Seasonal patterns of ∂^{15}N and ∂^{18}O of NO_3^- in the Murderkill River Watershed and Estuary, DE

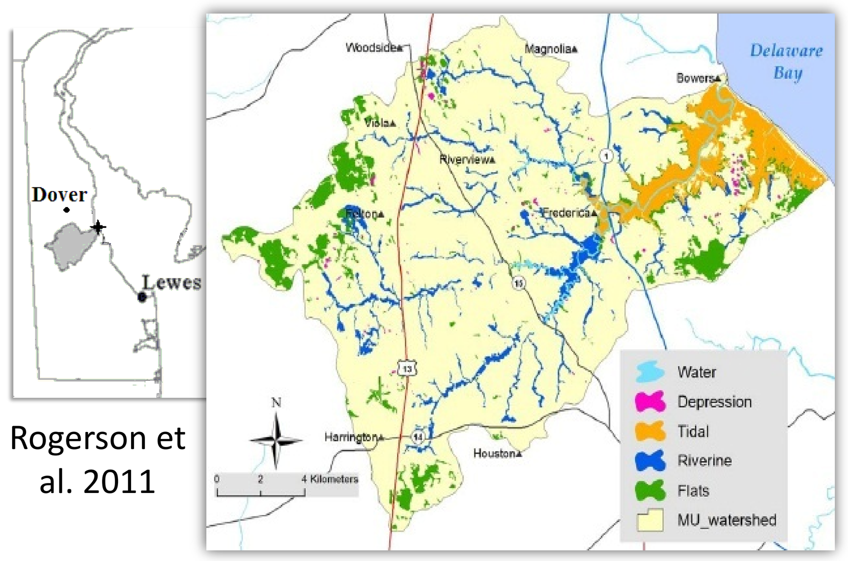
Sarah J. Fischer[a], William Gagne-Maynard[b,a], William J. Ullman[a], Joanna K. York[a]

[a] School of Marine Science and Policy, University of Delaware, Lewes DE 19958, [b]Carleton College, Northfield, MN 55057

Introduction

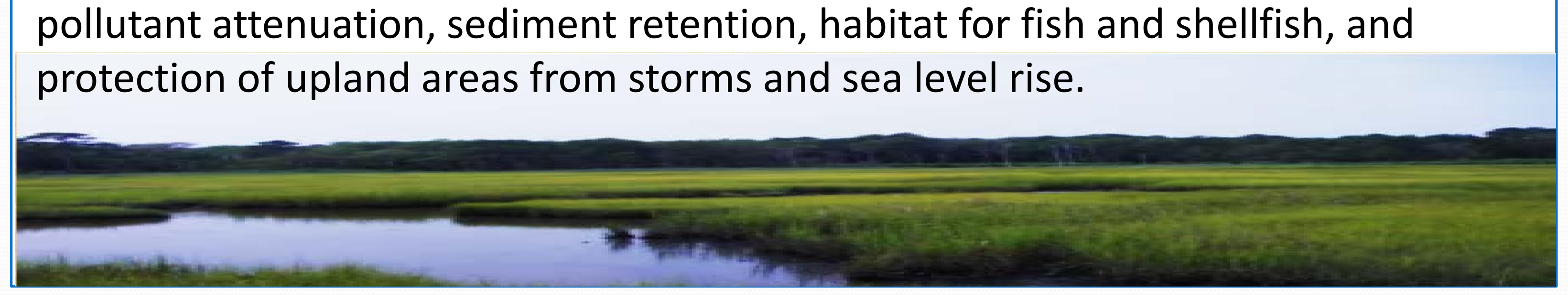
The Murderkill Watershed and its marsh-dominated estuary

Three major tributaries in the Murderkill Watershed – **Browns Branch**, **Black Swamp Creek**, and **Spring Creek** discharge to the **Murderkill Estuary** through a series of ponds. The estuary is approximately 16 km long and discharges to Delaware Bay at Bowers, Delaware.



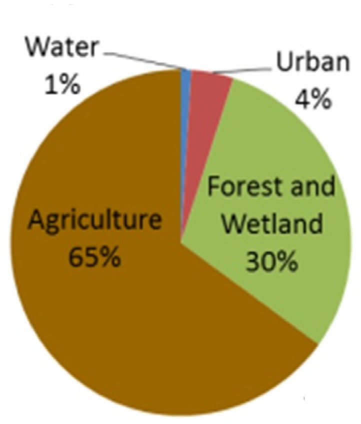
Rogerson et al. 2011

The Murderkill Estuary is surrounded by tidal marshes (Rogerson et al 2011). Wetlands and marshes provide important **ecosystem services**, including pollutant attenuation, sediment retention, habitat for fish and shellfish, and protection of upland areas from storms and sea level rise.

