Identification of the Sources of Nitrate in the Illinois River

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.
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
Cl vs K for All IL River Data
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

\[ \text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{NO} \]
\[ \text{N}_2\text{O} \rightarrow \text{N}_2 \]
Microbial Reduction of Nitrate

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

\[ \delta^{18}O \text{ (‰)} \]

\[ \delta^{15}N \text{ (‰)} \]

- Rain water
- Swg treatment/septic
- NO3-N fertilizer
- Year-round tile

Synthetic NO3 Fertilizer

15% NO3 + 85% Reduced N Fert.

Reduced N Fertilizer

Denitrification trend

SOM

Manure & Sewage
Mississippi River Data

δ¹⁸O (‰)

δ¹⁵N (‰)

Mississippi River

NO₃ in Precipitation

Synthetic NO₃ Fertilizer

15% NO₃ + 85% Reduced N Fert.

Reduced N Fertilizer

SOM

Manure & Sewage

Denitrification trend
NO$_3$ During Drought of 2005
NO$_3$ Isotopes for Summer 2005
NO$_3$ Isotopes for Spring ‘04-'05
Halide Results
Na vs Cl for All IL River Data
Cl/Br vs Cl for Miss. River Data

- Field Tiles and River Water
  Draining Agricultural Lands
- Road Salt
- WWTP
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.
• 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.