Identification of the Sources of Nitrate in the Illinois River

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Introduction

- Row crop agriculture has been blamed for nitrogen contamination in the Mississippi River and the Gulf of Mexico based on mass loading estimates.
- Other sources of nitrogen may play a role and include human and animal waste.
- Identifying sources and fate of N is important for calculating N loading of the Illinois River and its contributions to the Mississippi River.
- Direct evidence of the sources is lacking and role of denitrification uncertain.

Objectives of Investigation

- To determine the origin and fate of N (particularly nitrate) in the Illinois River using isotopes and chemical composition.
- To examine the seasonal variability of nitrate sources within the watershed of the Illinois River.
- To determine the role of denitrification (and other mechanisms) on reducing nitrate concentrations in the Illinois River.

Study Area: Illinois River Basin

The **Illinois River basin** drains approximately 78,000 km2 or 44% of the land area of Illinois.

Methods

- **River water** sampling 6 times/year for 2 yrs.
- **Precipitation** sampling 6 times/year for 2 yrs.
- **Tile drain** sampling 6 times/year for 2 yrs.
- **Treated waste water** sampling 3 times/yr for 1 yr at 3 different plants.
- **Analyzed** water samples for:
  - Nitrogen isotopes of nitrate ions.
  - Cations and anions.
  - Halides.

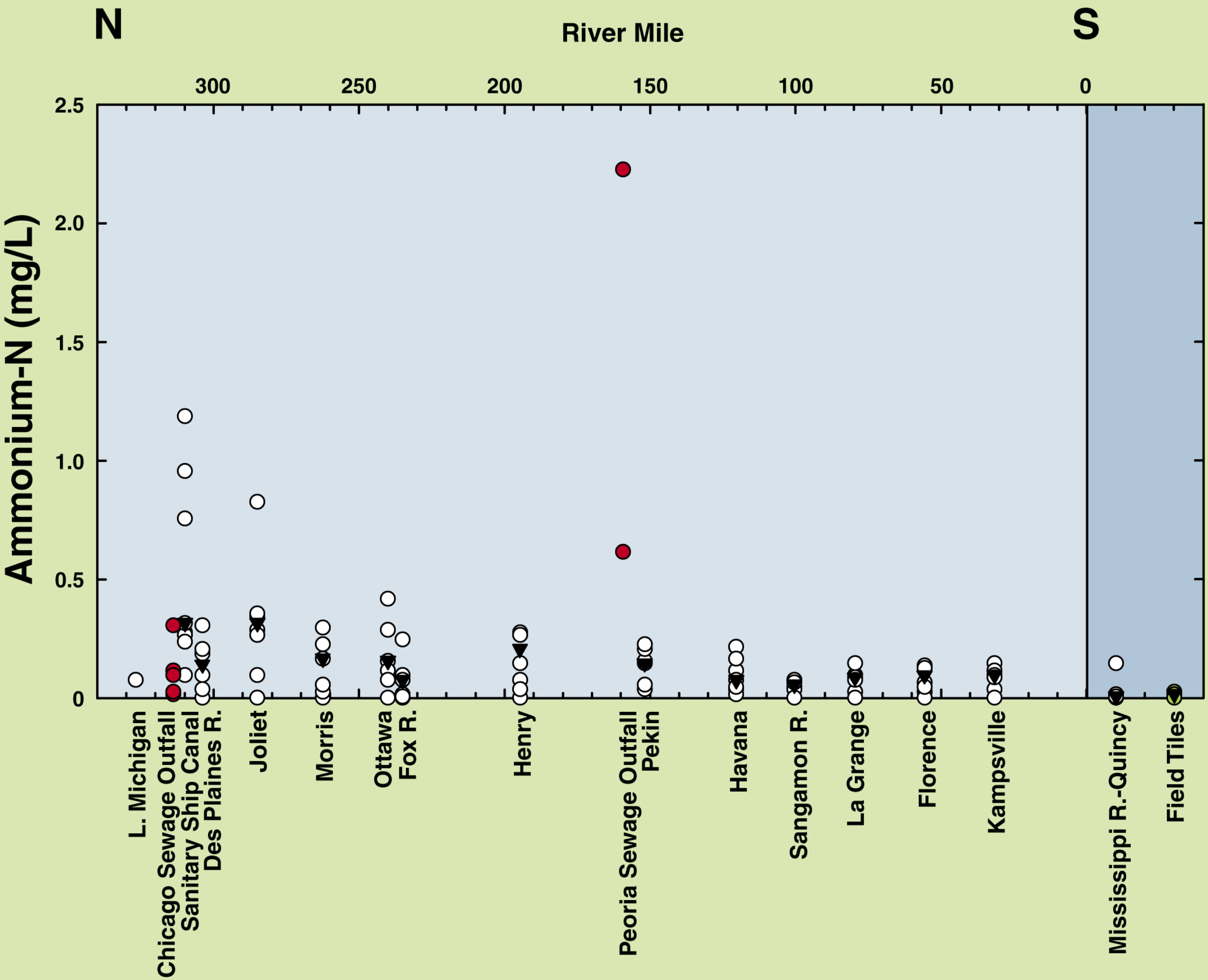
Precipitation Collectors in Chicago and Tile Drain in E-Central IL

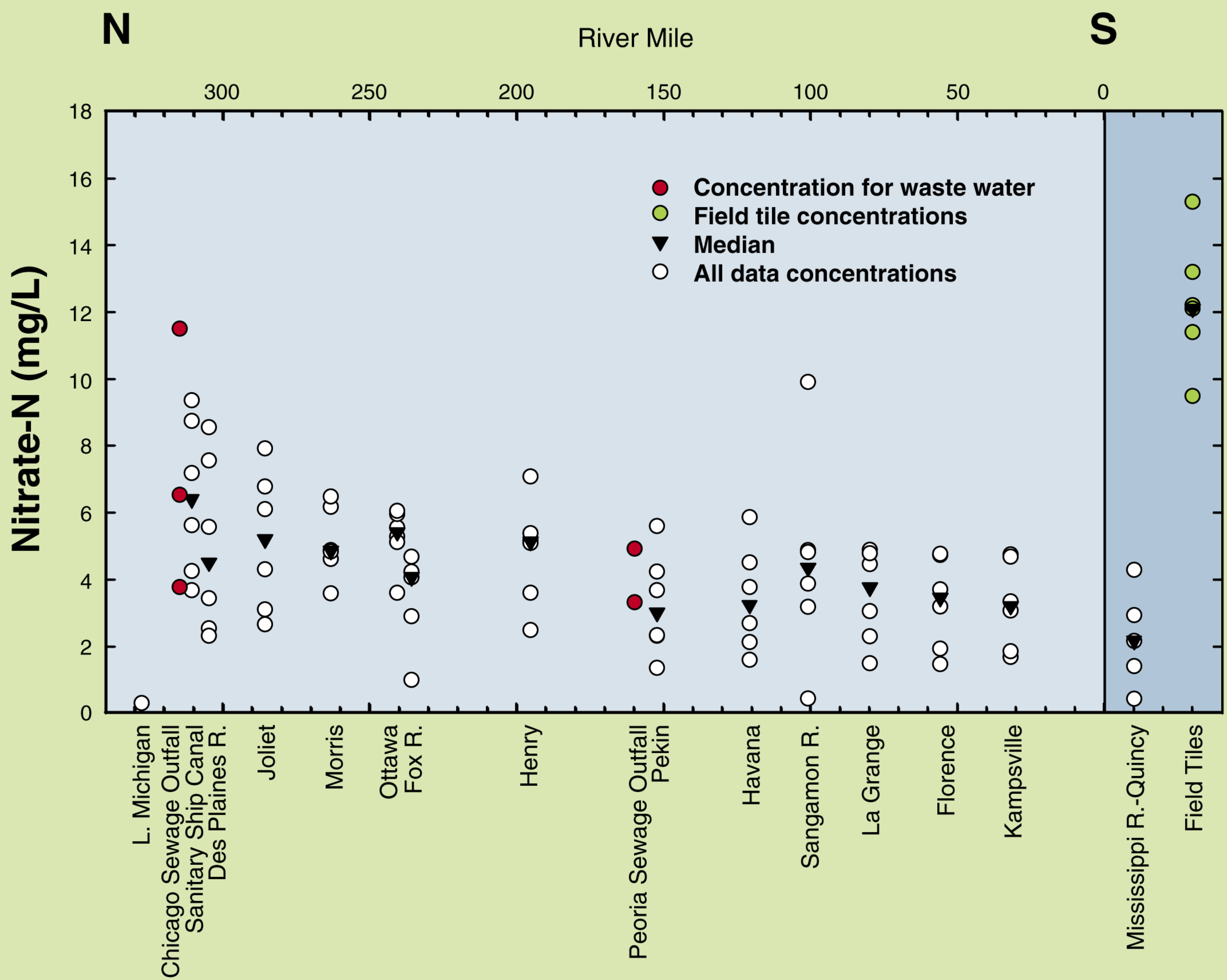
An ISGS Boat was used to Sample the Centroid of the River

