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# Results of Precision and Bias studies of USGS Total Nitrogen Methods

**Briefing to Chesapeake Bay Program**
**Analytical Methods and Quality Assurance Workgroup (AMQAW)**
**April 24, 2013**

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**U.S. Department of the Interior**
**U.S. Geological Survey**


Citation

Rus, D.L., Patton, C.J., Mueller, D.K., and Crawford, C.G., 2013, Assessing total nitrogen in surface-water samples—Precision and bias of analytical and computational methods: U.S. Geological Survey Scientific Investigations Report 2012–5281, 38 p.

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# A Bit of History

- Initial problem identification - 2005
- BQS laboratory experiment – 2008
- Initial OWQ recommendations
- NAWQA / NASQAN field study – 2009-10
- Draft SIR Completed 2012
- OWQ Tech Memo needs “policy / guidance” 2013

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# Nitrogen analytes and Total N

- $NO_X$: Nitrate plus nitrite, as N
- DN: Dissolved N measured by A-P digestion
- PN: Particulate N
- TKN: Total Kjeldahl N (ammonia + organic)
- TN-A: Total N measured by A-P digestion
- TN-C: Total N computed from DN + PN
- TN-K: Total N computed from TKN + $NO_X$

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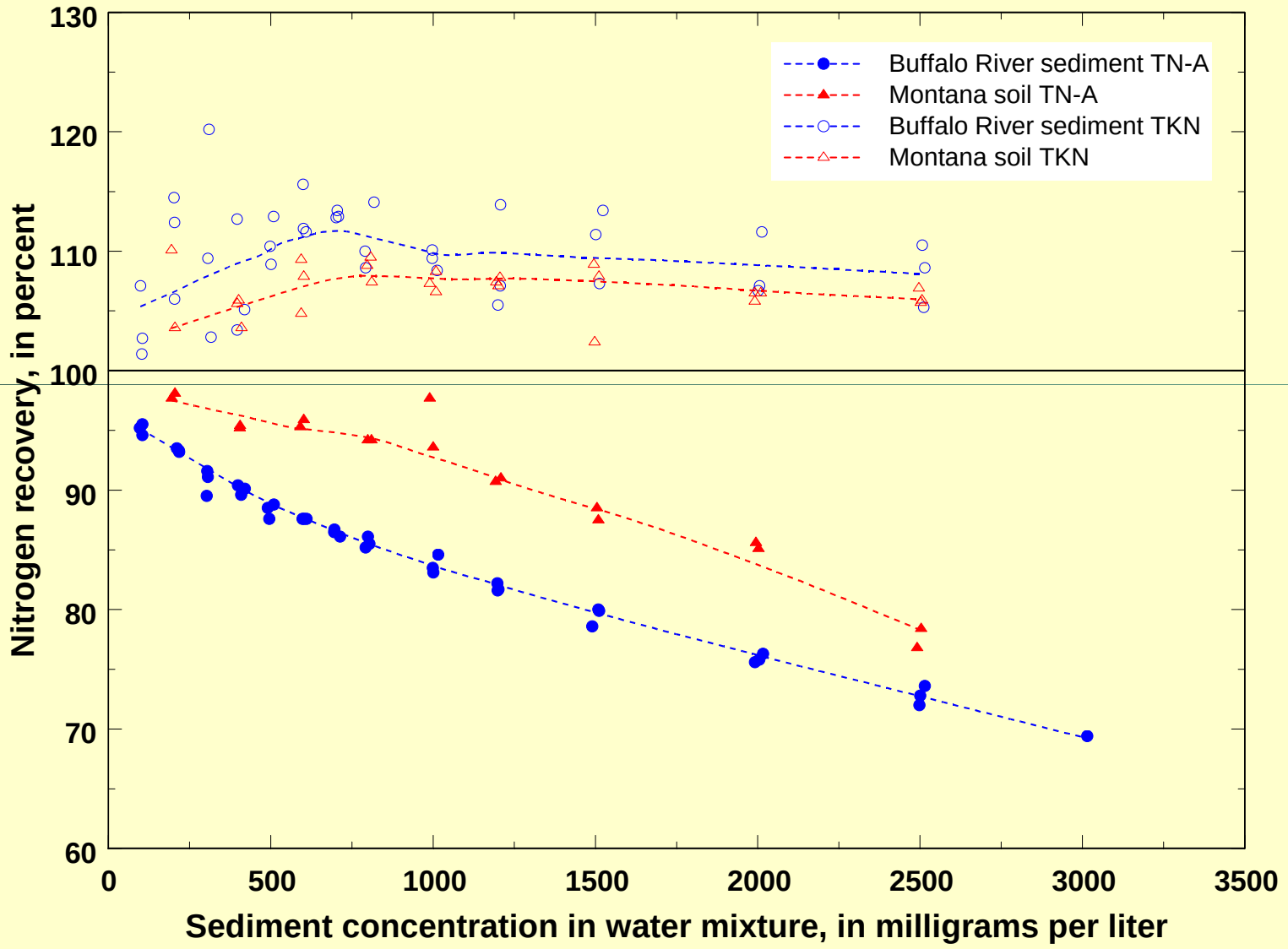
Buffalo River sediment TN-A
Montana soil TN-A
Buffalo River sediment TKN
Montana soil TKN
Nitrogen recovery, in percent
130
120
110
100
90
80
70
60
0
500
1000
1500
2000
2500
3000
3500
Sediment concentration in water mixture, in milligrams per liter

