

Detecting Nitrogen Sources and Flow Paths in the Great Bay Watershed



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Detecting Nitrogen Sources and Flow Paths in the Great Bay Watershed

Presentation Outline

- Review Nitrogen impacts in the Great Bay Watershed
- Highlight Main Objectives of this 3-yr *Collaborative Science* project
- Summarize Methods
- *Preliminary Data*

Nitrogen inputs have impaired the Great Bay

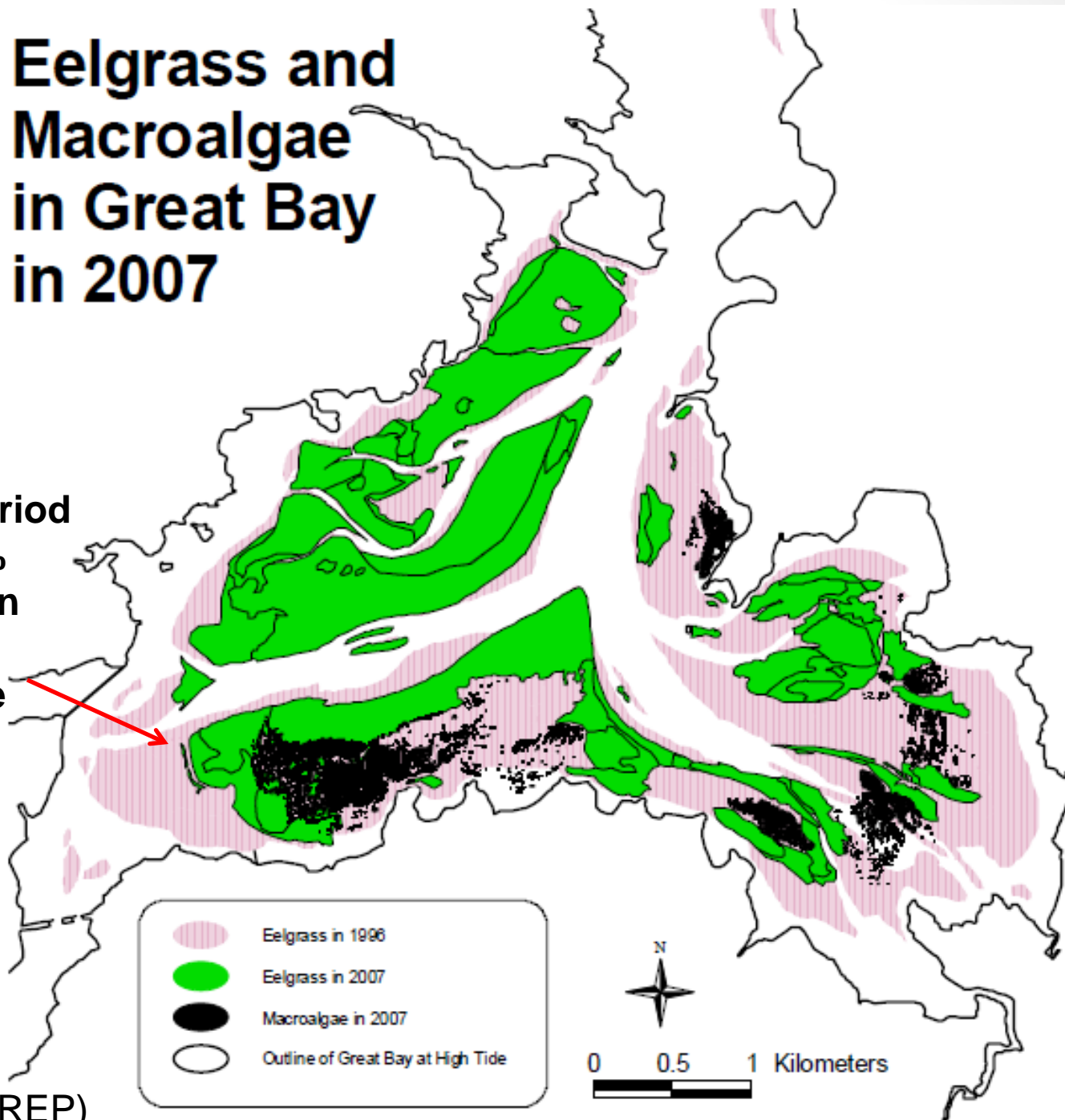
- Dissolved Inorganic Nitrogen up 42% over the last 5 years (PREP)
- Increases in nitrogen (N) loads drive habitat degradation
- Water clarity and dissolved oxygen levels declining
- Adult oyster populations decreased from 125,000 (1997) to 10,044 (2009)

Eutrophication
consequence
Menhaden Fish Kill
Neuse River, NC 2008



Eelgrass and Macroalgae in Great Bay in 2007

9 year period
Over 50%
Reduction
Eelgrass
Coverage



(Source, PREP)

