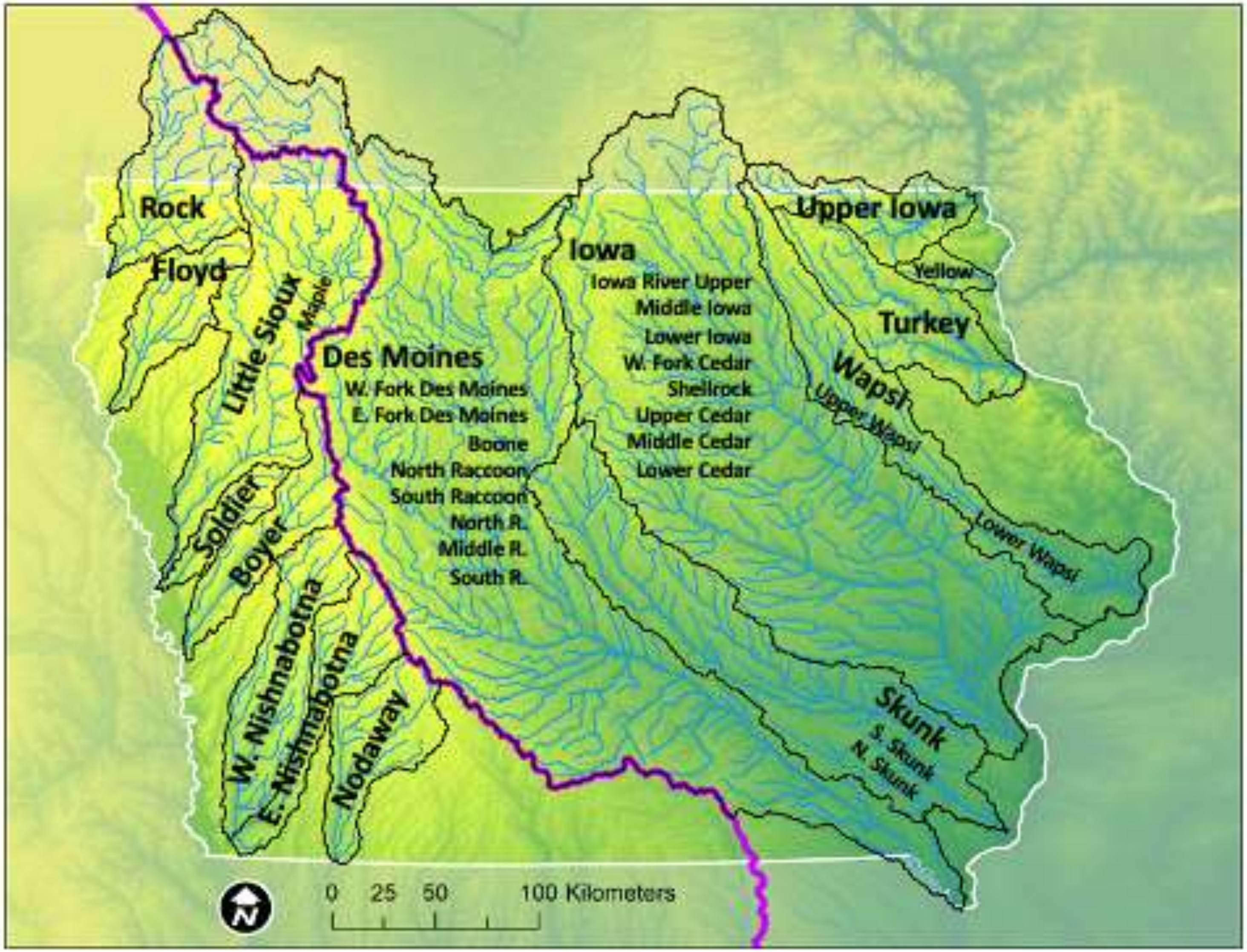
Plant	Potential Violations
CR NW Plant	5
CR J Ave	0
Oskaloosa	0
Ottumwa	55
CUIC	0
UI	187