Sampling at Western Springs and Joliet

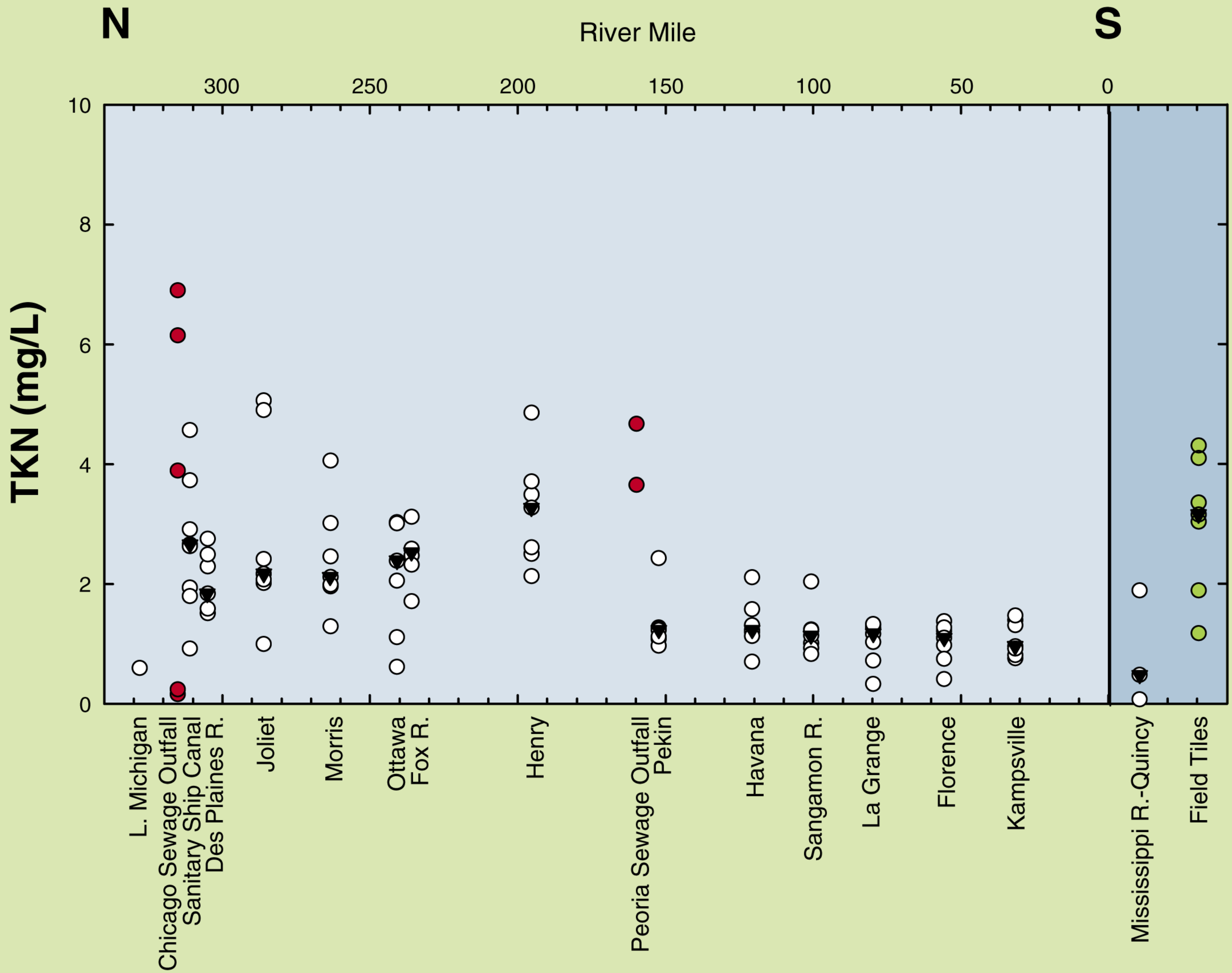
Winter Sampling Locations

Cation–Anion Results

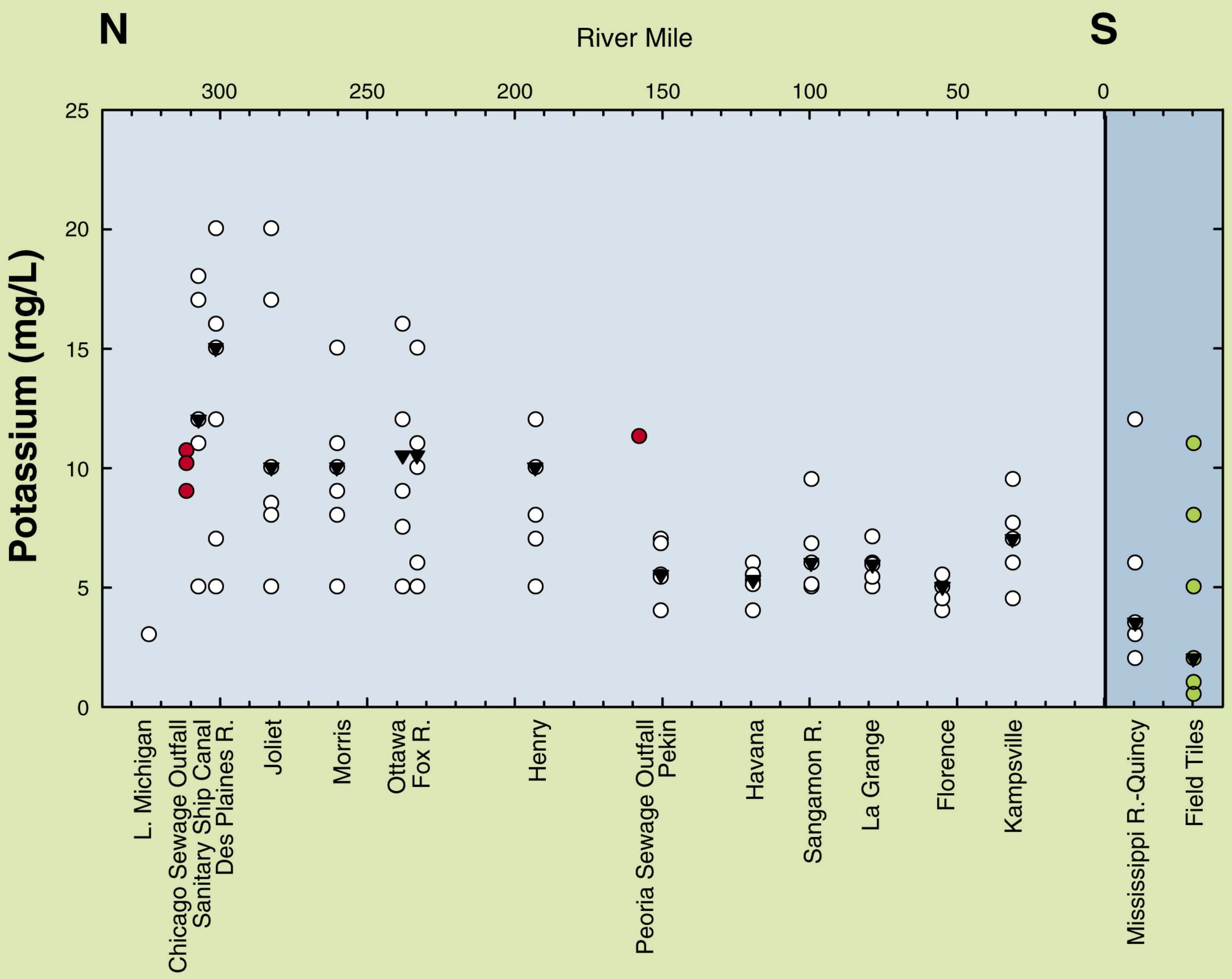

N
River Mile
S
300
250
200
150
100
50
0
2.5
2.0
1.5
1.0
0.5
0
Ammonium-N (mg/L)
L. Michigan
Chicago Sewage Outfall
Sanitary Ship Canal
Des Plaines R.
Joliet
Morris
Ottawa
Fox R.
Henry
Peoria Sewage Outfall
Pekin
Havana
Sangamon R.
La Grange
Florence
Kampsville
Mississippi R.-Quincy
Field Tiles



N
River Mile
S
300
250
200
150
100
50
0
18
16
14
12
10
8
6
4
2
0
Nitrate-N (mg/L)
Concentration for waste water
Field tile concentrations
Median
All data concentrations
L. Michigan
Chicago Sewage Outfall
Sanitary Ship Canal
Des Plaines R.
Joliet
Morris
Ottawa
Fox R.
Henry
Peoria Sewage Outfall
Pekin
Havana
Sangamon R.
La Grange
Florence
Kampsville
Mississippi R.-Quincy
Field Tiles