Types of Nitrogen Source Inputs

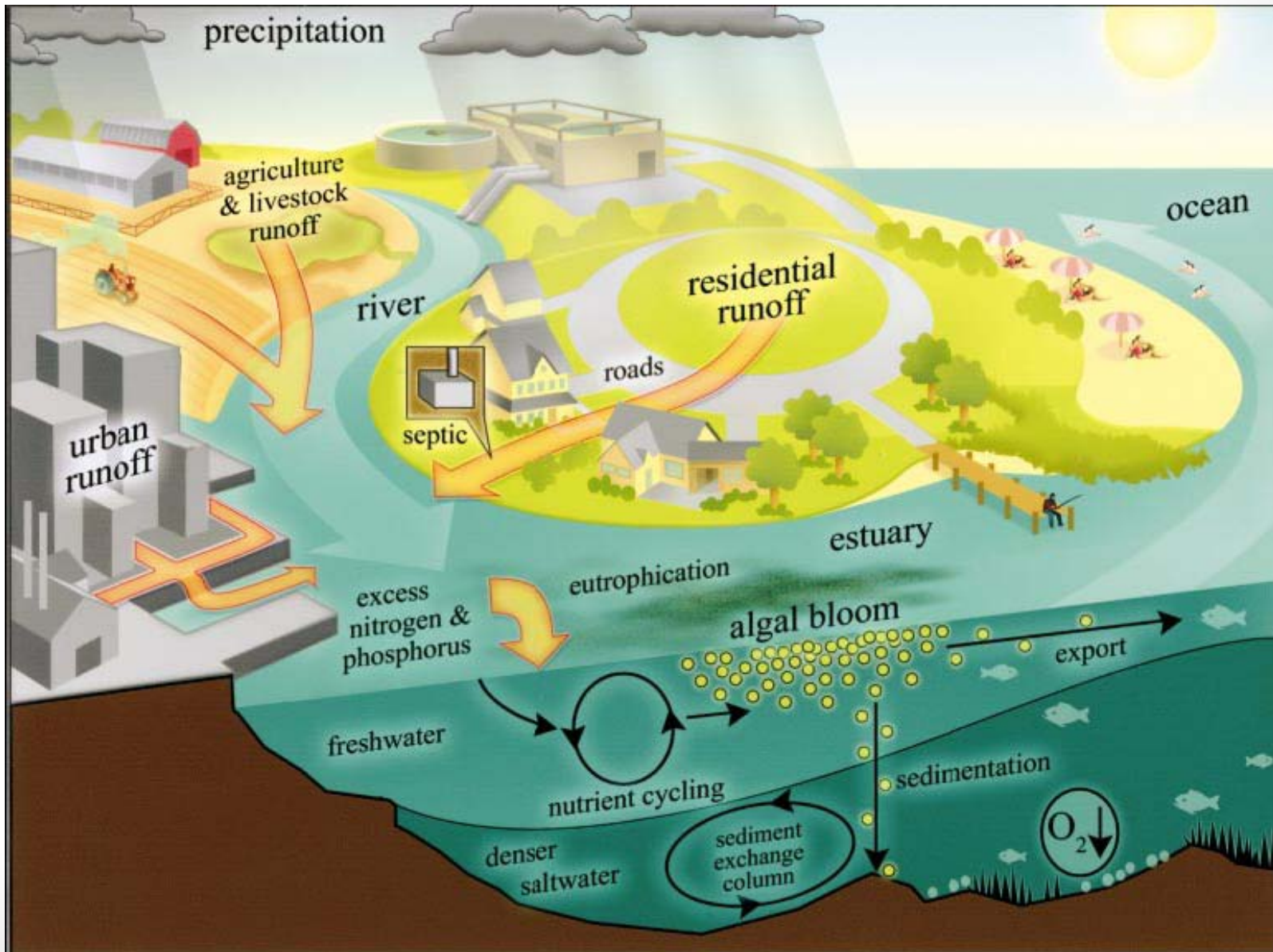
Non-Point Source (NPS) N: DIFFUSE in nature and transported in water in various forms (NO_3^- , NH_4^+)

- Fertilizer - Natural and Synthetic, agricultural crops, homeowner, golf courses
- Storm water runoff (urban)- Mixture (fertilizers, pet waste, NO_x auto emissions, parking lots)
- Septic – Sewage leakage, On-site waste disposal
- Manure - Animal farm applications
- Precipitation/Atmospheric- Deposited in aquatic systems

Point source pollution: Originates from a single source (“pipe”)