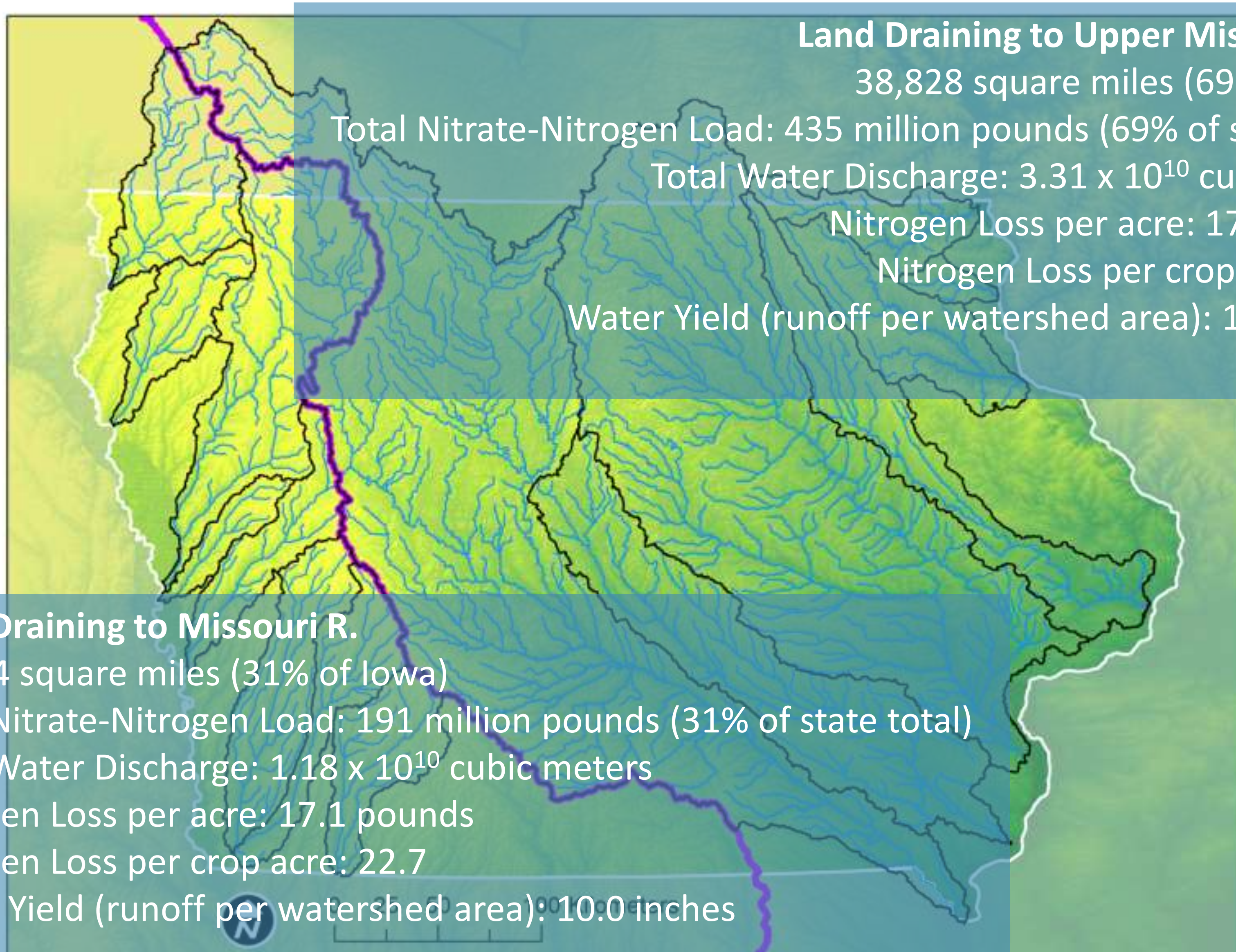
Conclusions

- Sensors are adequate proxy for lab analysis
- Compliance monitoring frequency is not adequate to capture all potential MCL violations
- Sensor: $20,000
- 1 year of daily lab analysis: $14,600
- Sensors can inform plant operations
- Real-time data can inform water customers on the quality of their water

Statewide N Loading 2020

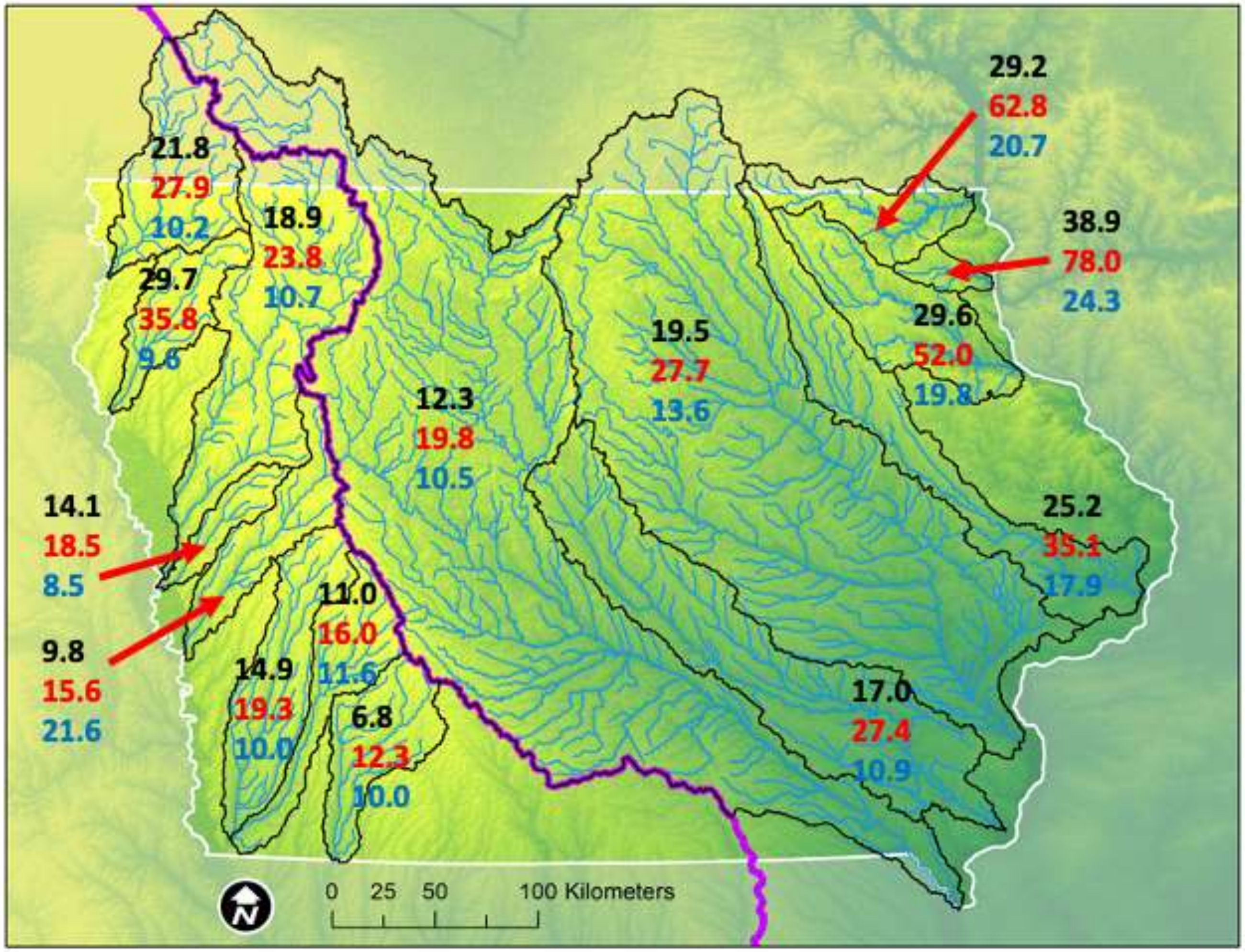
2020 Stream Nitrate Data





Land Draining to Upper Mississippi R.
38,828 square miles (69% of Iowa)
Total Nitrate-Nitrogen Load: 435 million pounds (69% of state total)
Total Water Discharge: 3.31 x 10^{10} cubic meters
Nitrogen Loss per acre: 17.5 pounds
Nitrogen Loss per crop acre: 27.0
Water Yield (runoff per watershed area): 13.0 inches