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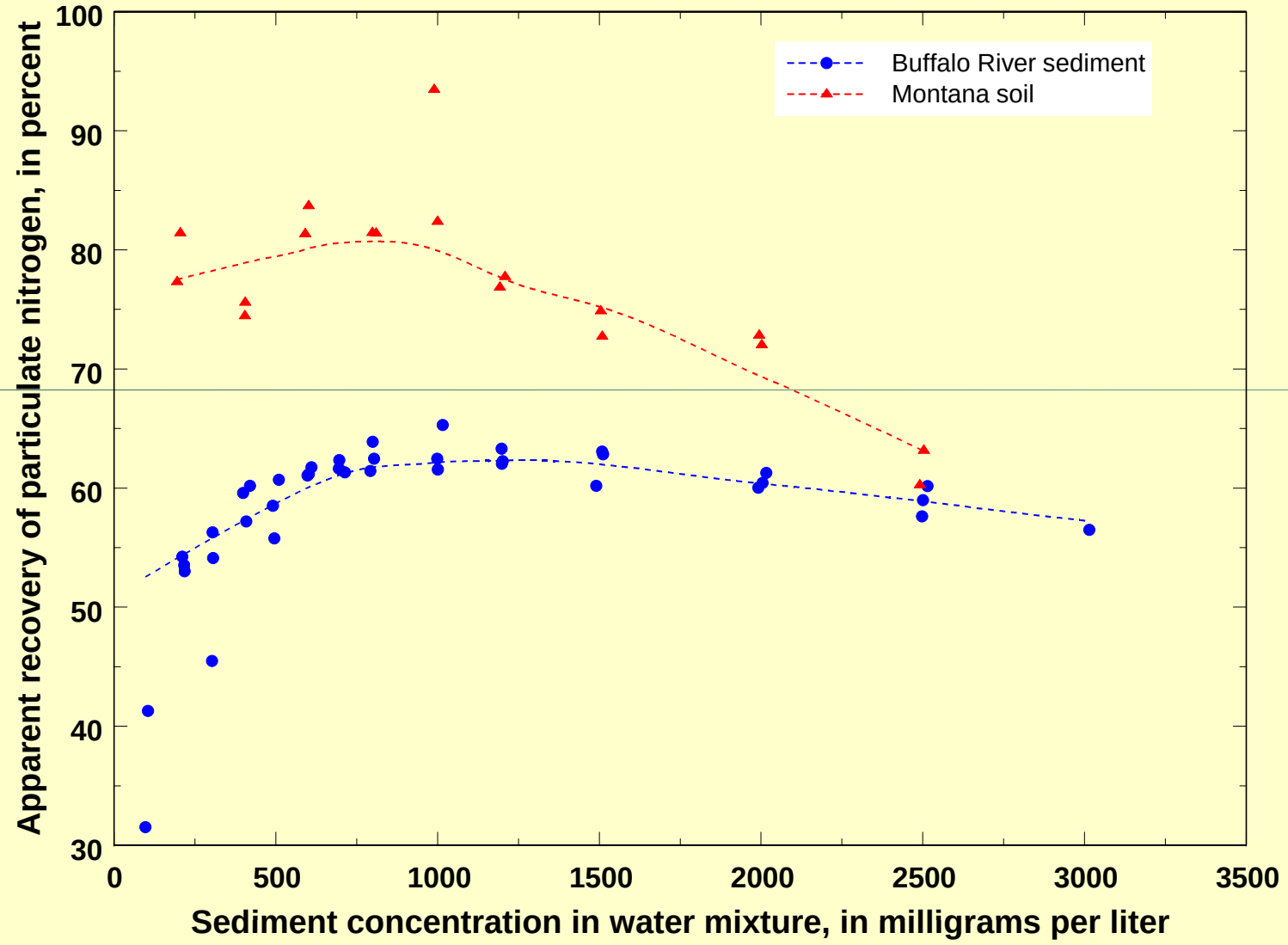
Buffalo River sediment
Montana soil
Apparent recovery of particulate nitrogen, in percent
100
90
80
70
60
50
40
30
0
500
1000
1500
2000
2500
3000
3500
Sediment concentration in water mixture, in milligrams per liter