- Industrial, WWTP

Source inputs to the hydro & atmosphere



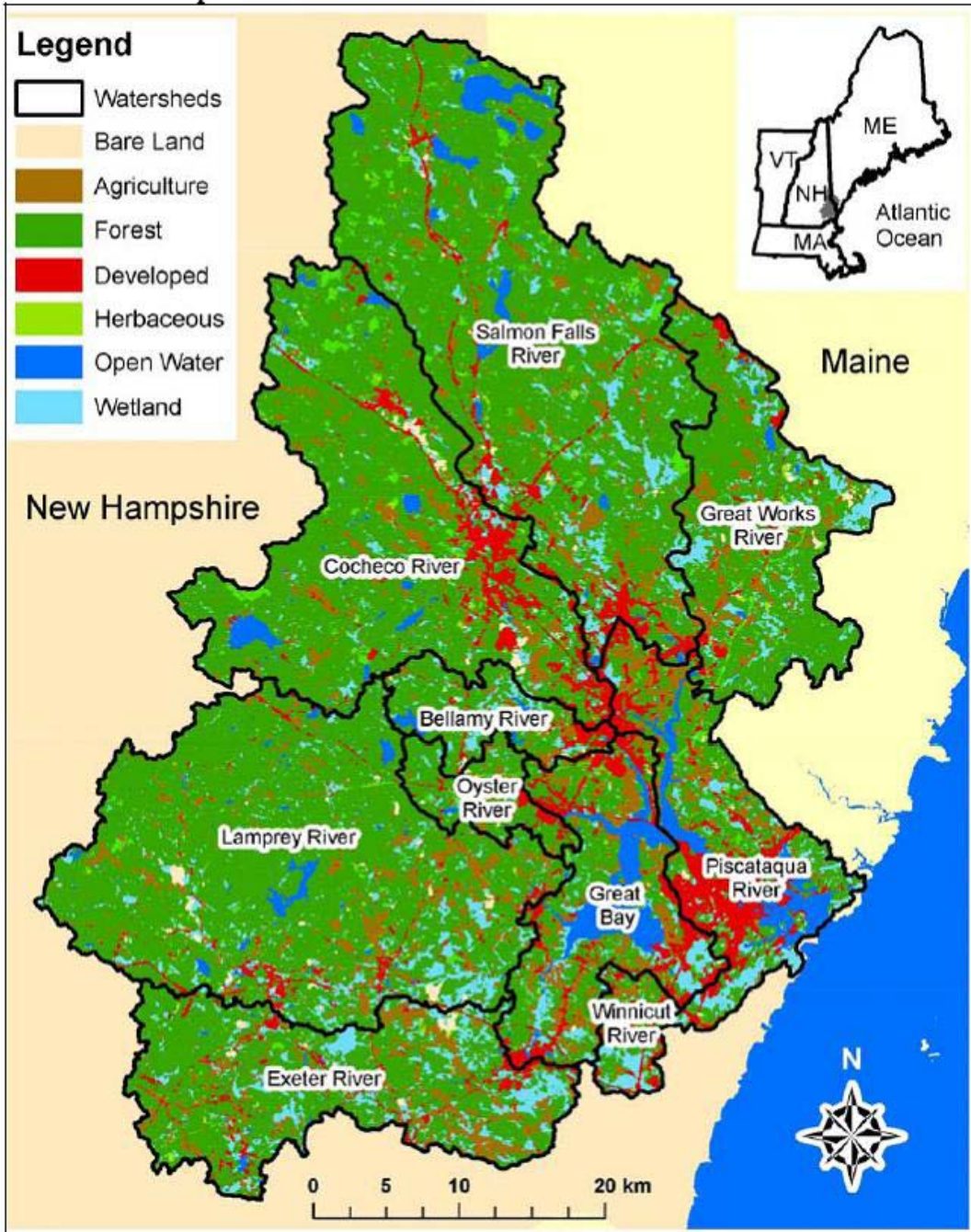
What previous studies have found

- Studies of watersheds in the northeastern US show that 60-80% of the N added to catchments is *not exported* to large estuarine systems such as the Great Bay
- Of the N entering the Great Bay, it is unclear what % of which NPS's are responsible for habitat impairment
- Land-use conversion (impervious surface construction) and human population density linked to total N input

Main Objectives

- Objective 1: ***Identify N hot spots in surface waters of the Great Bay Watershed***
- Objective 2: ***Identify Non-Point Source N that result in hot spots***
- Objective 3: ***Characterize the flow paths that deliver N to these hot spots***
- Objective 4: ***Collaborate with stakeholders every step of the process and make results useful to local environmental managers***

I. Reference Map:



Study Area Great Bay [Piscataqua River] Watershed –

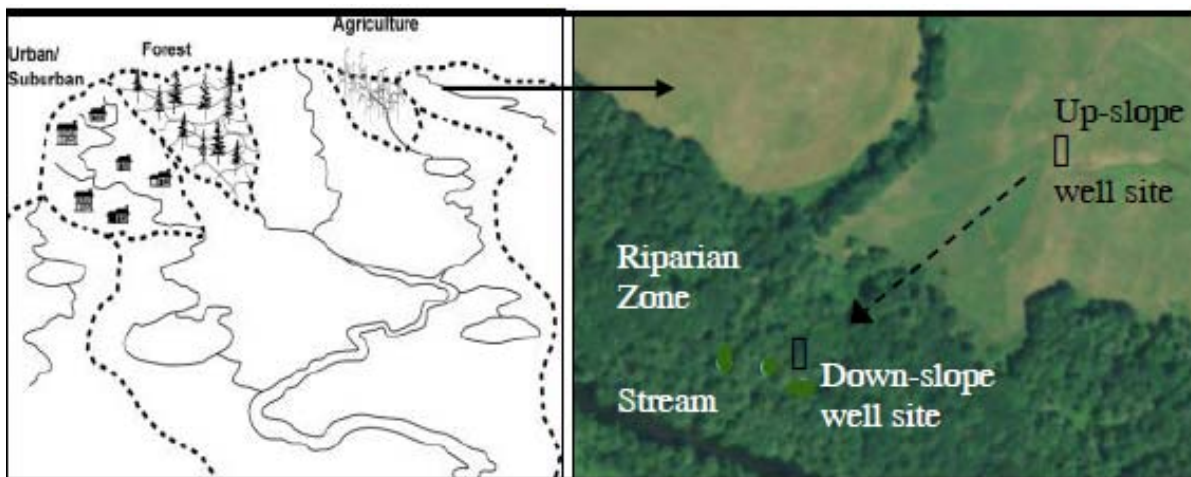
- Composed of 7 tidal rivers and covers 1025 mi²
- Mesotidal estuary with average tidal range 8.2 ft at the mouth to 6.6 ft at Dover Point

Objectives 1-2:

- **1: Identify N hot spots in surface waters of the Great Bay Watershed**
- Synoptic sampling of 250 stream sites in tributaries
- Samples analyzed for water chemistry (*e.g.*, $\text{NO}_3^- \text{ N}$, $\text{NH}_4^+ \text{ N}$, TN) and spatially related to land-use characteristics (impervious surface, human pop density)
- **2: Identify NPS N that result in hot spots**
- Target sites (20-30) that have a range of NO_3^- levels and land-use
- Examine water chemistry and source signatures of surface and groundwater nitrate seasonally
- Model the spatial variability of NPS N using a multi-tracer approach (Isotopic, Chemical, and Microbiological)

Objective 3

- ***Characterize the flow paths that deliver N to these hot spots***
- Water samples analyzed from shallow groundwater wells (1-3 m depth), upslope and downslope along the flow path that passes through the riparian zone
 - Compare chemical signatures (Caffeine and Optical Brighteners) with isotopic and microbiological markers to delineate flow paths
- ***Examine nitrate attenuation potential in streams and river channels***
- Document reduction of N as water moves through the riparian zone.
 - Mass balance of higher order (4th-5th) streams
 - $\delta^{15}\text{N}$ tracer experiments in smaller streams (1st -3rd)



Objective 4

- *Collaborate with stakeholders along with the scientific process*
- *Integrate scientific results and make them useful to environmental managers and stakeholders*

Methods (1): Isotope Tracer Approach

- By measuring the NATURAL ABUNDANCE of environmental stable isotopes ($\delta^{15}\text{N}$) *relative* to that of the more abundant $\delta^{14}\text{N}$ in water and organic matter
 - Source relationships can be distinguished
 - NPS's of nitrate have different $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values
 - Correlate isotopes from the different source with nitrate levels at study sites
 - δ values, expressed in units of permil (‰). The standard for N isotopes is Air ~ 0 ‰.