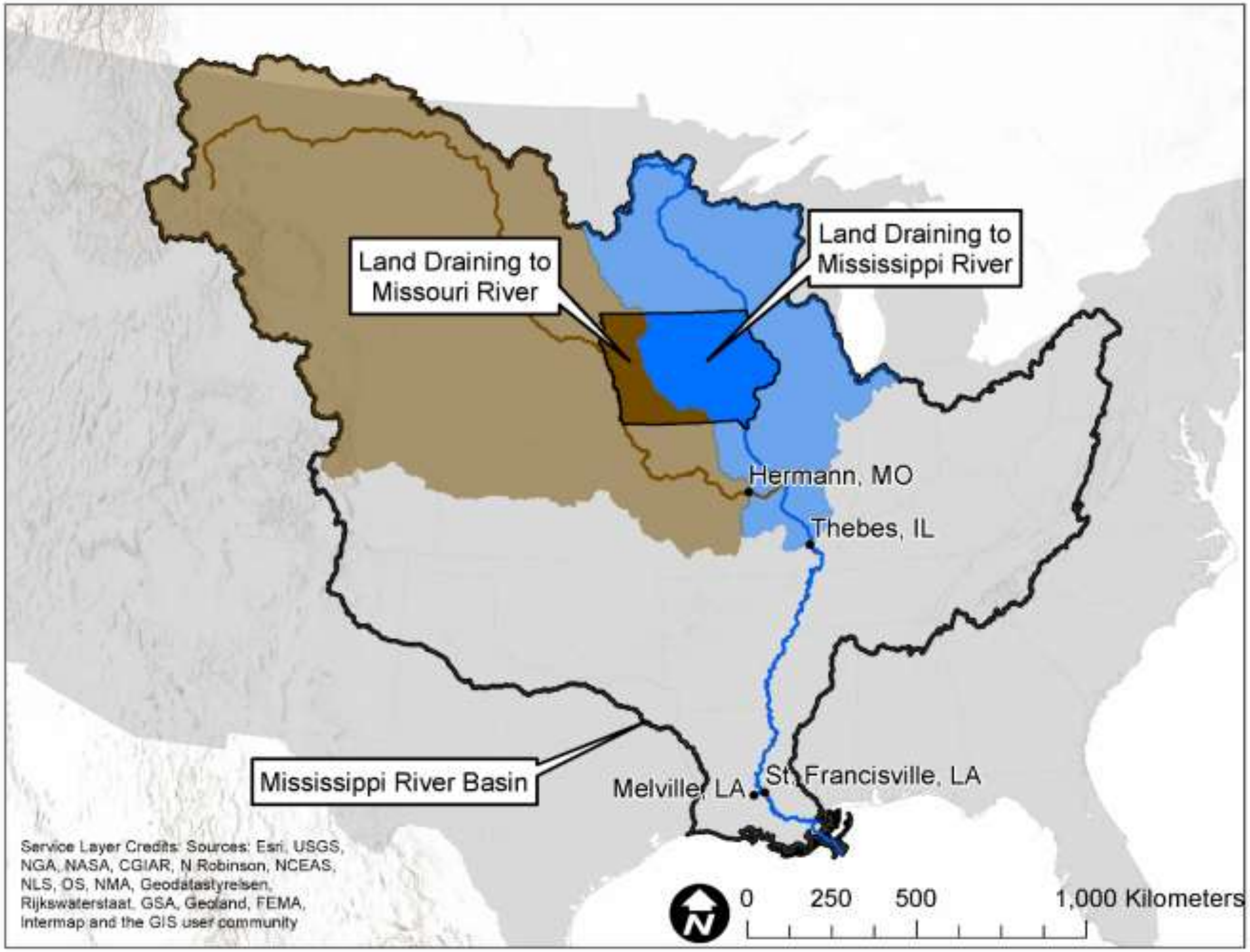
Land Draining to Missouri R.
17,444 square miles (31% of Iowa)
Total Nitrate-Nitrogen Load: 191 million pounds (31% of state total)
Total Water Discharge: 1.18 x 10^{10} cubic meters
Nitrogen Loss per acre: 17.1 pounds
Nitrogen Loss per crop acre: 22.7
Water Yield (runoff per watershed area): 10.0 inches



Black: lbs/acre

Red: lbs/crop-acre

Blue: Runoff (inches)