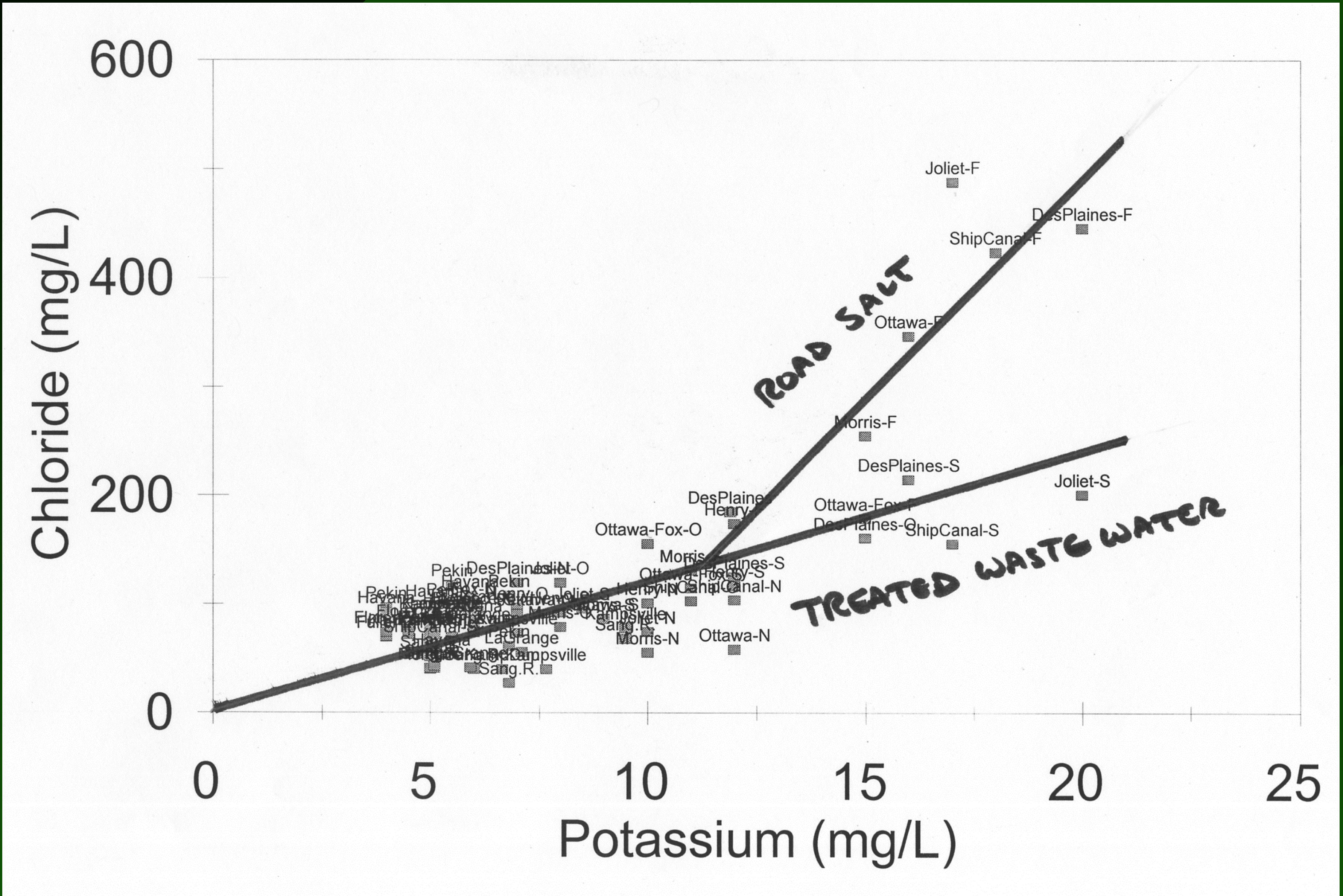


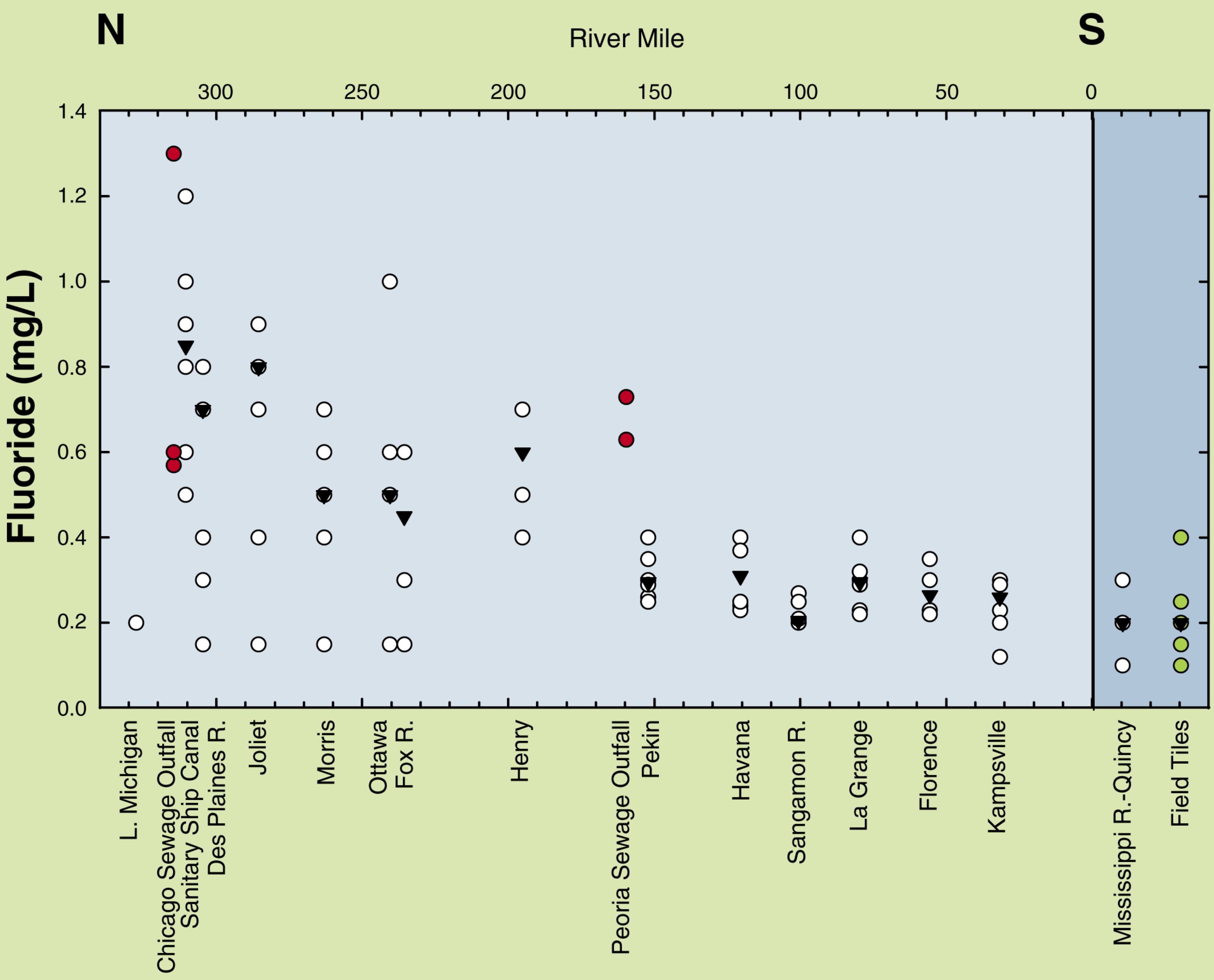
N
River Mile
S
300
250
200
150
100
50
0
10
8
6
4
2
0
TKN (mg/L)
L. Michigan
Chicago Sewage Outfall
Sanitary Ship Canal
Des Plaines R.
Joliet
Morris
Ottawa
Fox R.
Henry
Peoria Sewage Outfall
Pekin
Havana
Sangamon R.
La Grange
Florence
Kampsville
Mississippi R.-Quincy
Field Tiles

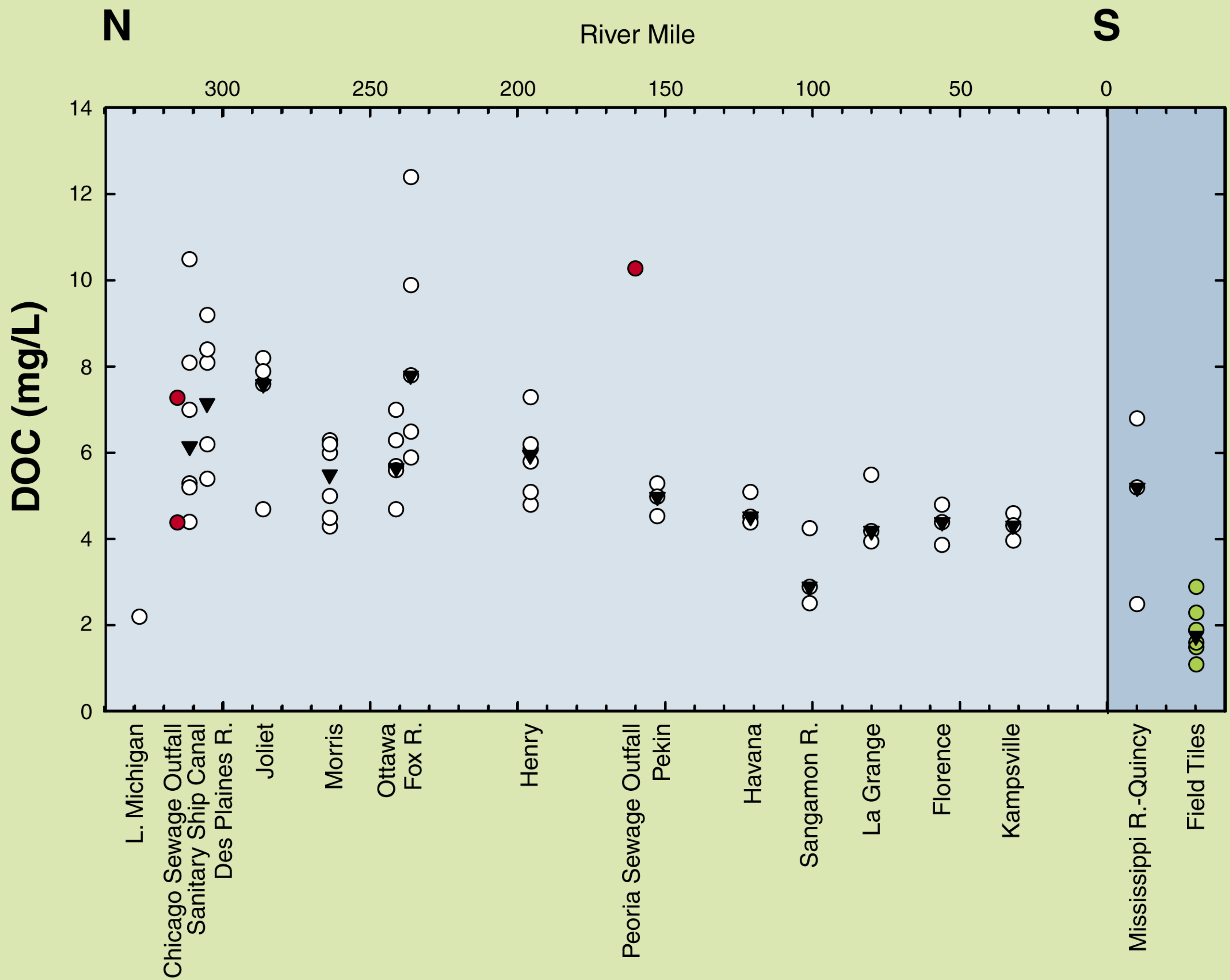


N
River Mile
S
300
250
200
150
100
50
0
25
20
15
10
5
0
Potassium (mg/L)
L. Michigan
Chicago Sewage Outfall
Sanitary Ship Canal
Des Plaines R.
Joliet
Morris
Ottawa
Fox R.
Henry
Peoria Sewage Outfall
Pekin
Havana
Sangamon R.
La Grange
Florence
Kampsville
Mississippi R.-Quincy
Field Tiles

Cl vs K for All IL River Data




N
S
River Mile
300
250
200
150
100
50
0
Fluoride (mg/L)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
L. Michigan
Chicago Sewage Outfall
Sanitary Ship Canal
Des Plaines R.
Joliet
Morris
Ottawa
Fox R.
Henry
Peoria Sewage Outfall
Pekin
Havana
Sangamon R.
La Grange
Florence
Kampsville
Mississippi R.-Quincy
Field Tiles



N
River Mile
S
300
250
200
150
100
50
0
14
12
10
8
6
4
2
0
DOC (mg/L)
L. Michigan
Chicago Sewage Outfall
Sanitary Ship Canal
Des Plaines R.
Joliet
Morris
Ottawa
Fox R.
Henry
Peoria Sewage Outfall
Pekin
Havana
Sangamon R.
La Grange
Florence
Kampsville
Mississippi R.-Quincy
Field Tiles

Nitrate Isotopes Results

What Are Isotopes?