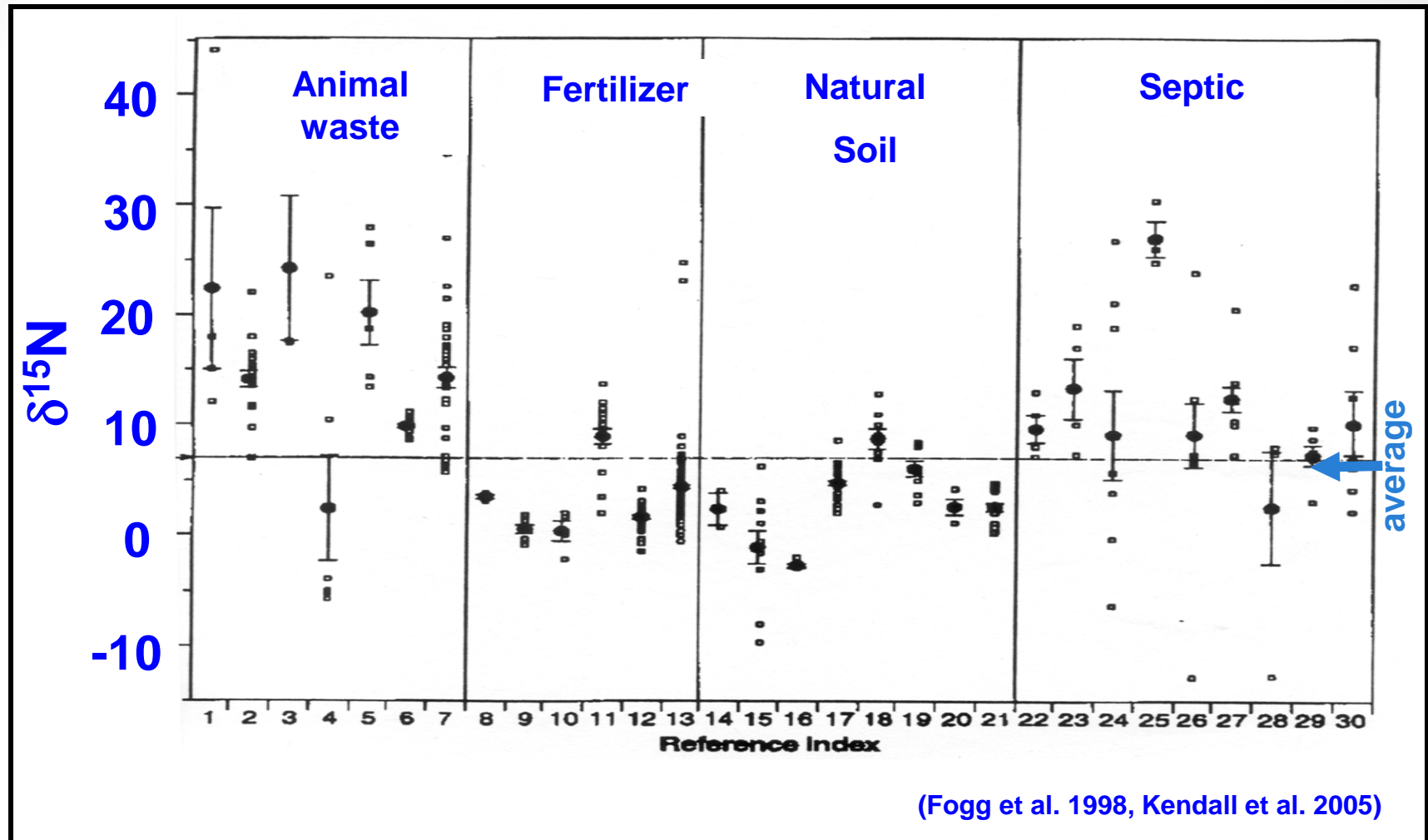
$$\text{Delta } (\delta) \text{ value} = \frac{\text{Ratio}_{\text{sample}} - \text{Ratio}_{\text{standard}}}{\text{Ratio}_{\text{standard}}} \times 1000$$

How well can we Interpret Sources with A Single Isotopic Approach



**Input Parameter:
Source Mixing Model**

Fertilizer vs animal waste source of nitrate: $\delta^{15}\text{N}$



Nitrate derived from fertilizer ($\sim 0\%$) can be distinguished from nitrate derived from animal and human waste (10-20%). **End members.**

Septic waste vs. Animal manure:

Would NOT work using only nitrate- $\delta^{15}\text{N}$.