Land Draining to Missouri River
Land Draining to Mississippi River
Hermann, MO
Thebes, IL
Mississippi River Basin
Melville, LA
St. Francisville, LA
Service Layer Credits: Sources: Esri, USGS, NGA, NASA, CGIAR, N Robinson, NCEAS, NLS, OS, NMA, Geodatastyrelsen, Rijkswaterstaat, GSA, Geoland, FEMA, Intermap and the GIS user community
N
0
250
500
1,000 Kilometers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National Water-Quality Assessment (NAWQA) Project
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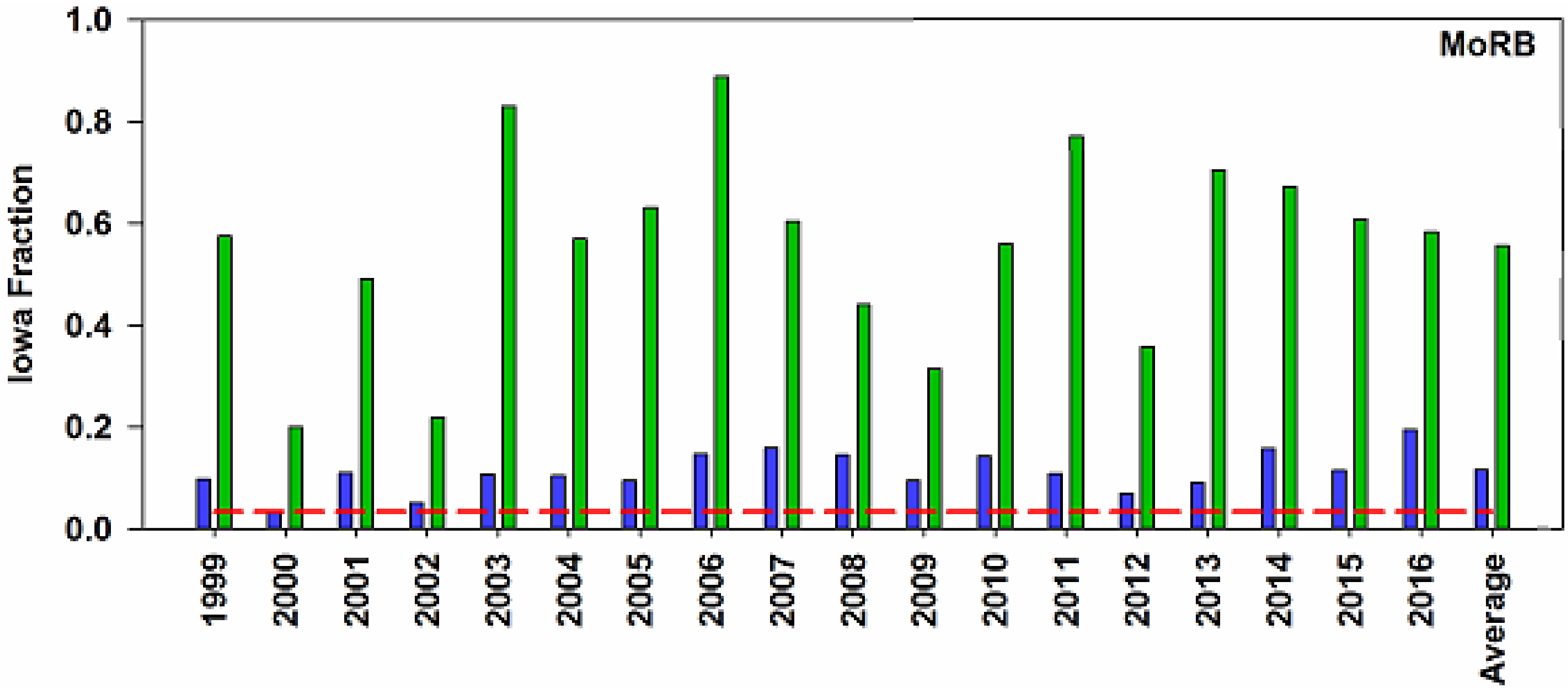
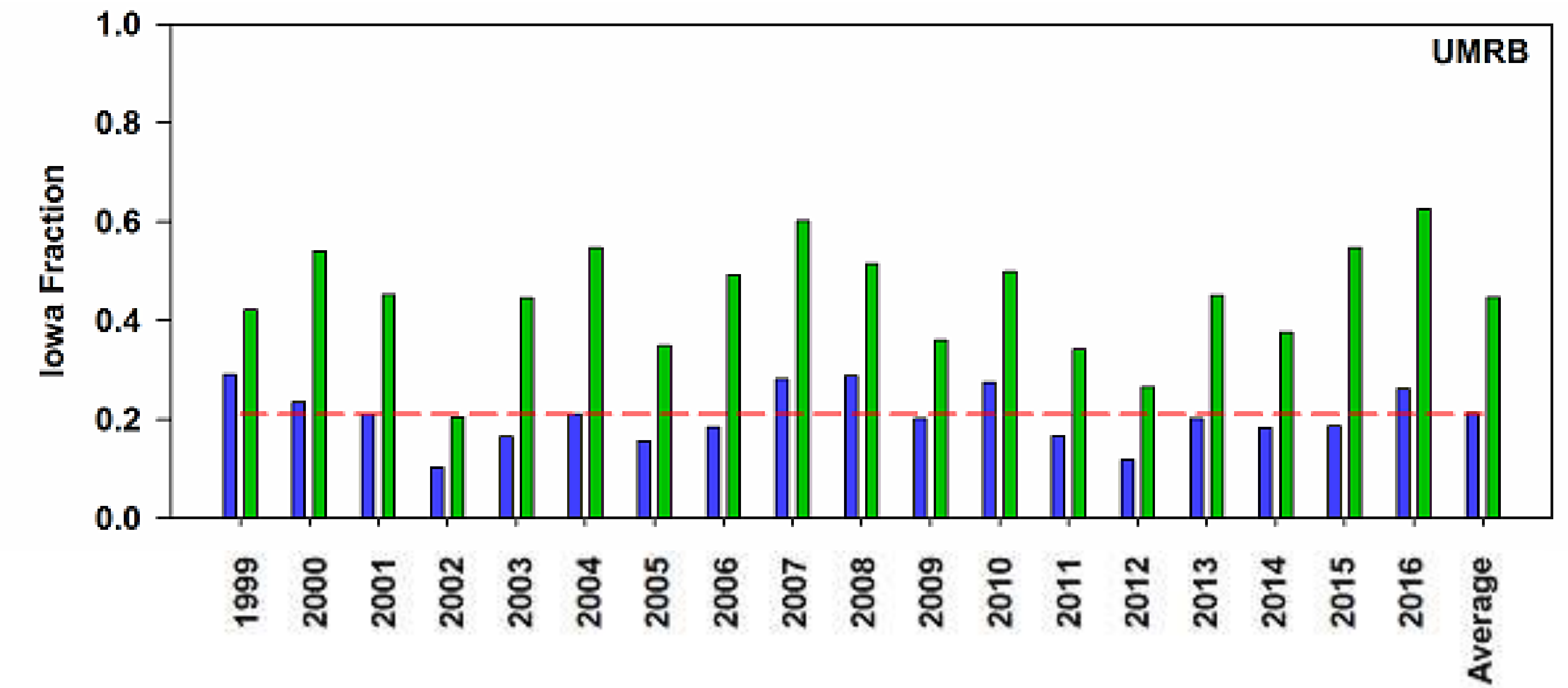
Informing Decision Make