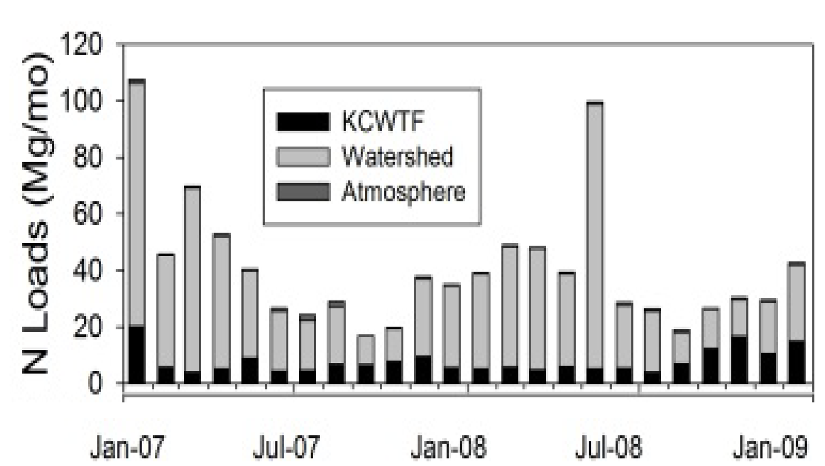


Sources of Anthropogenic Nitrate (NO_3^-)

Watershed Land Cover



N Loads in the Murderkill Estuary



NOAA 2011, Ullman et al 2011

Surface waters in the Murderkill watershed currently exceed state and federal guidelines for NO_3^- concentration. This is attributed to agriculture and wastewater discharge (DNREC 2005, Ullman et al 2011). Agricultural discharges are focused to the tributaries but may also contribute to the tidal marshes and directly to the watershed through dispersed groundwater seepage. The Kent County Wastewater Treatment Facility (KCWTF) discharges directly to the saline reaches of the estuary. Combined with concentration-based analyses, the ∂^{15}N and ∂^{18}O of NO_3^- can indicate sources and the extent of NO_3^- processing within the estuary (Kendall 1998).

Objectives

1. Identify the characteristic isotopic signatures of NO_3^- sources to the estuary.
2. Assess nutrient concentrations and alteration of ∂^{15}N to ∂^{18}O ratio in NO_3^- throughout the watershed: from freshwater to estuarine regions.
3. Determine the extent of natural N addition or removal processes (e.g., nitrification, dentrification, assimilation) in different zones of the watershed.

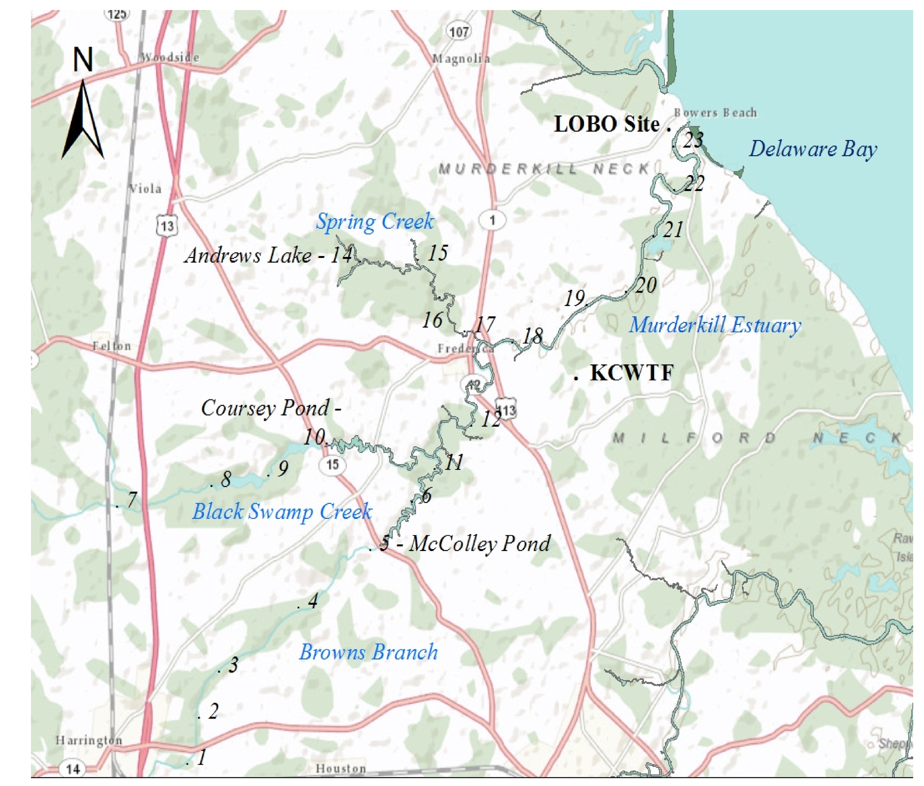
Methods

Water Sampling of tributaries, estuary, and KCWTF Effluent

Field surveys were conducted on:

- June 6th, 2012
- July 25th, 2012
- November 30th, 2012

Samples are collected for and analyzed for chlorophyll a, NO_3^- + NO_2^-, Si, NH_4^+, PO_4^{3-}, total dissolved nitrogen (TDN), and total dissolved phosphorus (TDP) PP. Dissolved oxygen (DO), conductivity and temperature are determined using a YSI probe.