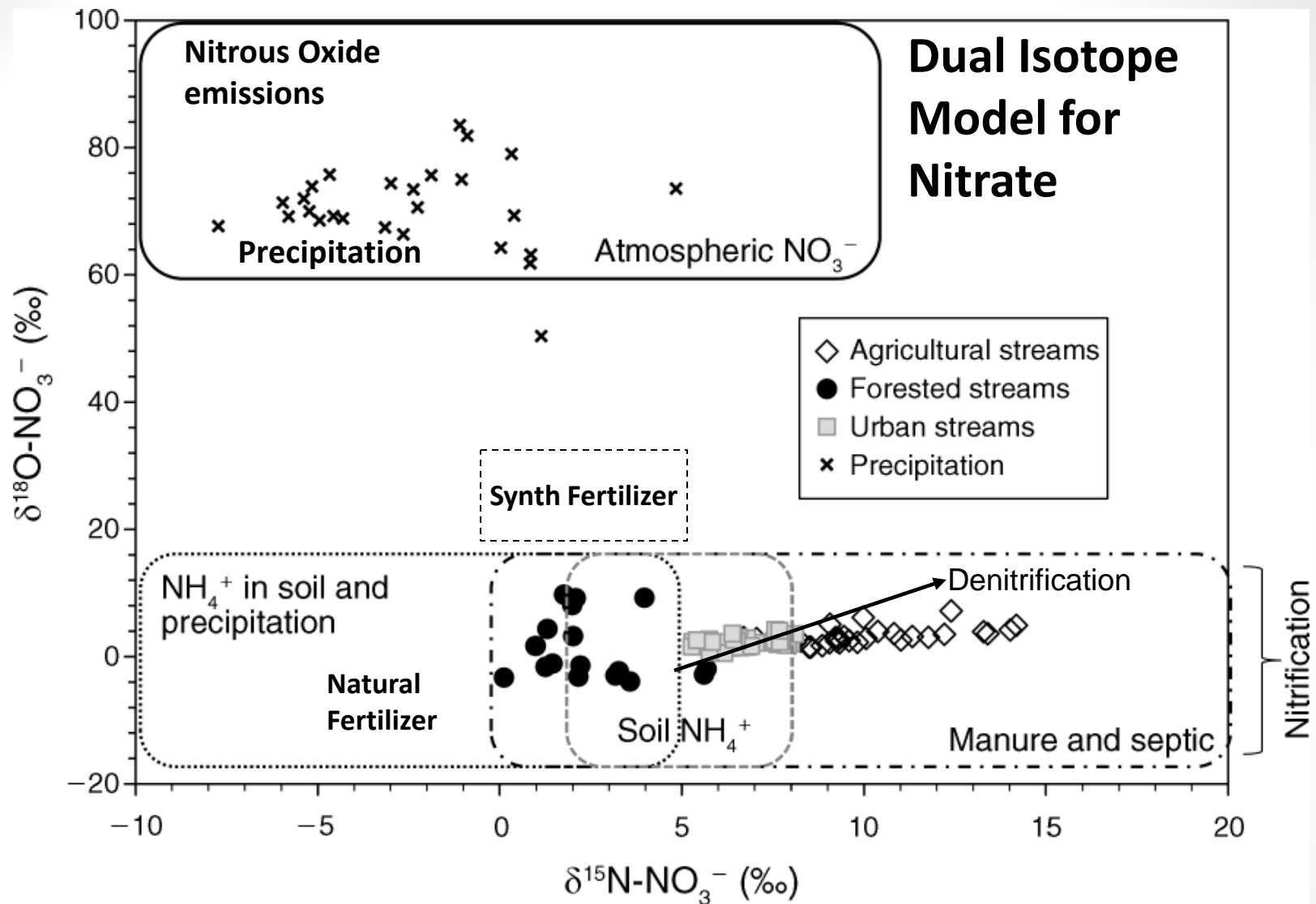
(because the nitrate- $\delta^{15}\text{N}$ values are usually overlapping).

These types of waste may be distinguished if:

- A dual isotopic approach is needed.
- other chemical tracers needed that are specific for the different sources used (caffeine, brighteners).

A Dual Isotopic Approach (^{18}O and ^{15}N of Nitrate) to *further* distinguish source relationships

**Develop:
Source Mixing Model**

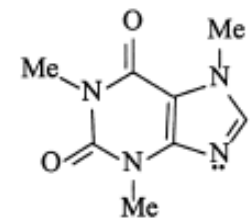


Nitrate in water from precipitation, fertilizer, manure and septic waste has distinct $^{18}\text{O}-\text{NO}_3$ signatures (Kendal et al. 2000, Barnes and Raymond 2010).