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# Conclusions from the laboratory experiment:

- The alkaline-persulfate method has a negative bias, probably some particulate nitrogen is not oxidized during digestion
- The Kjeldahl method has a positive bias, probably because some $NO_X$ is reduced to ammonia during the digestion
- The Kjeldahl method is substantially less precise than the alkaline persulfate method

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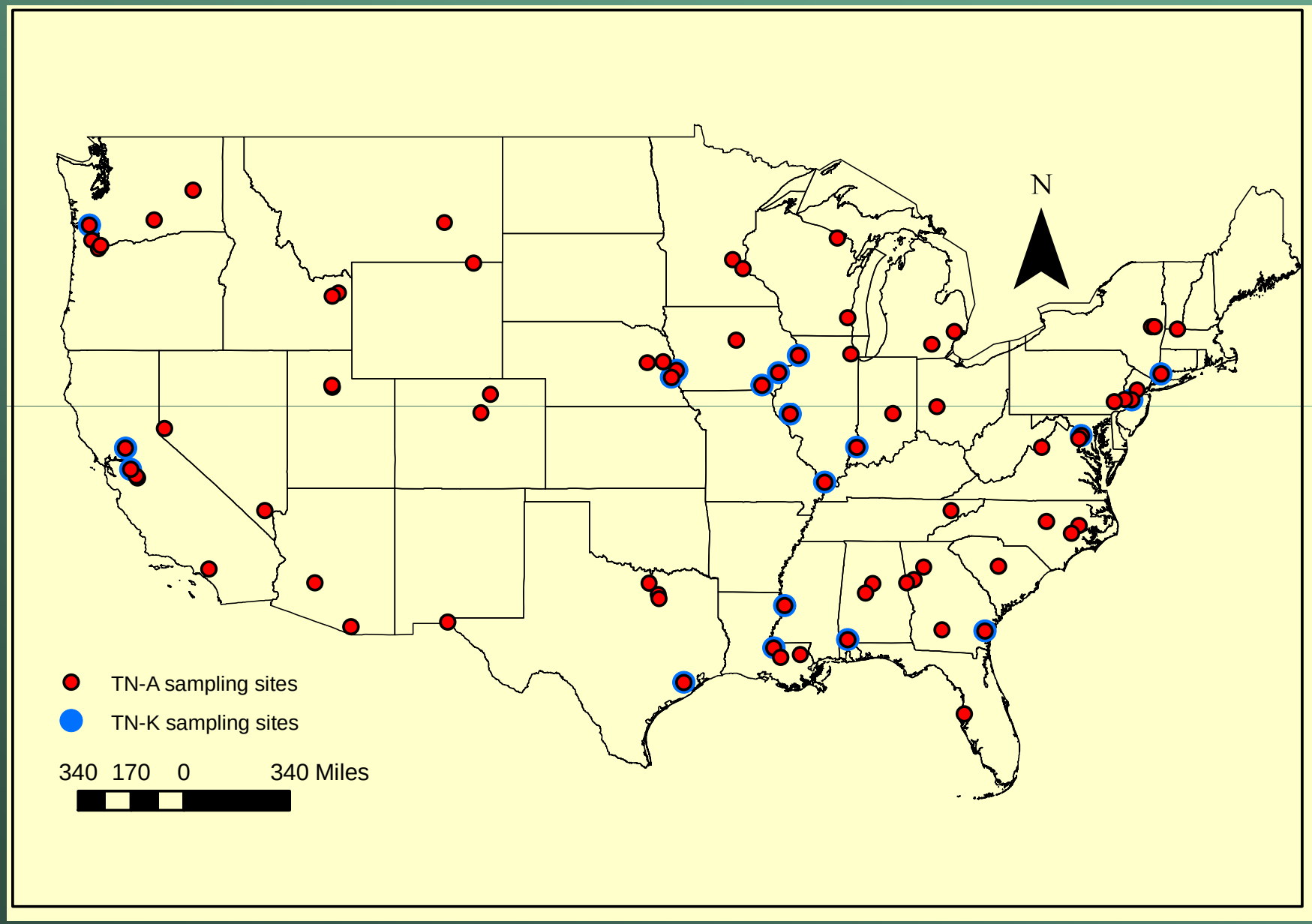