- Isotopes are atoms of the same element with different numbers of neutrons in the nucleus.
- Isotopes may be stable or radioactive. Most elements have two or more isotopes. We focused on oxygen (^{16}O,^{18}O),) and nitrogen (^{14}N, ^{15}N).
- Small differences in the concentration of isotopes exist in chemically identical compounds because of differences in the origin or certain processes that have occurred after the compounds was produced. These characteristics make isotope analyses useful for determining the source of certain compounds in the environment and/or determining the geochemical reactions that have affected their concentrations.

Denitrification

$NO_3^- \rightarrow NO_2^- \rightarrow NO$
$N_2O \rightarrow N_2$

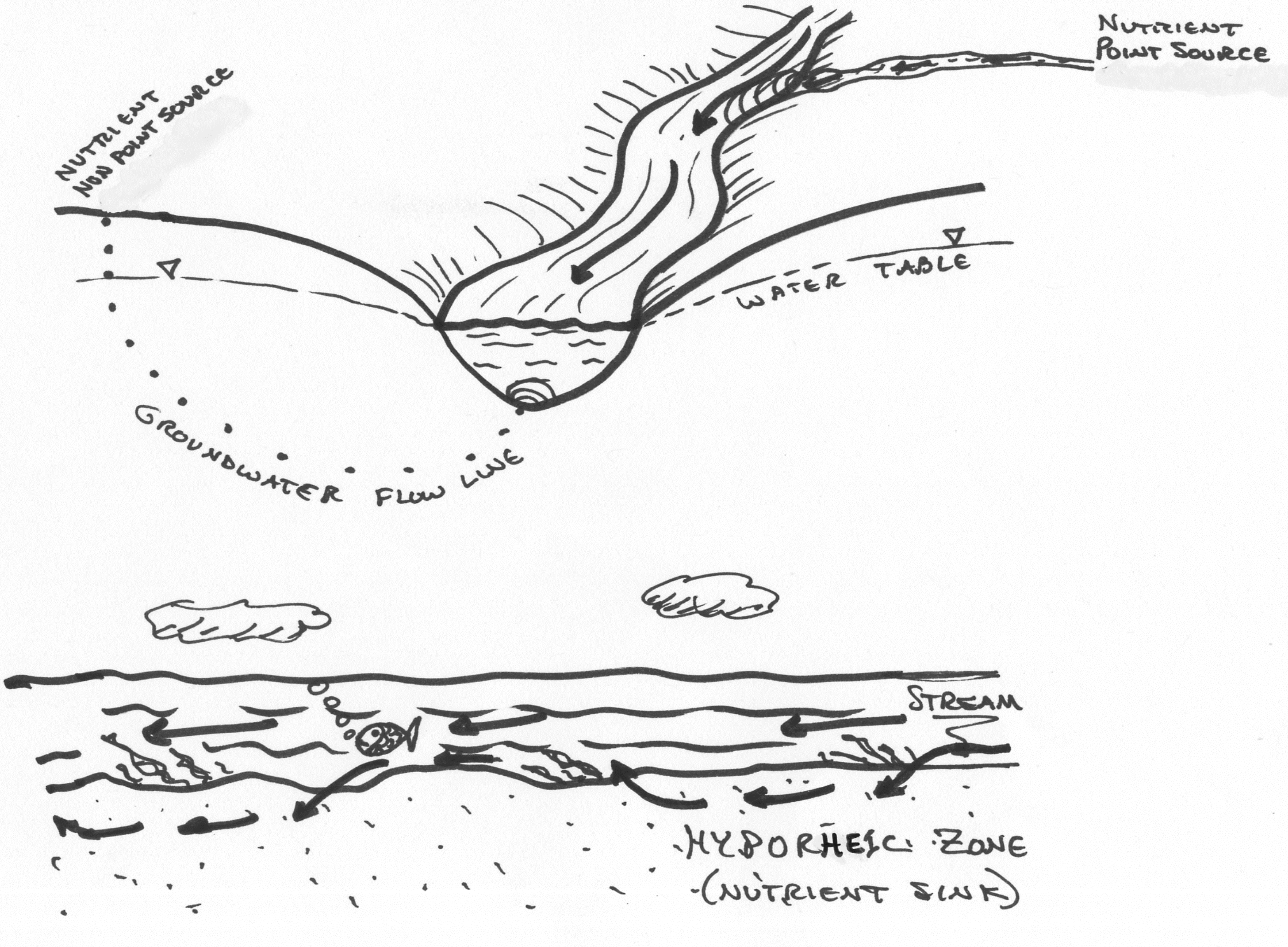
Microbial Reduction of Nitrate

- Microorganisms prefer ^{14}N-Nitrate to ^{15}N-Nitrate
- ^{14}N bond is easier to break
- As nitrate is consumed fraction remaining becomes enriched in ^{15}N and is thus “Heavier”
- Same Relationship holds true for $^{18}O/^{16}O$

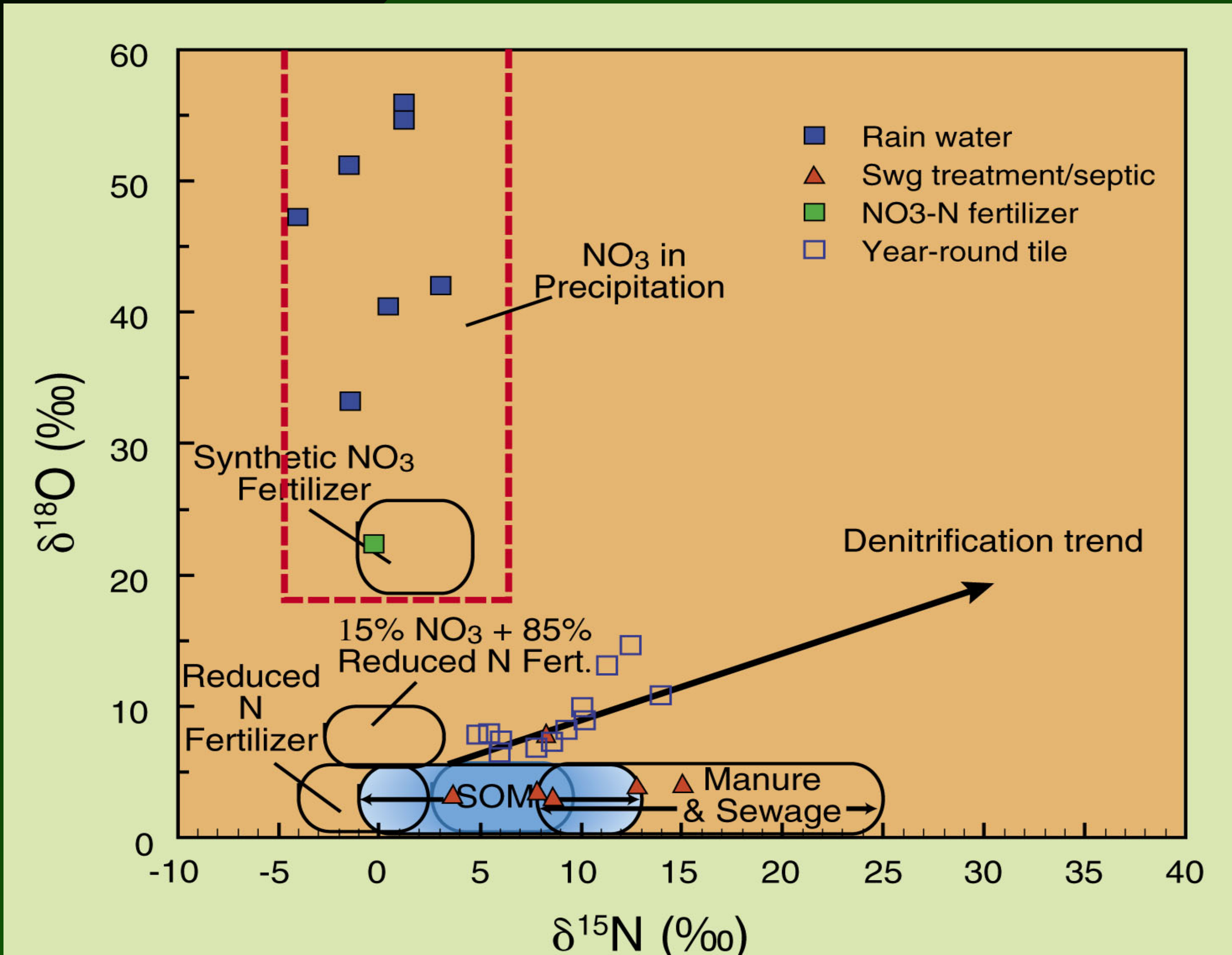
Denitrification Process

- The produced N_2 is enriched in the lighter isotope relative to the reacting NO_3.
- The remaining NO_3 becomes enriched in the heavier isotope.
- We measure the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios to monitor this effect.