Missouri



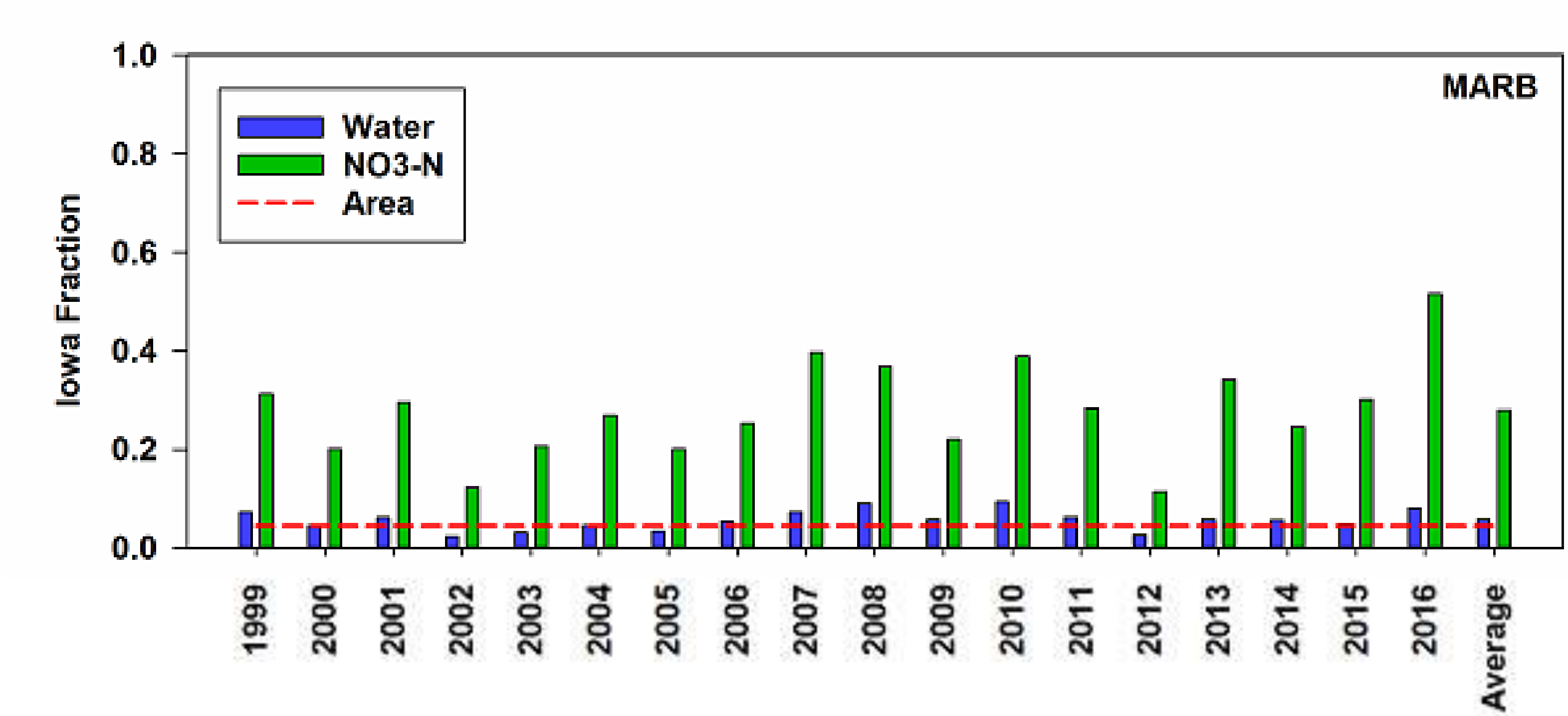
3.3% of the land
12% of the water
55% of the nitrate

Upper Mississippi



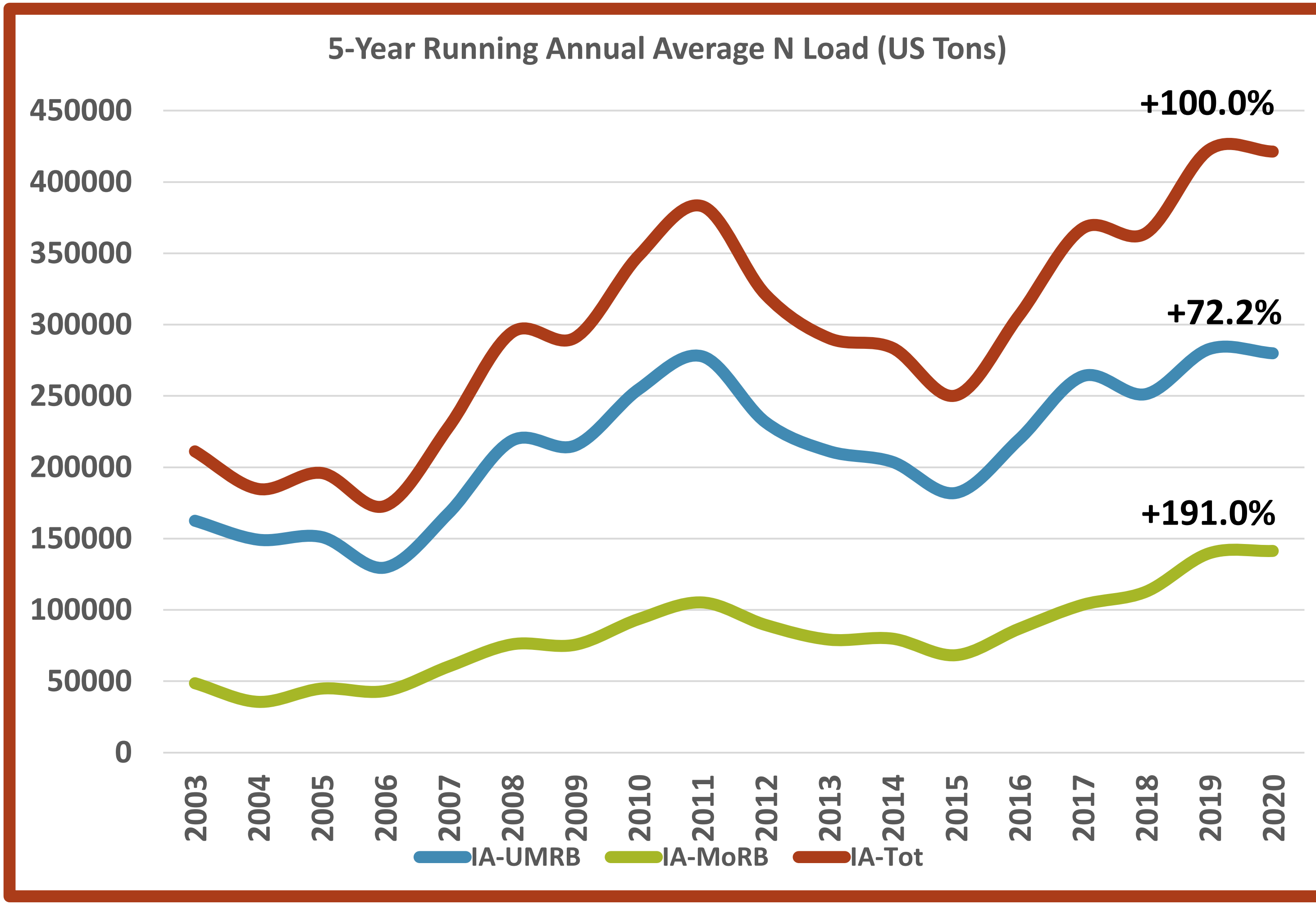
21% of the land
21% of the water
45% of the nitrate