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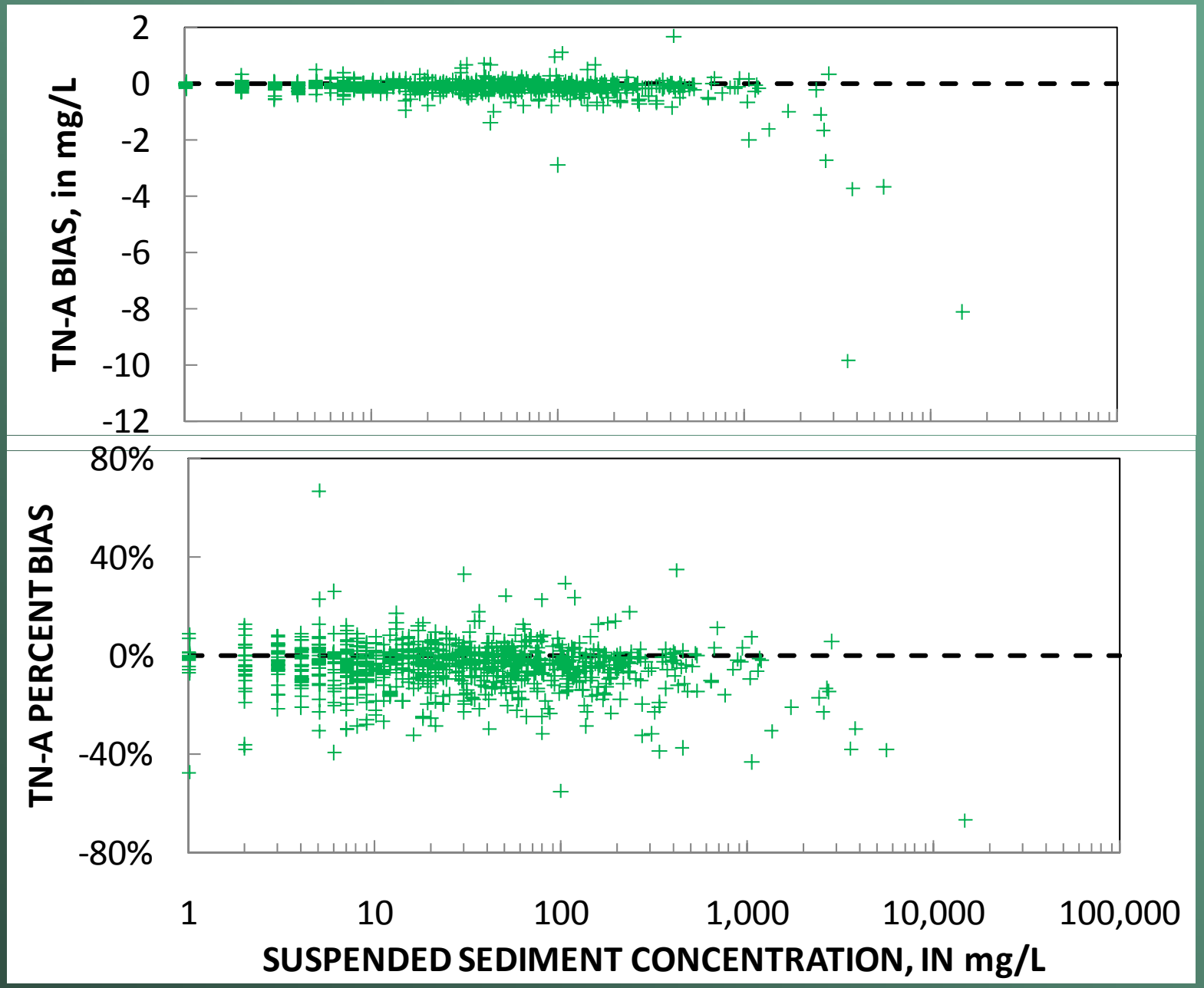
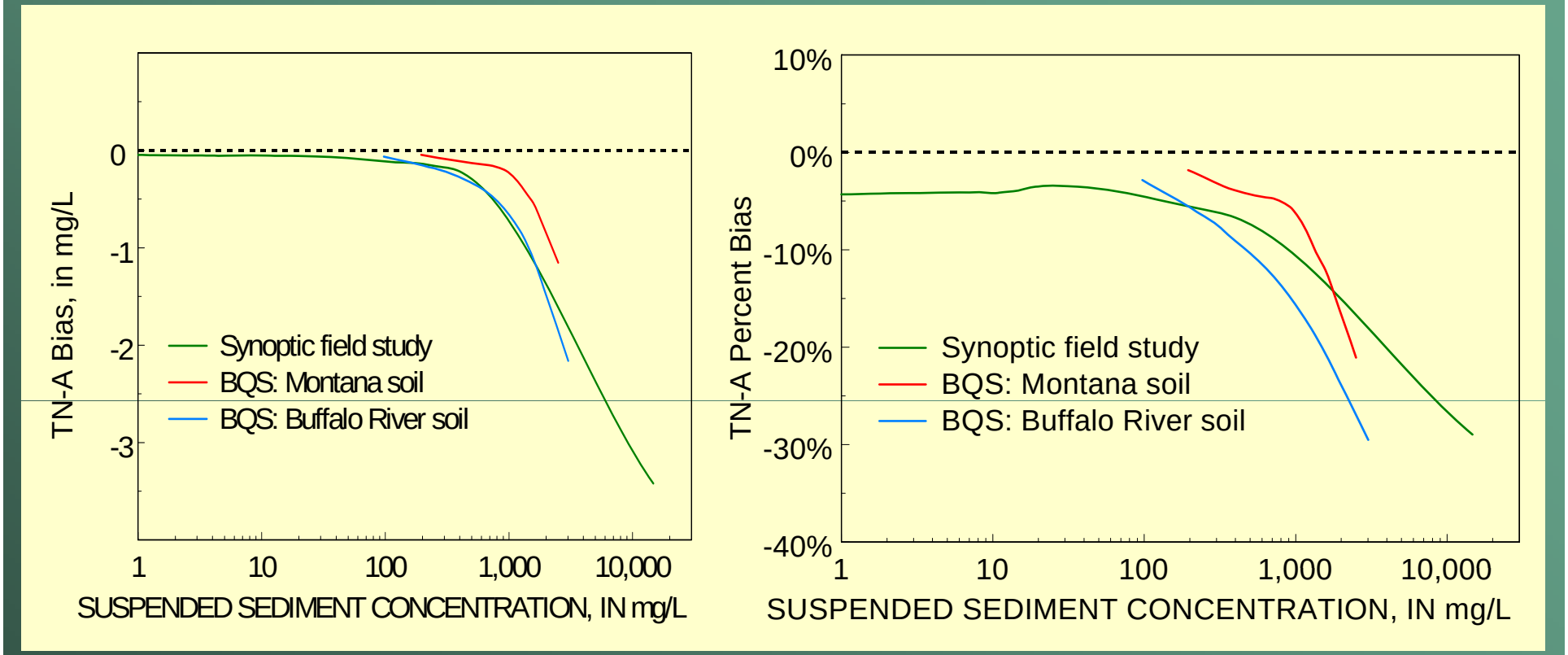