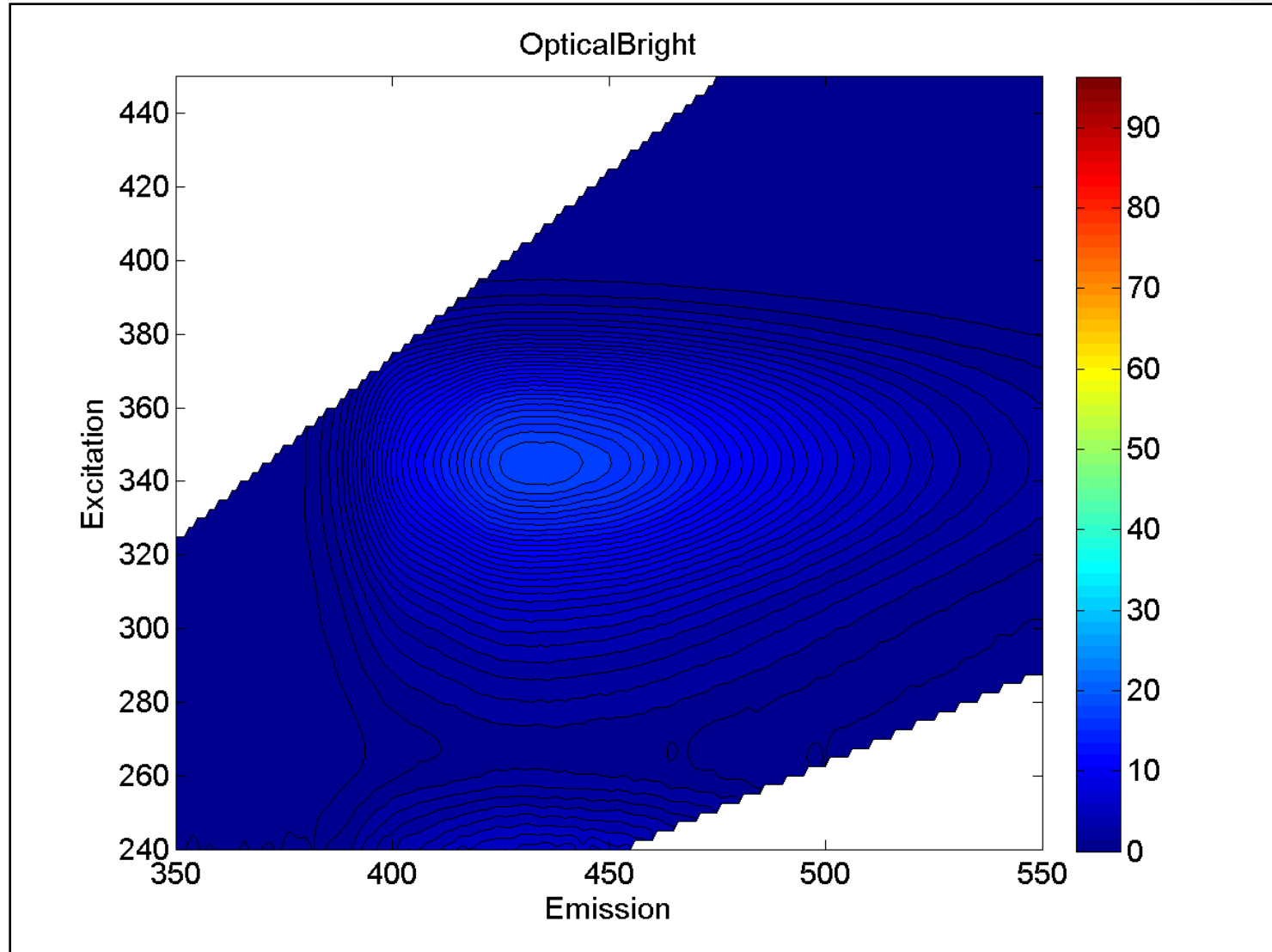
Methods (2): Chemical Tracers

- Detect Caffeine and Optical Brightener compounds using HPLC fluorescence and solid phase extraction
 - Indicates human waste source (caffeine in domestic wastewater measured 200-300 µg/liter)
- Laundry products - Fluorometric Detection of Optical Brighteners: A septic and stormwater source
- ^{11}B oron – ID bleaching agent. Conservative tracer not prone to degradation
- Analyze stream, groundwater and runoff values with isotopic and microbiological markers

5-10% of caffeine (a widely consumed drug in the world) is excreted unchanged by humans (World Health).