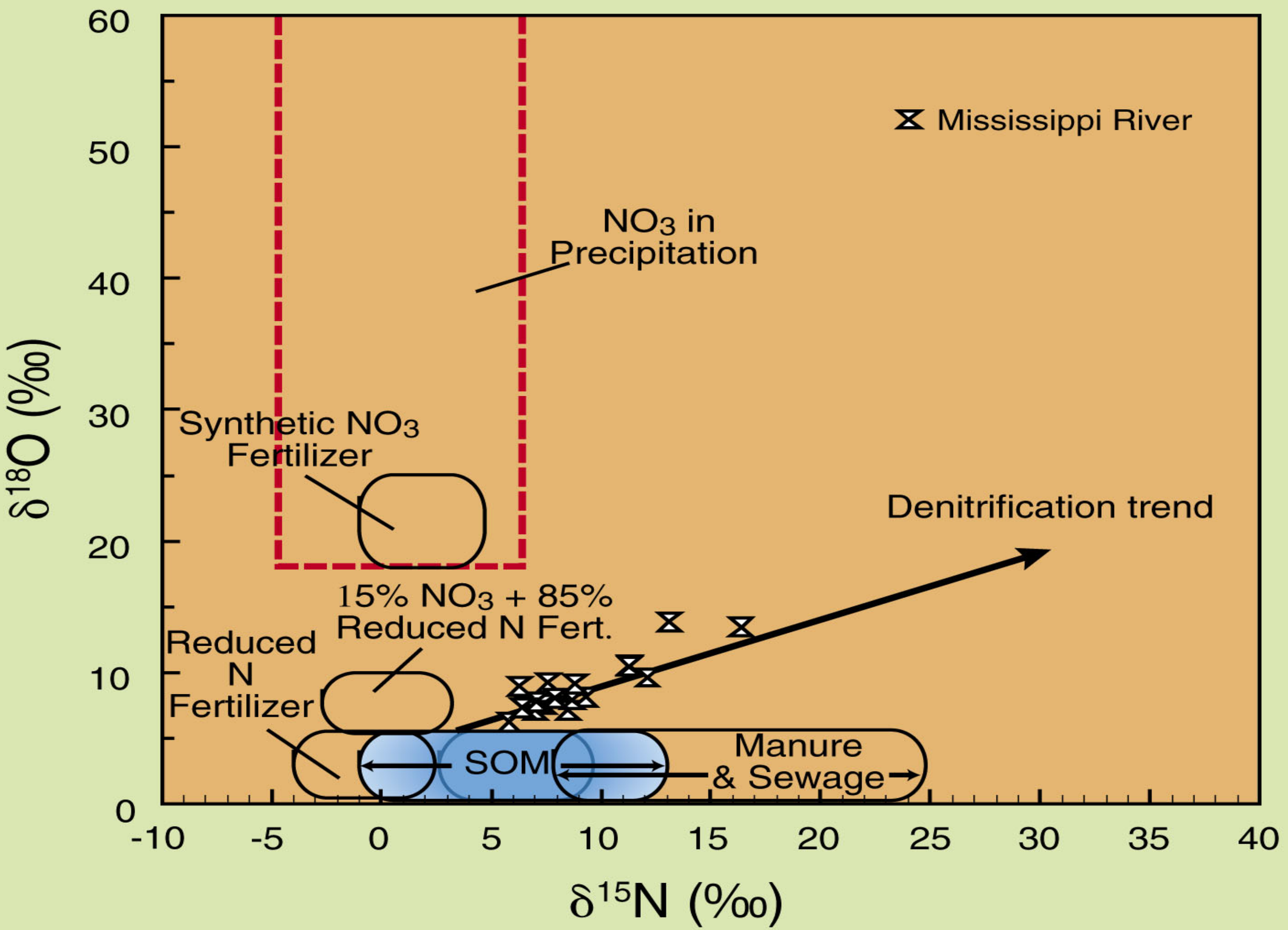
Movement of NO_3 in the Environment



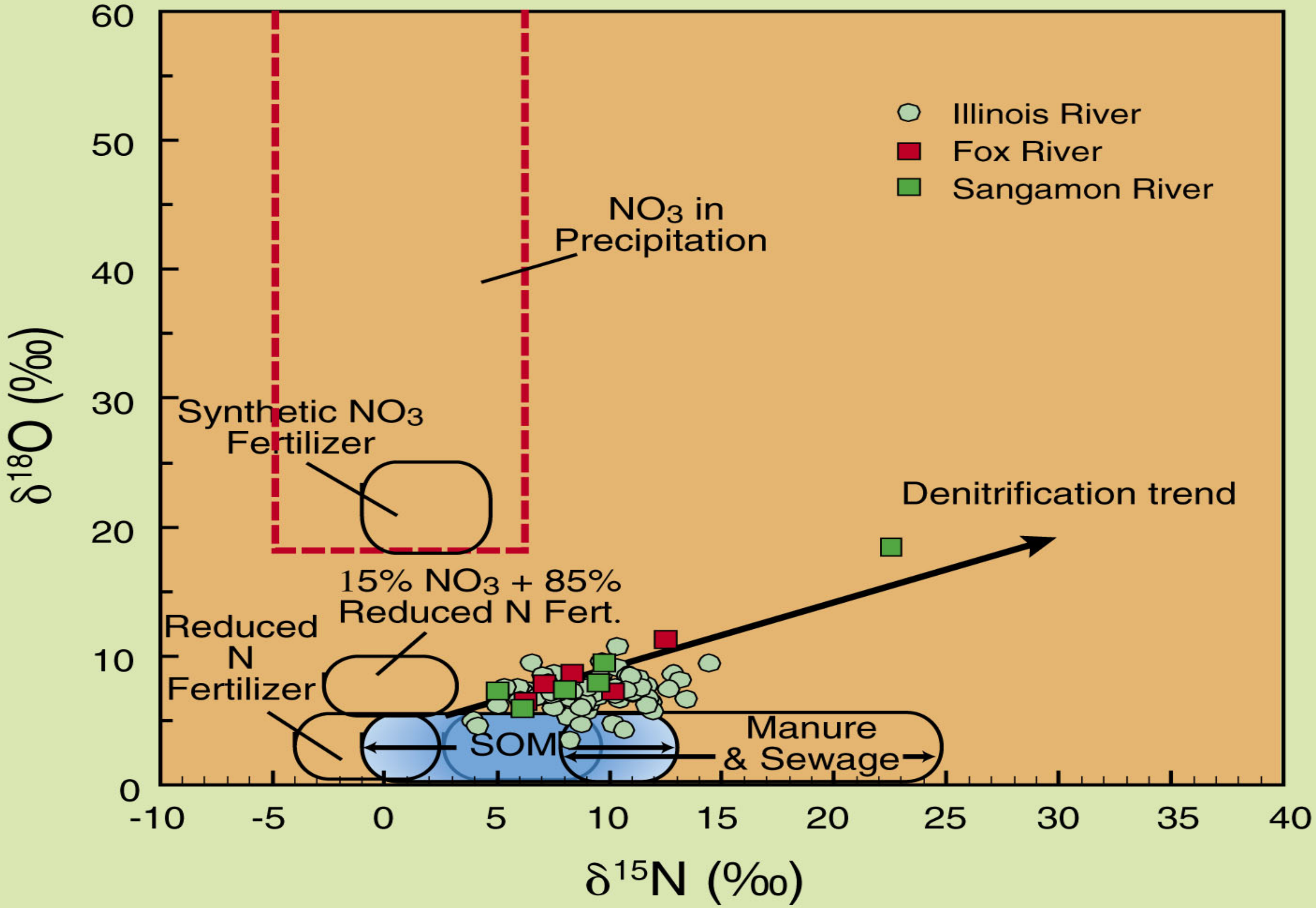
Sources/End Members of N



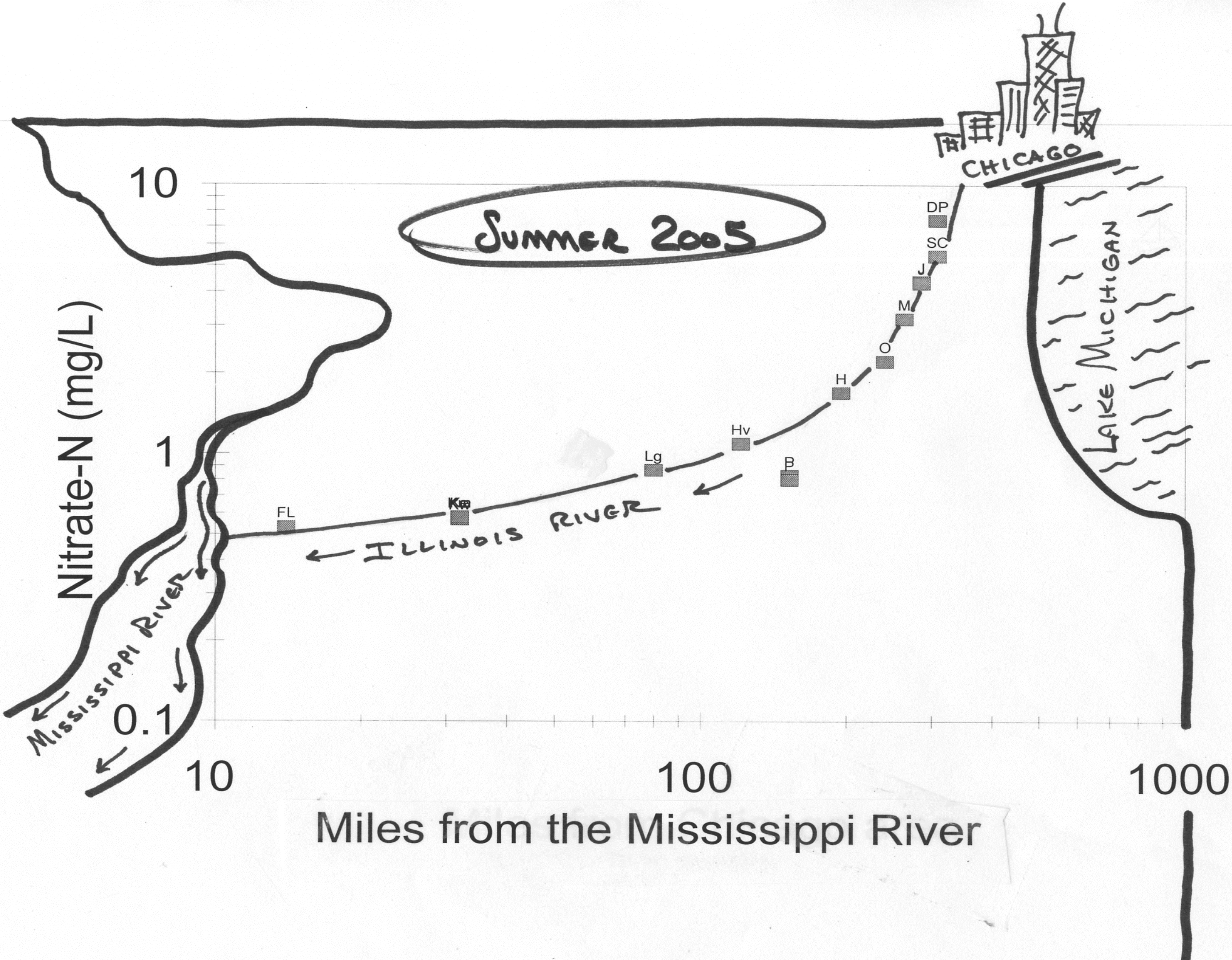
Mississippi River Data