TN-A BIAS, in mg/L
2
0
-2
-4
-6
-8
-10
-12
TN-A PERCENT BIAS
80%
40%
0%
-40%
-80%
1
10
100
1,000
10,000
100,000
SUSPENDED SEDIMENT CONCENTRATION, IN mg/L


TN-A Bias, in mg/L
0
-1
-2
-3
Synoptic field study
BQS: Montana soil
BQS: Buffalo River soil
1
10
100
1,000
10,000
SUSPENDED SEDIMENT CONCENTRATION, IN mg/L
TN-A Percent Bias
10%
0%
-10%
-20%
-30%
-40%
Synoptic field study
BQS: Montana soil
BQS: Buffalo River soil
1
10
100
1,000
10,000
SUSPENDED SEDIMENT CONCENTRATION, IN mg/L

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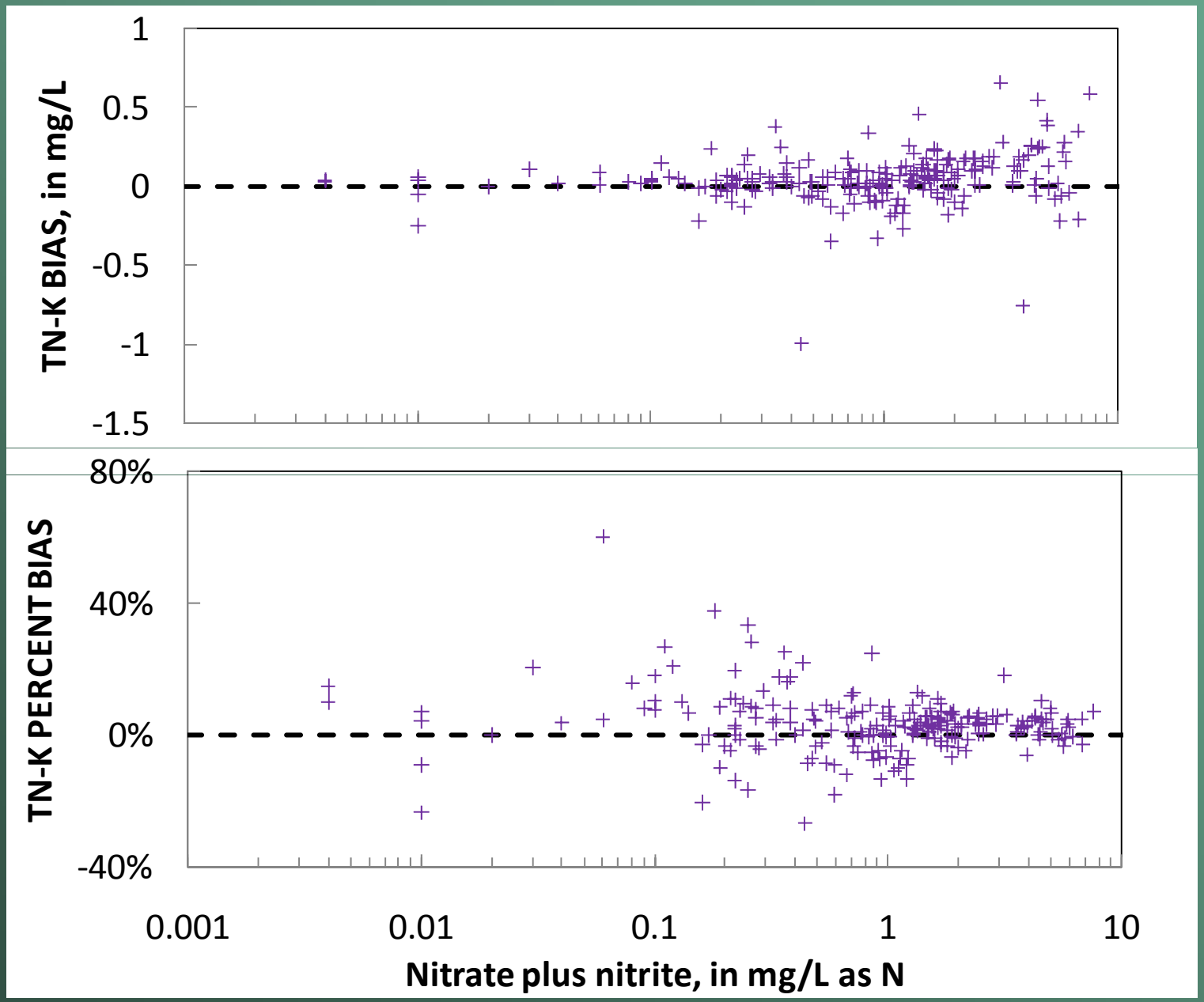
TN-K BIAS, in mg/L
1
0.5
0
-0.5
-1
-1.5
TN-K PERCENT BIAS
80%
40%
0%
-40%
0.001
0.01
0.1
1
10
Nitrate plus nitrite, in mg/L as N