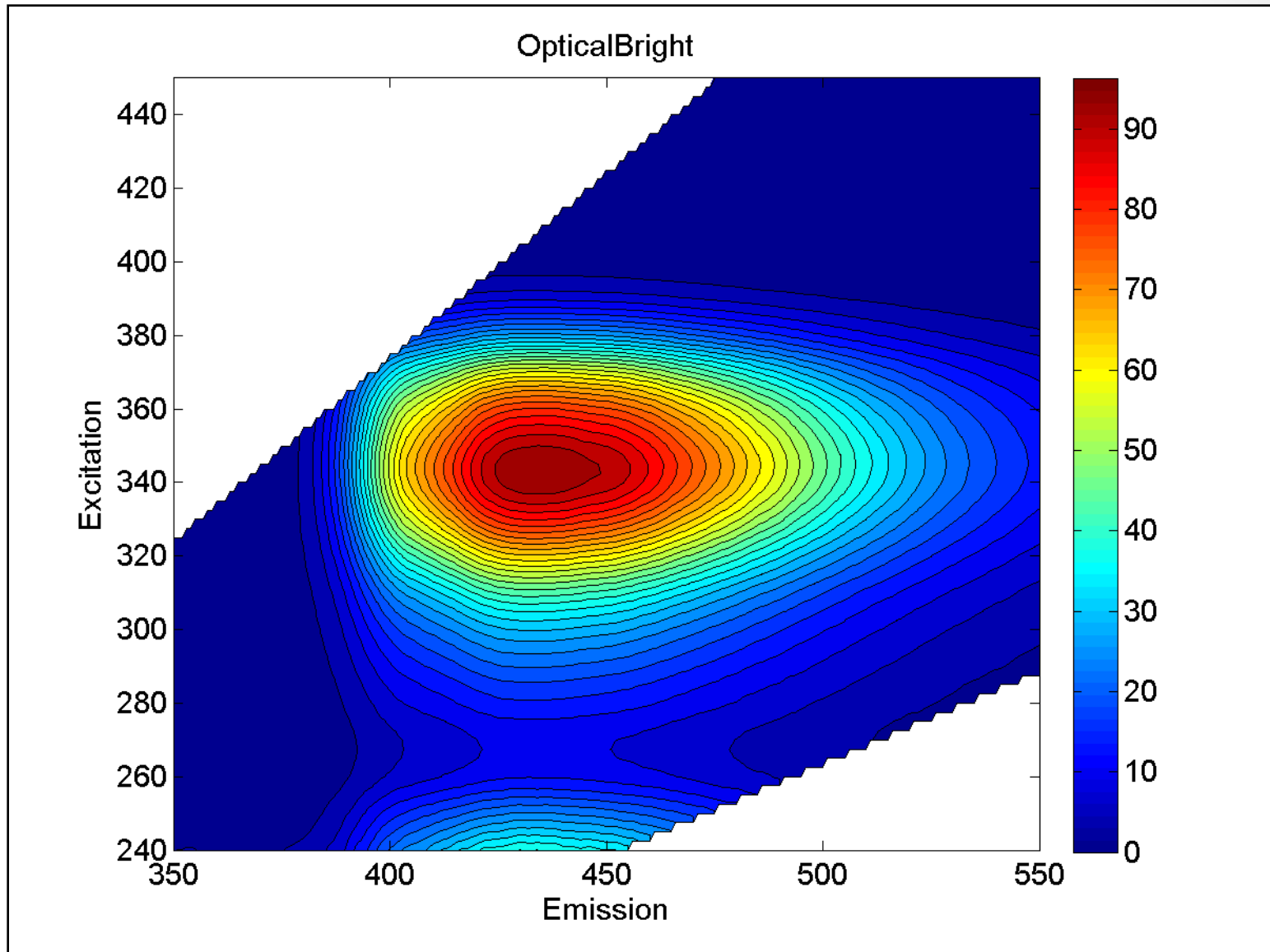


Methods (2): HPLC of Laundry Detergent



- Natural Brand (7th Generation) Signature

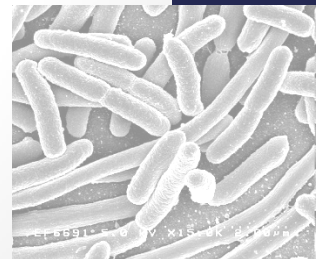
Methods (2) : HPLC of Laundry Detergent



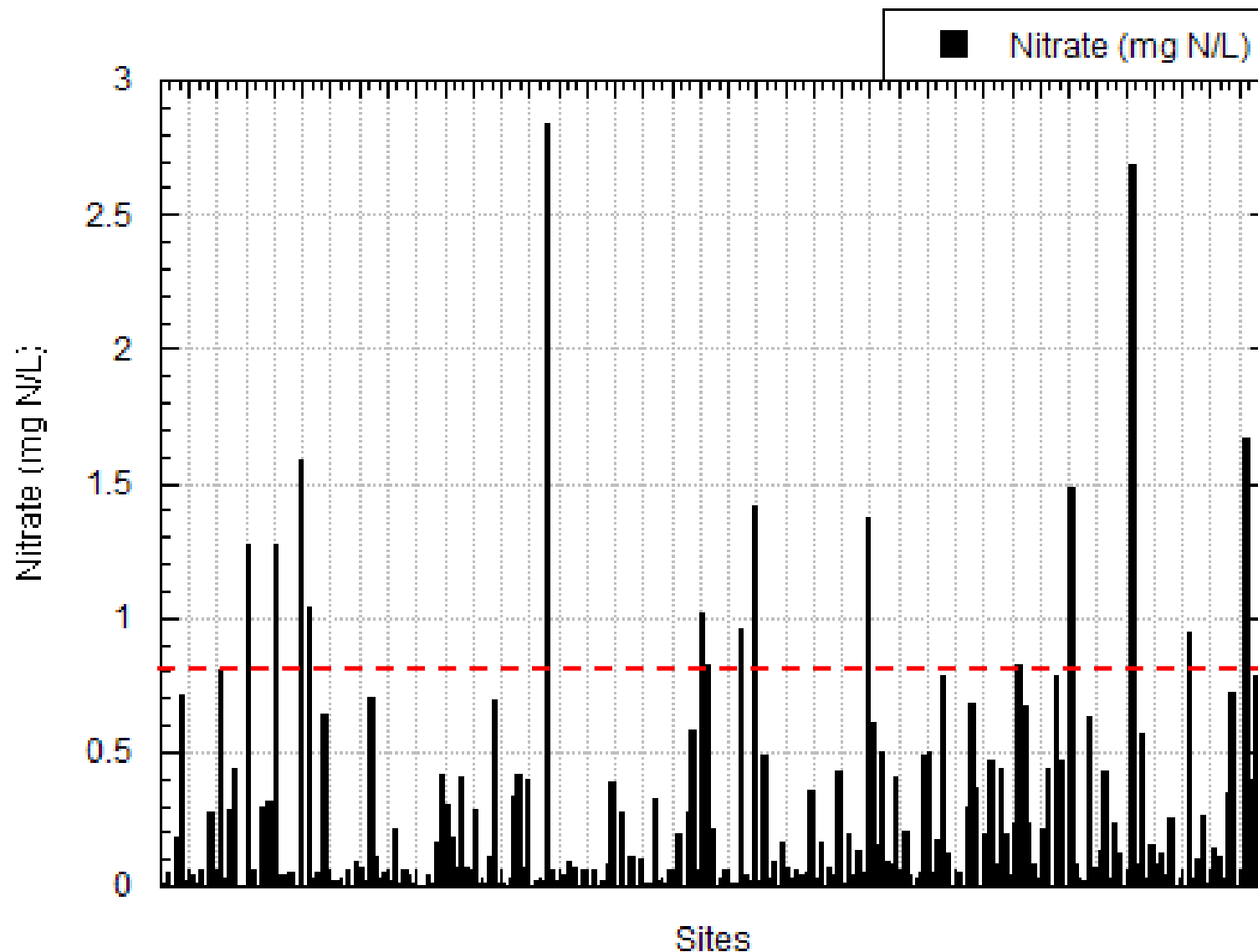
- Arm and Hammer Brand. Positive at OB 420-460nm range

Methods (3) Microbial Source Tracking

- How to confirm Animal vs. Human waste source ?
- Test water for high fecal counts (>126 cfu/100ml)
- Use Genotypic Method: (real-time PCR) of **mt** (mitochondrial) **DNA** to CONFIRM animal waste source (Human, Dog, Bovine, Geese) (Caldwell et al. 2007)
 - Eukaryotic (host) feces contain excess exfoliated epithelial cells
 - Amplify fecal mt DNA - many copies per cell
 - Identifies fecal source directly without culturing
 - Detectable DNA persists even after cellular death