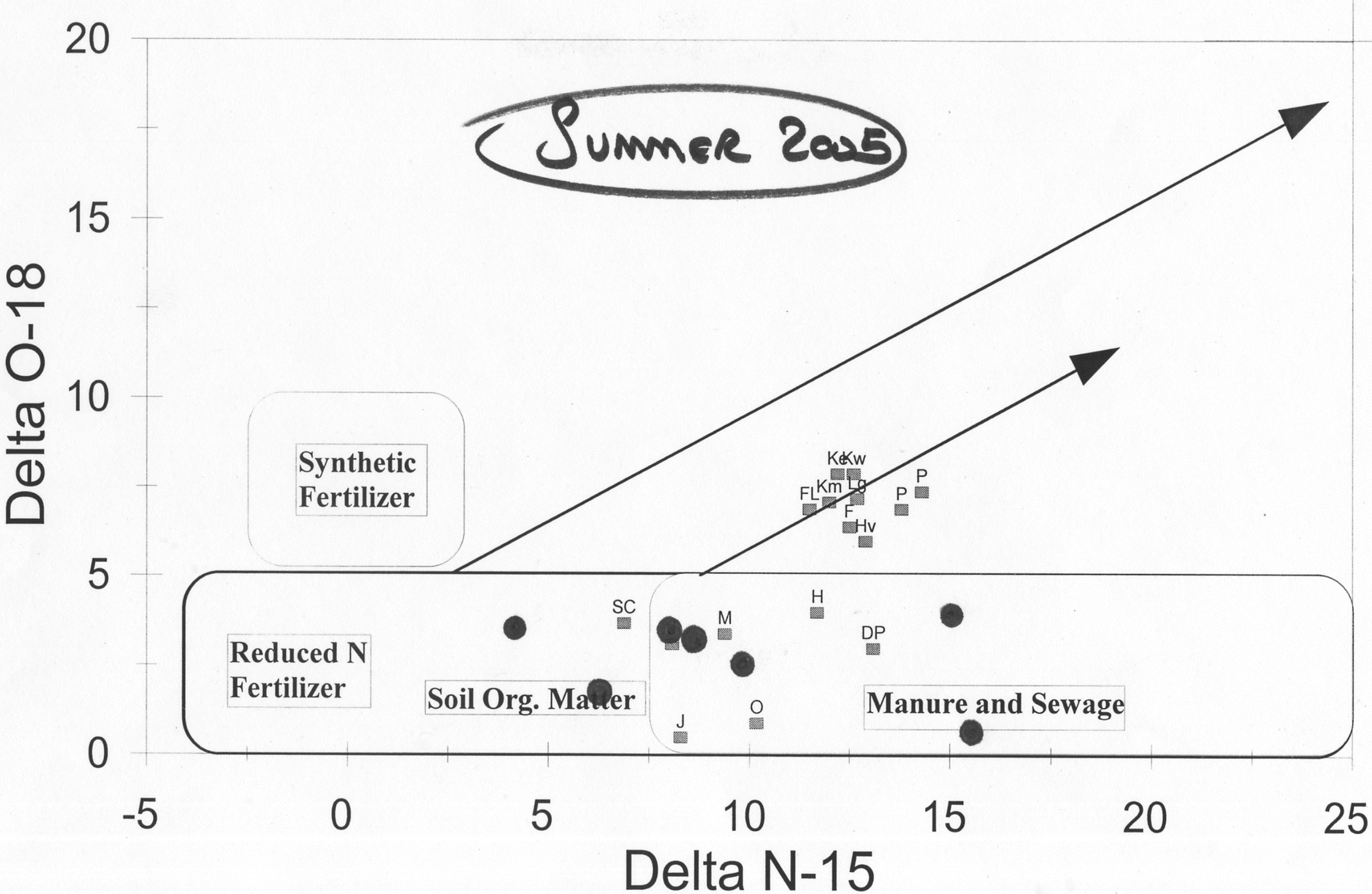
Illinois River: All Data



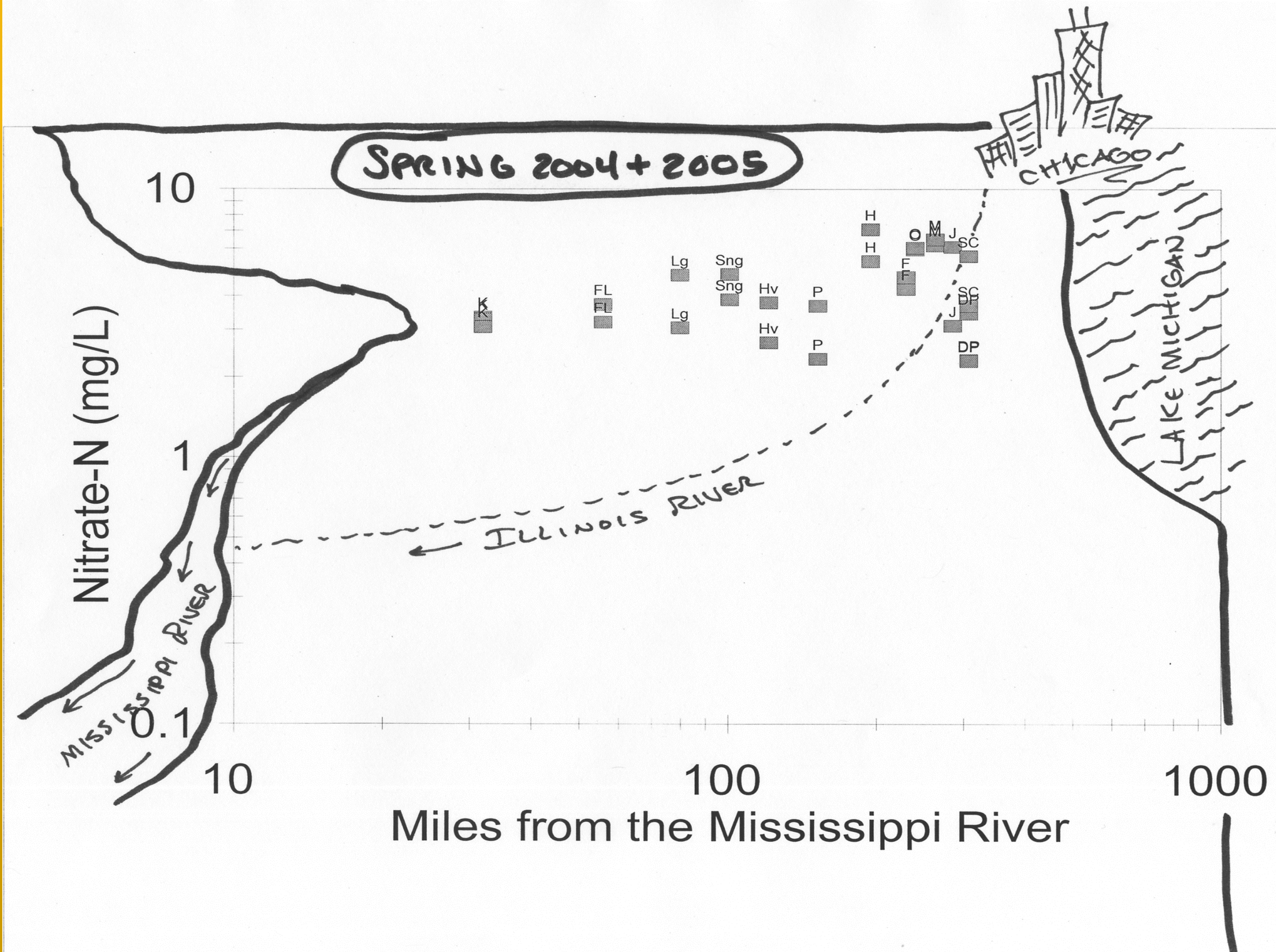
NO_3 During Drought of 2005



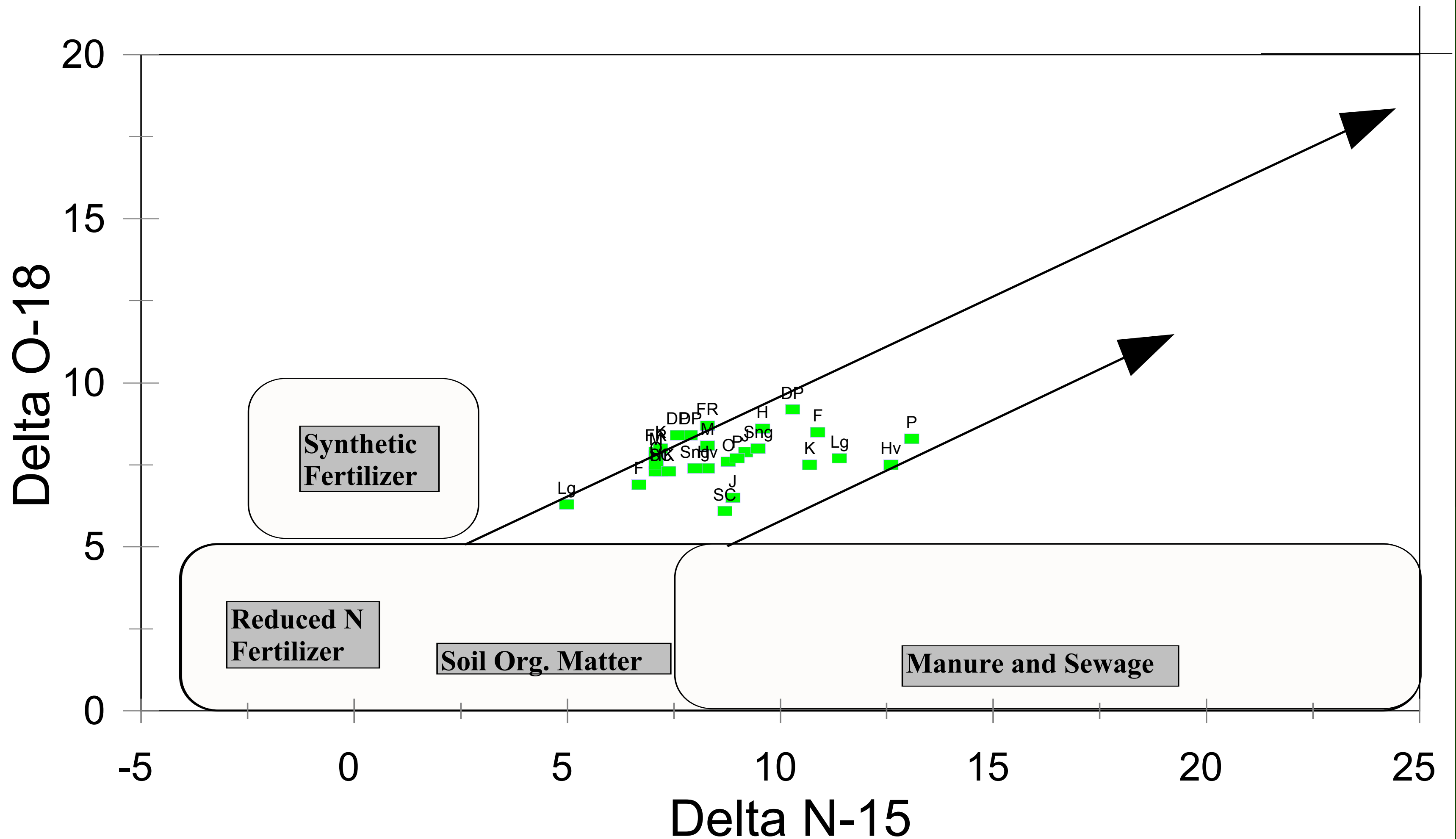
NO_3 Isotopes for Summer 2005



NO_3 During Spring (2004-2005)