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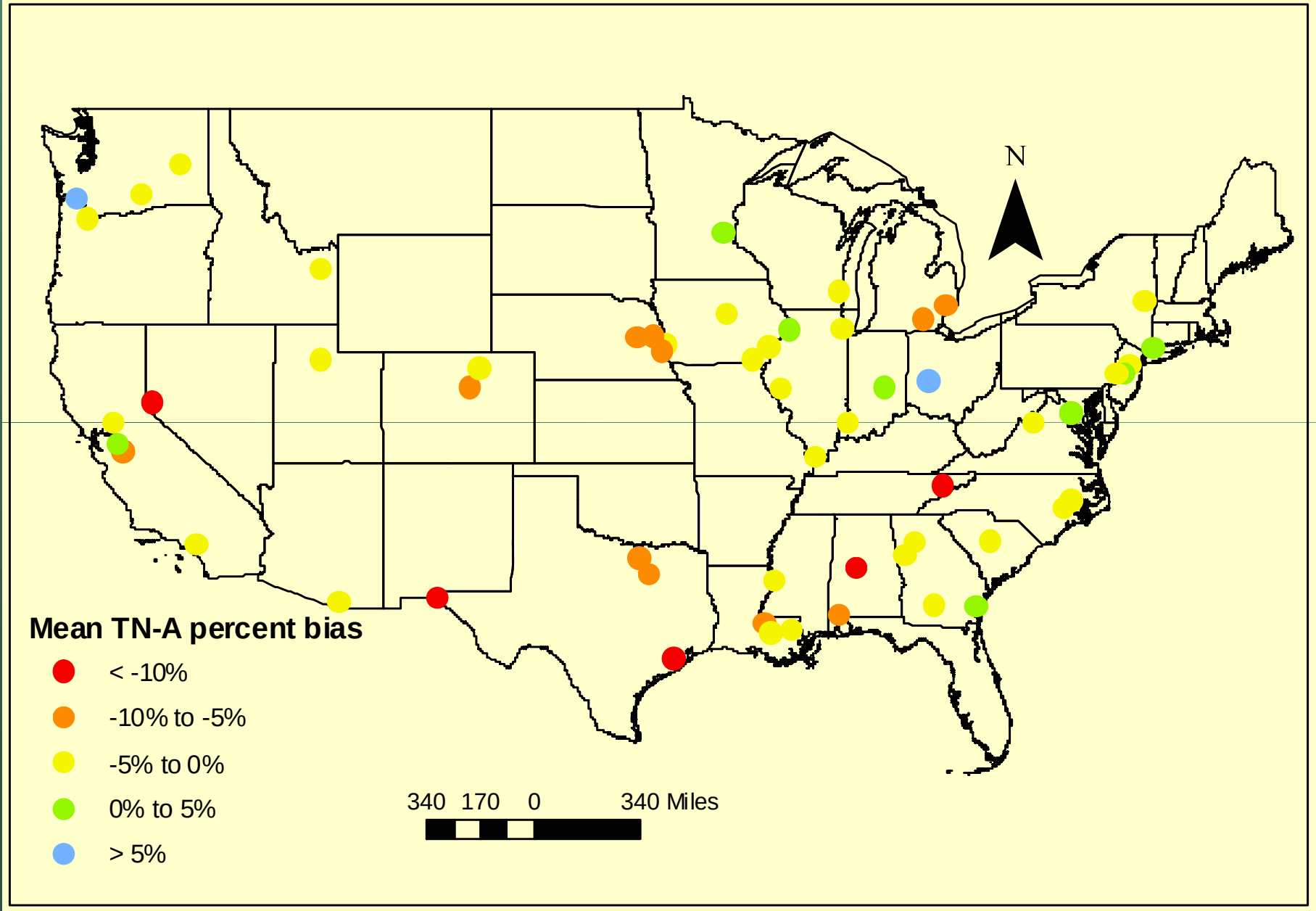
N
Mean TN-A percent bias
< -10%
-10% to -5%
-5% to 0%
0% to 5%
> 5%
340 170 0 340 Miles

