Exploring causes of increasing nitrate concentrations in the Lower St. Croix River

Brenda Moraska Lafrancois, Byron Karns, Wade Miller, Brian Schuetz, Elizabeth Peterson, and Will Daniels



K. Heideman

# Why N?



- Like P, N can be a limiting nutrient
- Excess N (or changes in N:P) can lead to nuisance blooms

# **Coastal Dead Zones**

#### Spread exponentially since 1960s

- 400 ecosystems
- Result of coastal eutrophication
- Fertilizer runoff
- Serious ecological consequences

Diaz and Rosenberg. 2008. Science 321:926-929.

# Gulf of Mexico Hypoxia



Goolsby (2000) Eos.

- Noticed since 1950s, monitored since 1970s
- Driven by increases in nitrate (NO<sub>3</sub>-N) – fertilizer
- 56% of nitrate from Upper Mississippi
- 30% reduction in N loading required

Rabalais et al. (2002) BioScience.

# Lake St. Croix Nitrate



Median values for SC 0.3 and MR 796.9, 2000-2004.

# Lake St. Croix Nitrate



#### **Potential Causes**



- Increases in fertilizer use
- Changes in wastewater treatment (NH<sub>3</sub>→NO<sub>3</sub>)
- Atmospheric deposition
- Changes in soil denitrification processes

# Stable Isotope Analysis

#### • What are stable isotopes?

- Different forms of the same element
- Not radioactive
- Common ones = C, N, O, S, H
- Relative proportions used to infer things about ecosystem structure and process
- Isotopes of N and O useful for tracking nitrate
  - $^{14}N$  and  $^{15}N$
  - <sup>16</sup>O, <sup>17</sup>O, and <sup>18</sup>O

# Nitrate Stable Isotopes



C. Kendall. 1998. Tracing nitrogen sources and cycling in catchments. Chapter 16 *in* C. Kendall and J.J. McDonnell, eds., Isotope tracers in catchment hydrology. Elsevier Science B.V.

# Study Goals

- 1. Characterize patterns in nitrate concentration
  - Mainstem Lake St. Croix
  - Tributaries
  - Wastewater Treatment Plants
- 2. Identify nitrate sources
- 3. Evaluate usefulness of biological proxies

# Hypotheses

- NO<sub>3</sub>-N concentrations are highest in downstream tributaries and WWTPs
- δ<sup>15</sup>N and δ<sup>18</sup>O suggest wastewater influence at upstream sites, fertilizer downstream
- δ<sup>15</sup>N is more stable in zebra mussels than in water or phytoplankton over season



• 14 sites

- 7 mainstem
- 5 tributaries
- 2 wastewater plants
- 5 sampling events
- 3 components
  - Water (nitrate)
  - Phytoplankton
  - Zebra mussels

# Methods









## Methods

- Water analyzed for nitrate concentration and stable isotopes of N and O
  - Diffusion technique ( $\delta^{15}N$ )
  - Denitrifier method ( $\delta^{15}N$  and  $\delta^{18}O$ )
- Phytoplankton and zebra mussel tissue analyzed for δ<sup>15</sup>N (δ<sup>13</sup>C)



# Mainstem Concentrations



Means and StDevs, May-Aug 2008 Note: detection limit = 0.2 mg/l

#### Tribs and WWTPs



# Stable Isotope Results (Hypothetical)



# **Preliminary Findings**



- Nitrate increases systematically
  - Largest increases downstream
  - Lake St. Croix tributaries and tributary land use important

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#### **Seasonal Patterns**



Long-term means (1976-2002)

## **Seasonal Patterns**

**Mainstem St. Croix Sites** 