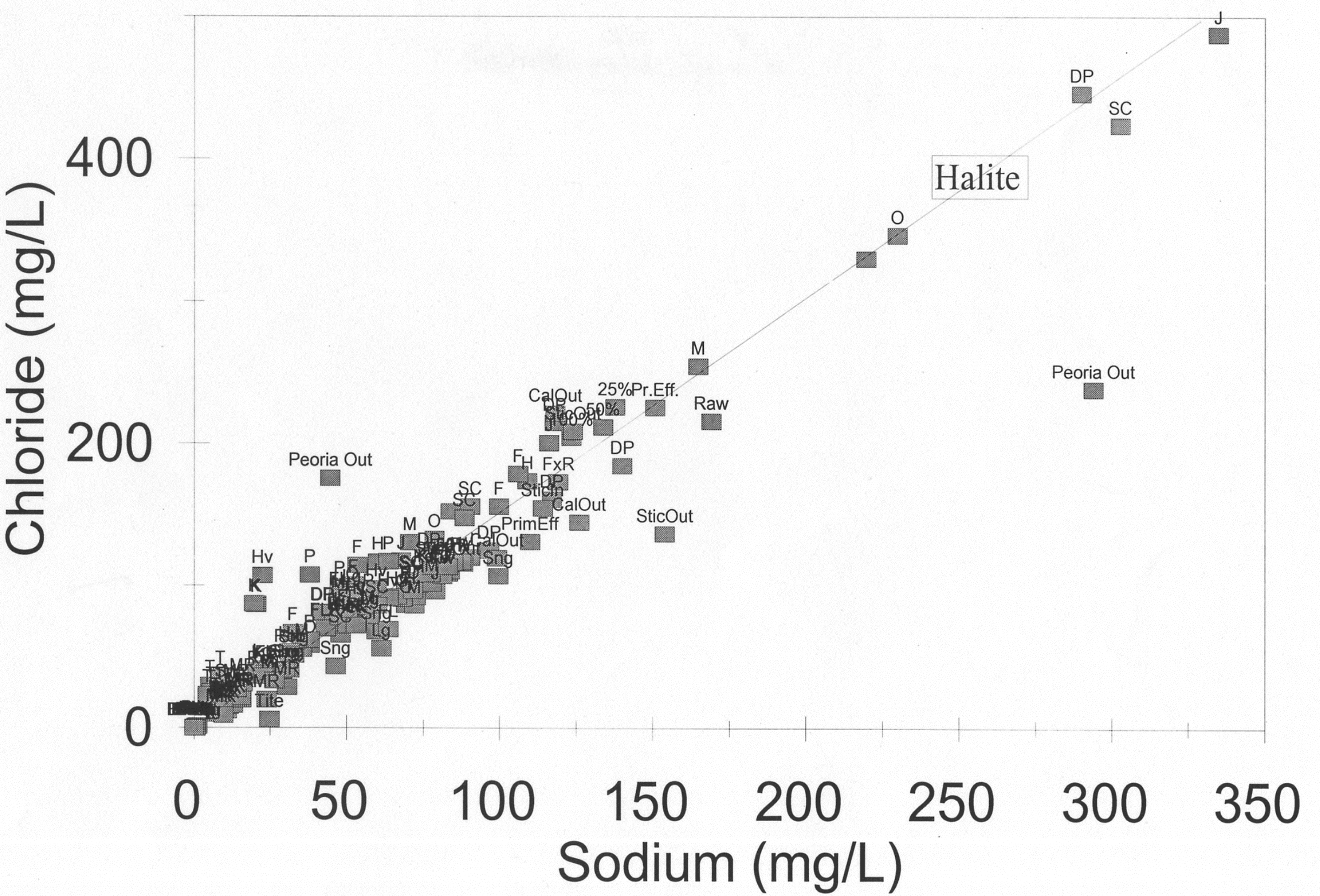


NO_3 Isotopes for Spring '04-'05

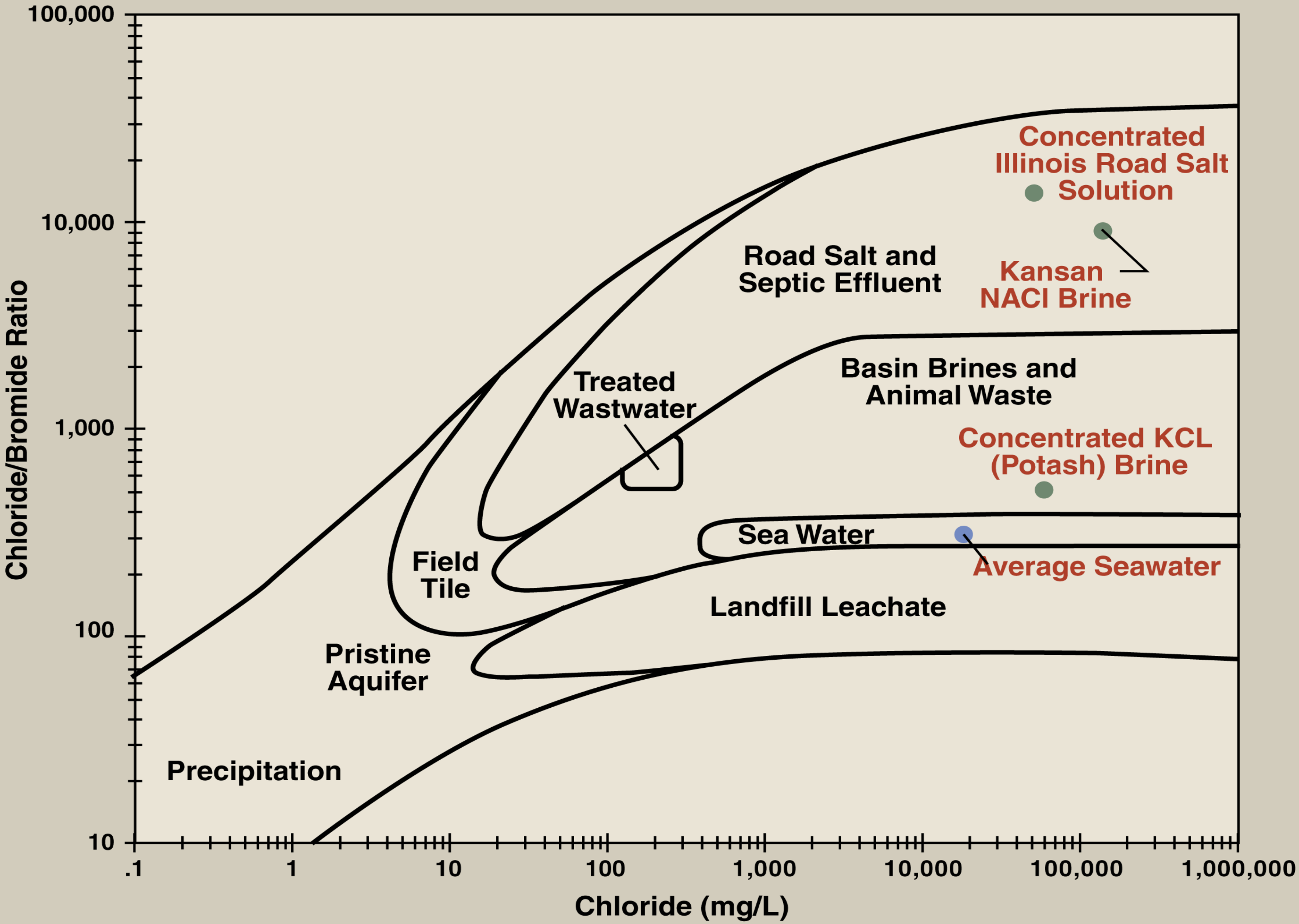


Halide Results

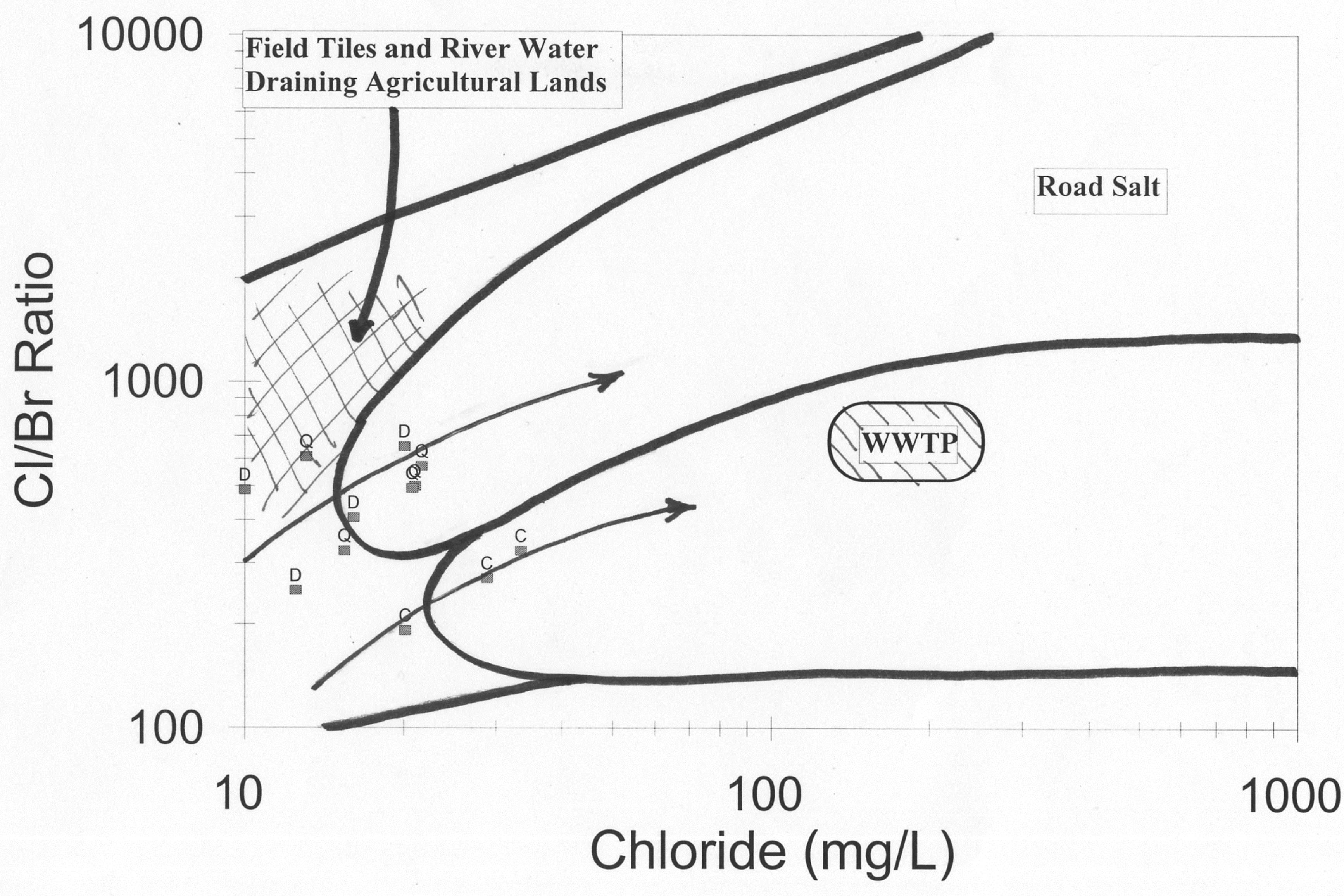
Na vs Cl for All IL River Data



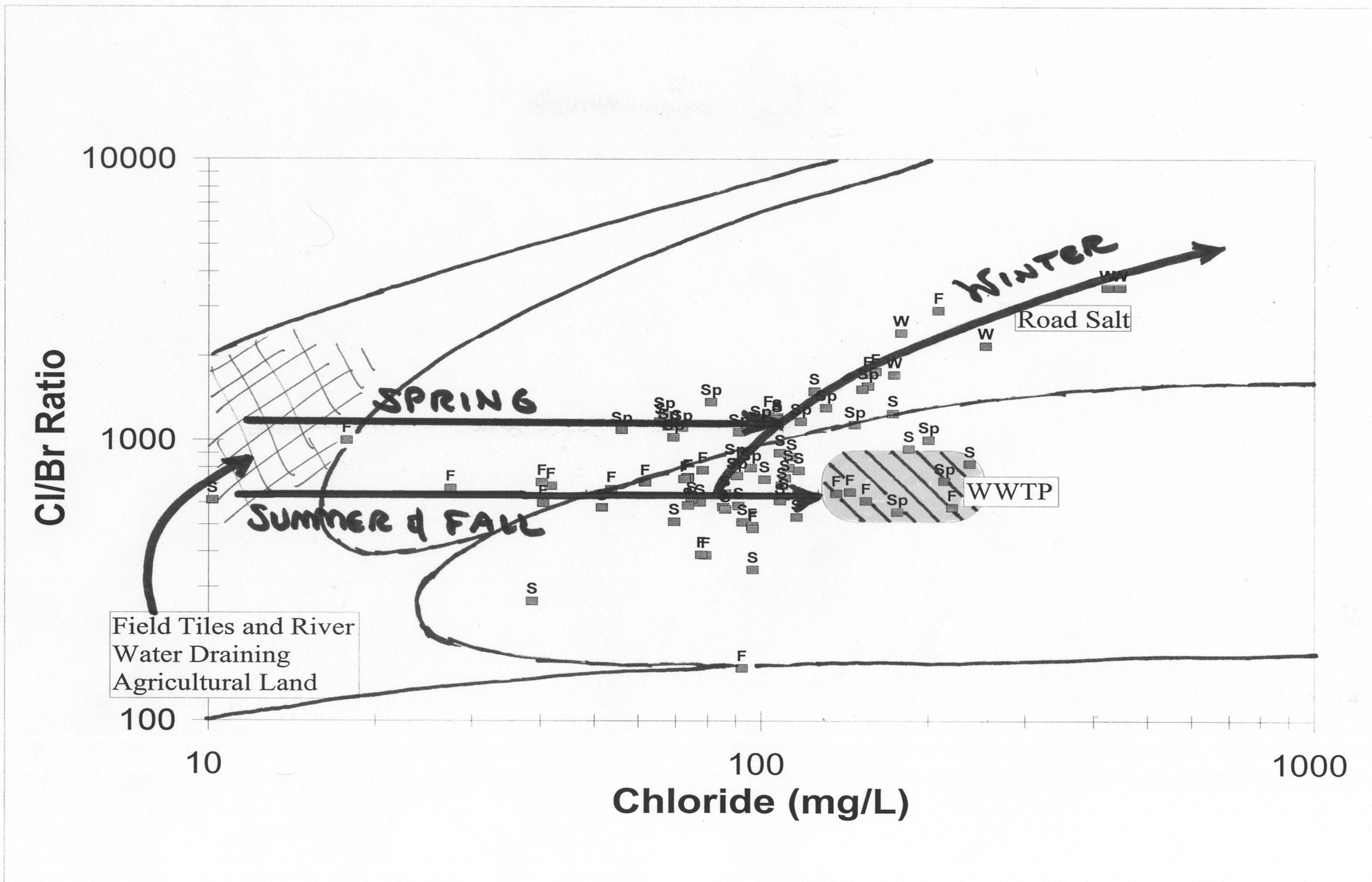
Cl/Br Plot for ID of Cl Sources



Cl/Br vs Cl for Miss. River Data



Cl/Br vs Cl for All IL River Data



Summary and Conclusions

- Surface waters in the Chicago area contain elevated concentrations of N species, Na, K, B, Cl, F, PO4 and DOC, and low DO.
- Concentrations of most contaminants originating at the waste-water treatment plants decrease with distance from the Chicago area.
- There is evidence of denitrification in drain tiles, tributaries, and perhaps along the Illinois River.
- Treated waste water has a significant effect on the nitrate isotopic composition of Illinois River water.

Summary and Conclusions cont.

- Results of this investigation support previous estimates that NO_3 in the Illinois River is derived from agricultural sources with a considerable contribution from municipal waste water.
- Cl/Br vs Cl plots reveal mixing trends among field tile waters, treated waste water, and road salt affected water.
- Mississippi River water shows the effects of the input of treated waste water from the Illinois River.

Additional Work

- We are currently comparing river discharge to chemical data in order to calculate mass loading of each N source.
- We are comparing land use throughout the watershed with chemical data in to further identify sources of N along the river.
- We are attempting additional integration of the halide data with the isotopic data in order to further identify the sources and fate of N in the Illinois River and its tributaries.