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# Conclusions from the field study:

- Conclusions of the laboratory experiment are supported by field data
- TN-A results are biased low regardless of suspended sediment concentration, but the bias increases at suspended-sediment concentrations greater than 750 mg/L
- TN-A bias is not related to drainage basin characteristics
- TN-K results have a positive bias at higher $NO_X$ concentrations

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# Evaluating the alternatives

- **Precision:**
  - **TN-A: 1.5%**
  - **TN-K: f(NOx,TKN) ~ 2.2 to 7.6%**
  - **TN-C: f(PN, DN) ~ 1.6 to 12.9%**
- **Bias (% from synoptic): mean, 5$^{th}$, 95th**
  - **TN-C: Assume 0**
  - **TN-A: -4.5%, +7.9%, -22.2%**
  - **TN-K: +3.3%, +18.2%, -9.8%**

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# Evaluating the alternatives (cont)

- Impact on field practices:
  - TN-A: Minimal for most existing programs
  - TN-K: Minimal for most existing programs
  - TN-C:
    - Procurement of PN filtering equipment/supplies
    - Field time to process/deconn the TPCN filters (~15-30 min/sample)

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# Resulting USGS Policy / Guidelines

- TN in whole-water should be calculated as the sum of dissolved nitrogen (DN), determined by alkaline-persulfate digestion of a filtered-water sample, and particulate nitrogen (PN)…

- Whole-water samples from environments with very low suspended sediment and organic matter (such as groundwater or oligotrophic lakes) may still be analyzed by the alkaline-persulfate digestion method since the negative bias generally is negligible in these conditions.

- TN calculated as the sum of TKN and nitrite-plus-nitrate should be avoided in most situations because of a positive bias….

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# Resulting USGS Policy / Guidelines

- Projects that need to change the approach used for determination of TN are encouraged to submit comparison samples ..... Stations with a primary or significant purpose of trend detection (for example, stations on the lower Mississippi River or its major tributaries or tributaries to Chesapeake Bay) should consider running paired samples longer than a year to definitively demonstrate the magnitude of the bias in the method being replaced.

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# Other Publications of interest

Patton, C.J., and Kryskalla, J.R., 2003, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Evaluation of alkaline persulfate digestion as an alternative to Kjeldahl digestion for determination of total and dissolved nitrogen and phosphorus in water: U.S. Geological Survey Water-Resources Investigations Report 03–4174, 33 p., accessed July 2011, at http://nwql.usgs.gov/Public/pubs/WRIR03-4174/WRIR03-4174.pdf .

U.S. Environmental Protection Agency, 1997, Determination of Carbon and Nitrogen in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis, Method 440.0, Revision 1.4, September 1997, U.S. Environmental Protection Agency, National Exposure Research Laboratory, Office of Research and Development, Cincinnati, Ohio, 10 p. at http://www.epa.gov/microbes/documents/m440_0.pdf

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