Preliminary Result – Extensive Sampling

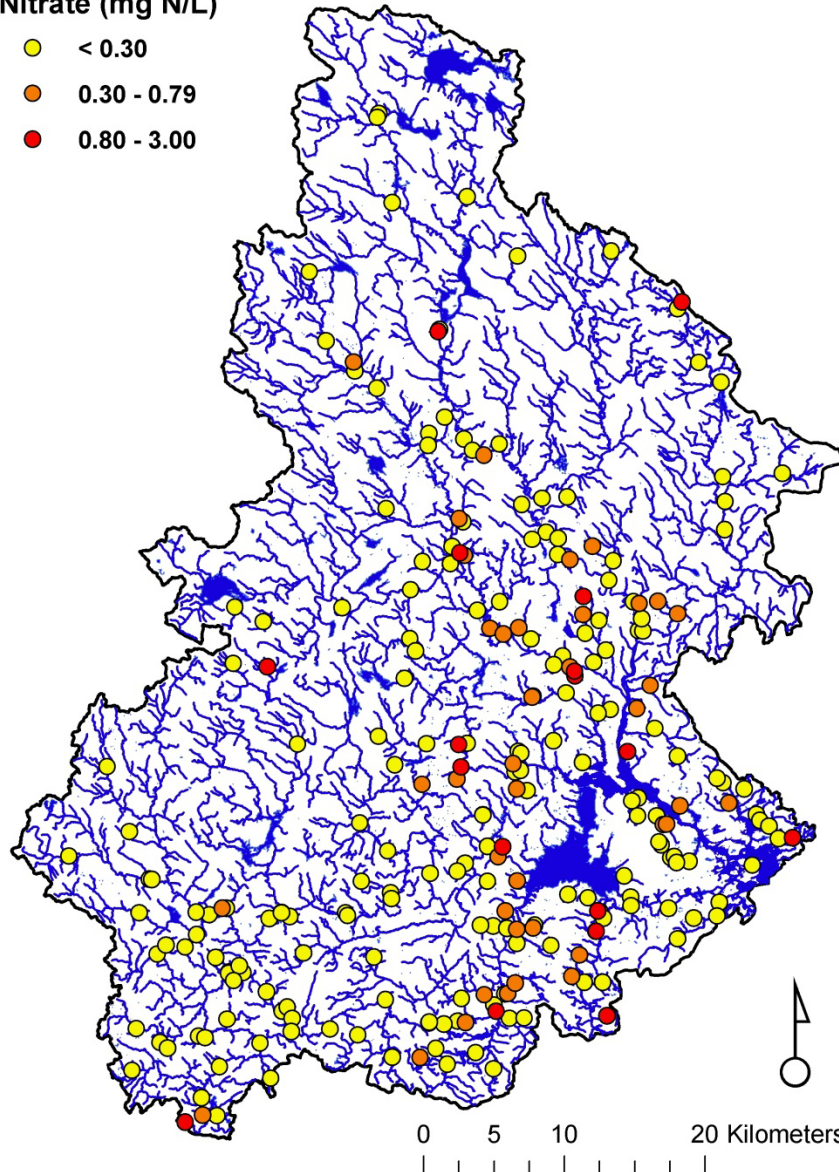


- Nitrate Data for sites (250) sampled across Great Bay Watershed (mean; 0.22 mg N/L \pm 0.3).
- High stream levels (> 0.8 mg N/L); Human public health (10 mg N/L).

Preliminary Result – Nitrate Concentration Map

Nitrate (mg N/L)

- < 0.30
- 0.30 - 0.79
- 0.80 - 3.00



➤ Map of Great Bay Watershed.

➤ Extensive sampling of stream surface water nitrate.

➤ Subsequent analyses will relate N water chemistry to spatial variables (i.e., % impervious surface, population density, land-use).

Summary

Collaboratively we will use innovative field and laboratory methods to identify hotspots of non-point source N entering the Bay

This approach will highlight impacts of land use on N fate and transport

Assist management on strategies to reduce N at critical areas that pose the greatest threat in the Great Bay

Acknowledgements

We would like to thank the faculty and students at UNH for their help on this project thus far.

We are especially grateful for the funding support from the NERRS Science Collaborative

Collaborative Science

The purpose of collaborative science in the context of this project is to bring together scientists, natural resource managers, policy-makers, local officials, and other stakeholders at all stages of scientific inquiry: from identifying the problem to ensuring that good science leads to good decision making.

Project Goal for Integration

Our goal is to engage stakeholders in dialogue about the research questions, the results-findings as they roll out, and how new information generated about NP Nitrogen hot spots and sources can inform and enhance management and decision-making.

The Stakeholders

Policy Makers

- NH-DES
- PREP
- GBNERR

Municipal Watershed Management Network

- Southeast Watershed Alliance
- Municipal Land Use Boards/Committees

Watershed Associations

- Lamprey, Cocheco, Oyster River, Hodgson Brook...

The Engagement Process

Phase 1: Engage stakeholders in developing the research questions and approach.

Phase 2: Share prelim. findings and incorporate stakeholder input into field implementation.

Phase 3: Share results and engage stakeholders in dialogue about what results mean for them.

Phase 4: Help stakeholders incorporate good science into plans/policies/outreach.

Next Steps

- Lunchtime discussion
- Focus Groups
- Availability to Present to Groups
- Website

How can we best use the website and other means to keep you engaged?

Website in Progress.....

<http://www.wrrc.unh.edu/greatbayNhotspots/index.html>