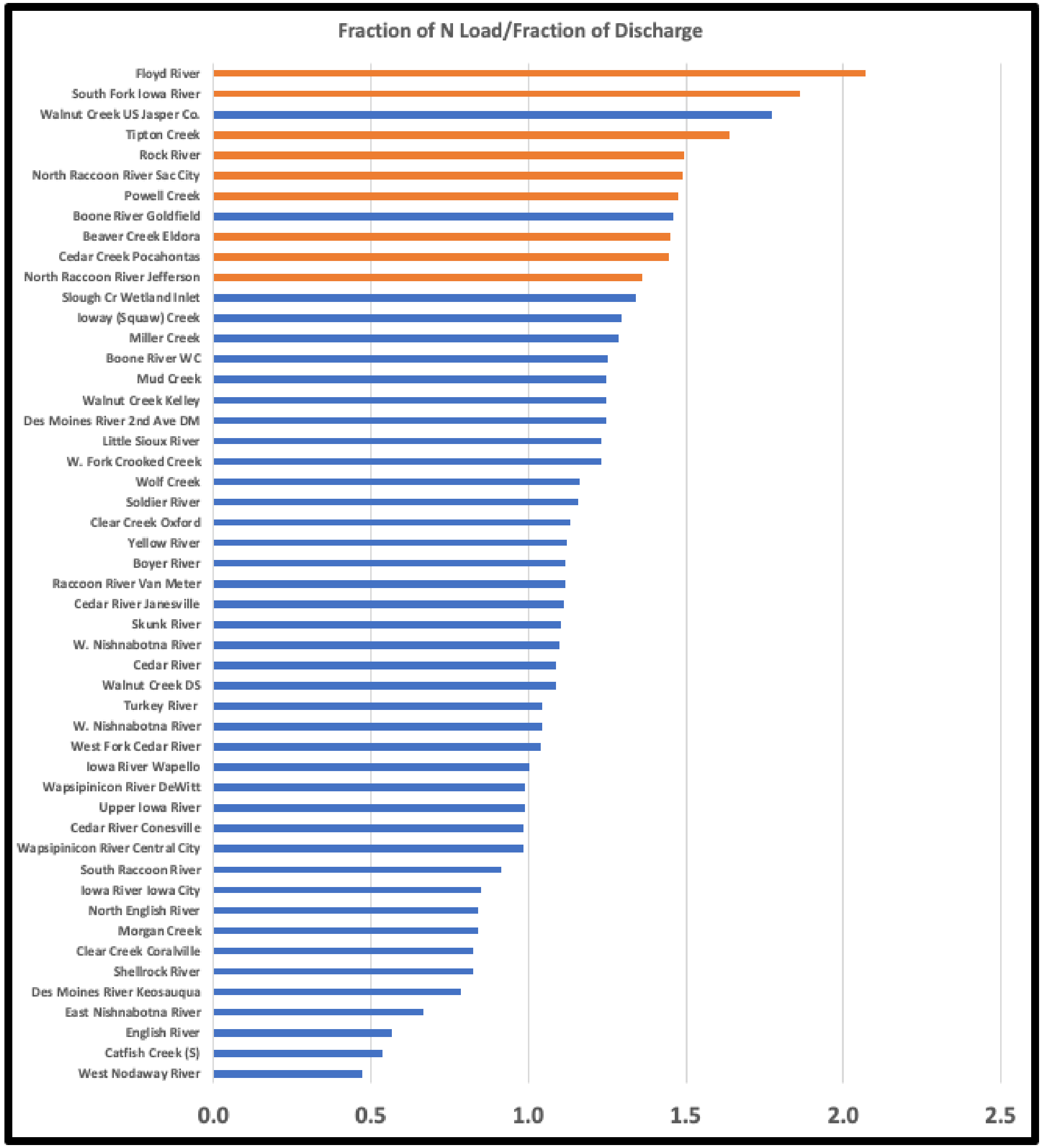
Mississippi-Atchafalaya-Gulf of Mexico

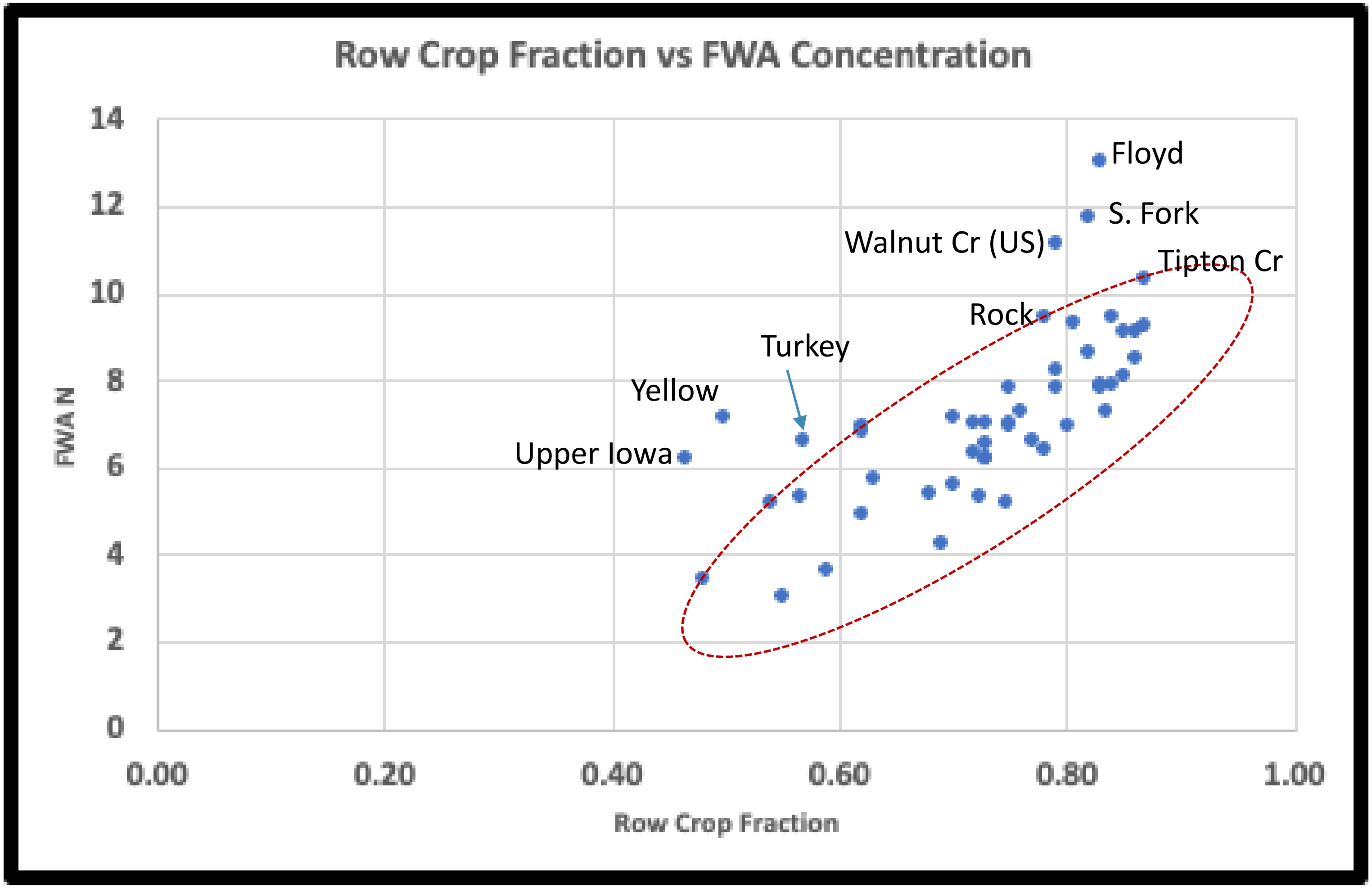


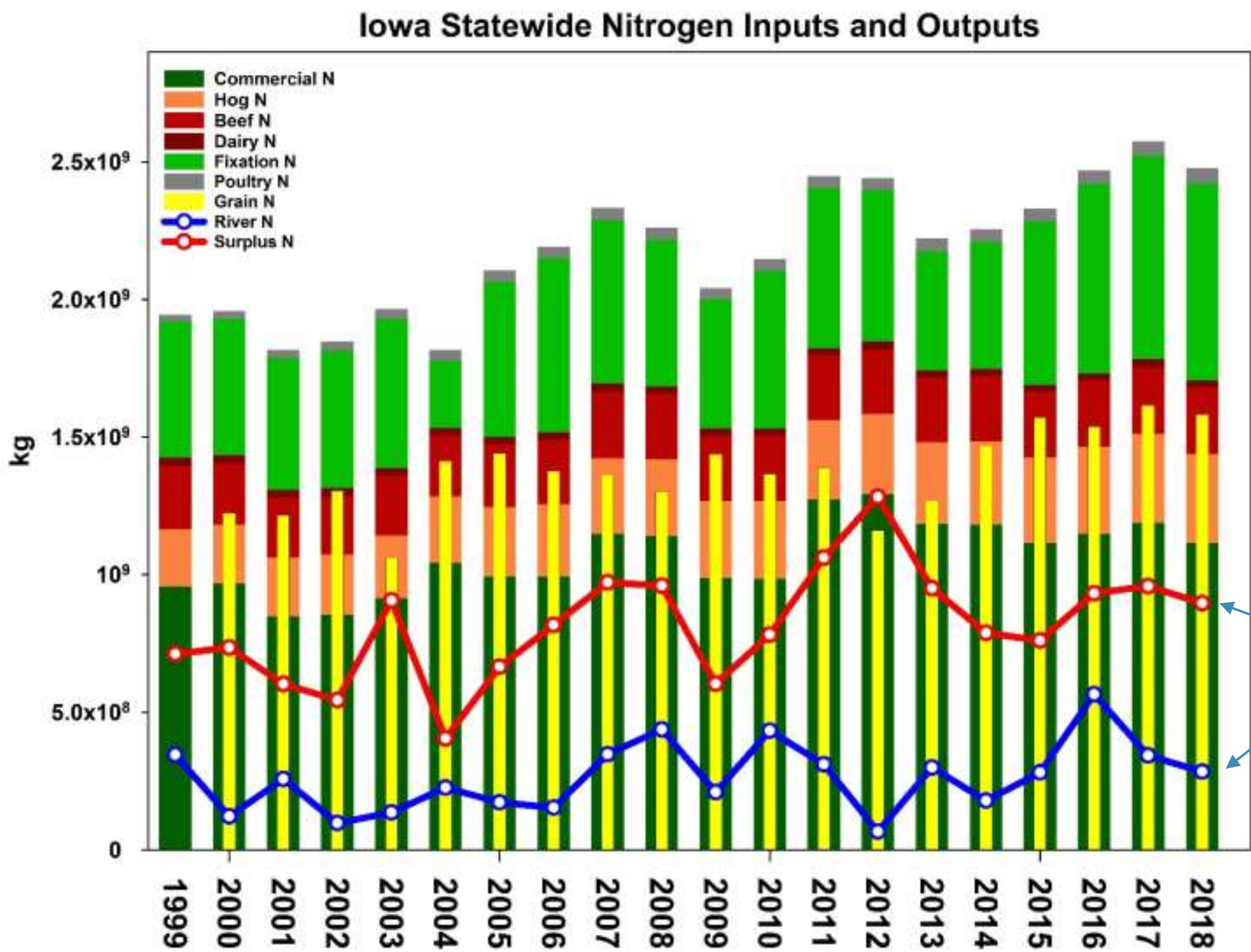
4.5% of the land
5.9% of the water
29% of the nitrate

How Much Nitrogen Leaves Iowa?




Fraction of N Load/Fraction of Discharge
Floyd River
South Fork Iowa River
Walnut Creek US Jasper Co.
Tipton Creek
Rock River
North Raccoon River Sac City
Powell Creek
Boone River Goldfield
Beaver Creek Eldora
Cedar Creek Pocahontas
North Raccoon River Jefferson
Slough Cr Wetland Inlet
Ioway (Squaw) Creek
Miller Creek
Boone River WC
Mud Creek
Walnut Creek Kelley
Des Moines River 2nd Ave DM
Little Sioux River
W. Fork Crooked Creek
Wolf Creek
Soldier River
Clear Creek Oxford
Yellow River
Boyer River
Raccoon River Van Meter
Cedar River Janesville
Skunk River
W. Nishnabotna River
Cedar River
Walnut Creek DS
Turkey River
W. Nishnabotna River
West Fork Cedar River
Iowa River Wapello
Wapsipinicon River DeWitt
Upper Iowa River
Cedar River Conesville
Wapsipinicon River Central City
South Raccoon River
Iowa River Iowa City
North English River
Morgan Creek
Clear Creek Coralville
Shellrock River
Des Moines River Keosauqua
East Nishnabotna River
English River
Catfish Creek (S)
West Nodaway River
0.0
0.5
1.0
1.5
2.0
2.5


Row Crop Fraction vs FWA Concentration
FWA N
Row Crop Fraction
0
2
4
6
8
10
12
14
0.00
0.20
0.40
0.60
0.80
1.00
Floyd
S. Fork
Walnut Cr (US)
Tipton Cr
Rock
Turkey
Yellow
Upper Iowa

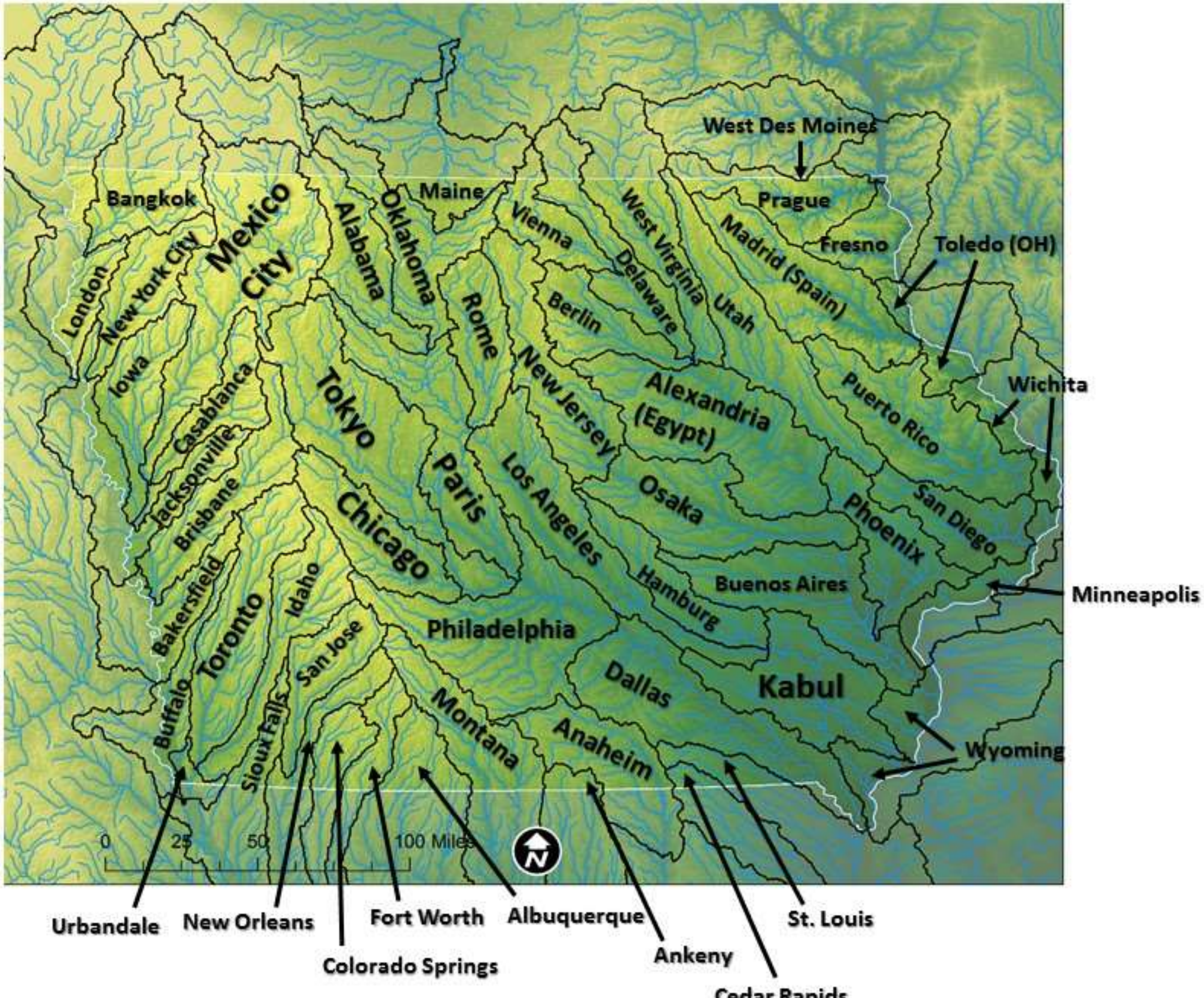


About 32% of “surplus” makes it to streams

Nitrogen Change (%) Since 1999

Can we "soil health" our way out of this?

N Category	% change
River	83
Chicken	76
Turkey	59
Hogs	59
Surplus	51
Fixation	41
total inputs	36
Commercial	34
Grain N	27
Beef	10
Dairy	-11


West Des Moines
Prague
Fresno
Toledo (OH)
Bangkok
Mexico City
Alabama
Oklahoma
Maine
Vienna
West Virginia
Delaware
Madrid (Spain)
Utah
Berlin
Rome
London
New York City
Iowa
Casablanca
Jacksonville
Brisbane
Tokyo
New Jersey
Alexandria (Egypt)
Puerto Rico
Wichita
Paris
Los Angeles
Osaka
Chicago
Phoenix
San Diego
Bakersfield
Toronto
Idaho
Hamburg
Buenos Aires
Minneapolis
Philadelphia
San Jose
Buffalo
Sioux Falls
Dallas
Kabul
Montana
Anaheim
Wyoming
0
25
50
100 Miles
N
Urbandale
New Orleans
Fort Worth
Albuquerque
St. Louis
Colorado Springs
Ankeny
Cedar Rapids

What Can Be Done?

1. Ban cropping in the 2-year Flood Plain

2. Ban fall tillage

3. Ban manure on snow and frozen ground

4. Make farmers adhere to ISU fertilization guidelines

5. Reformulate CAFO Regulations