Map of Sampling Sites

Isotopic Analysis: Dual Isotope ∂^{15}N-NO_3^- and ∂^{18}O-NO_3^-

Cultures of the denitrifying bacterium *Pseudomonas aureofaciens* were used for simultaneous determination of natural abundance levels of ∂^{15}N and ∂^{18}O in NO_3^- in surface water samples (Sigman et al 2001 and Casciotti et al 2002).

P. aureofaciens lacks the N_2O-reductase enzyme that would lead to complete reduction to N_2 (g), and instead produces N_2O (g) that retains the isotopic composition of both N and O in the original NO_3^- (aq).

9-day batch incubation of *P. aureofaciens* to grow culture and to remove background NO_3^-

Gas-tight vials of culture are purged with N_2 to remove O_2 and N_2O

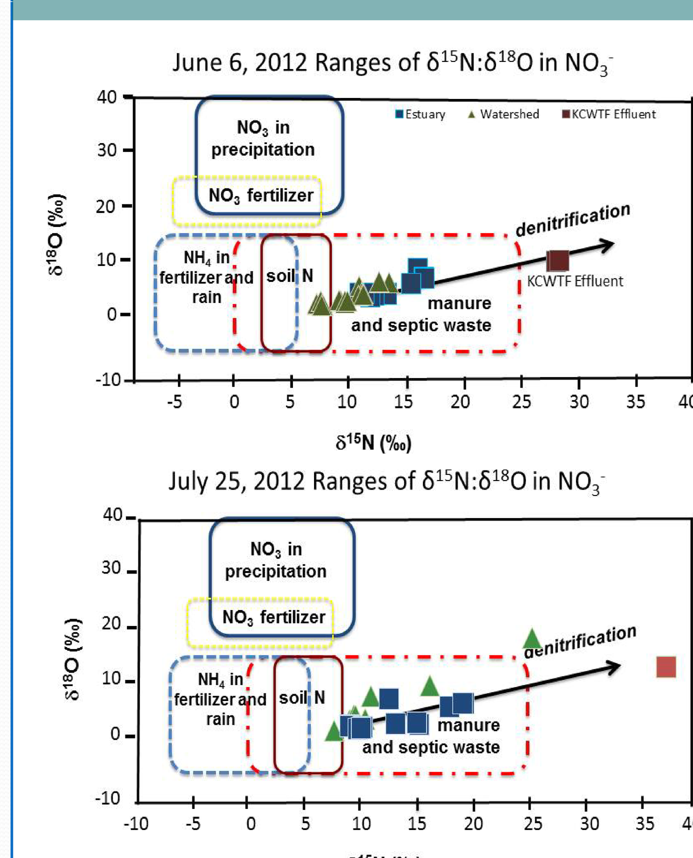
Standards and water samples are injected into *P. aureofaciens* vials

Denitrification of NO_3^- in samples to N_2O, isotopic signature retained: $2NO_3^-$ (aq) → $2NO_2^-$ (aq) → 2NO (aq) → N_2O (g)

N_2O extracted and ∂^{15}N and ∂^{18}O determined using a ThermoFinnigan GasBench + PreCon trace gas concentration system interfaced to a ThermoScientific Delta V Plus isotope-ratio mass spectrometer at the U.C. Davis Stable Isotope Facility.

NO_3^- and NO_2^-, Si, NH_4^+, PO_4^{3-}, total dissolved nitrogen (TDN), and total dissolved phosphorous (TDP) are determined by colorimetric analyses on a SEAL AutoAnalyzer 3.

Results: Isotopic signatures of sources

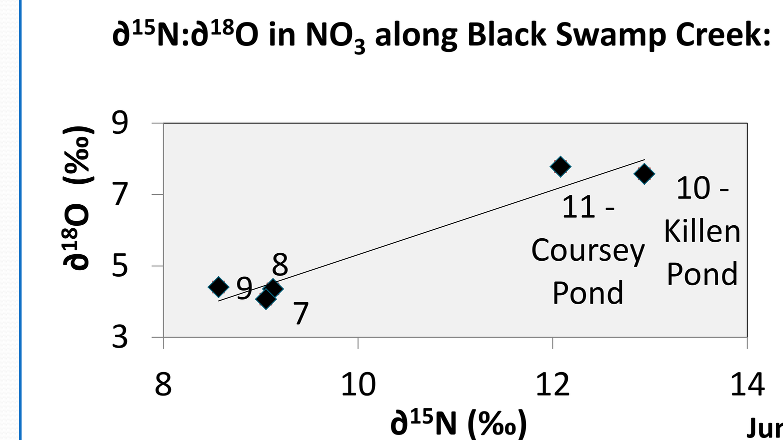


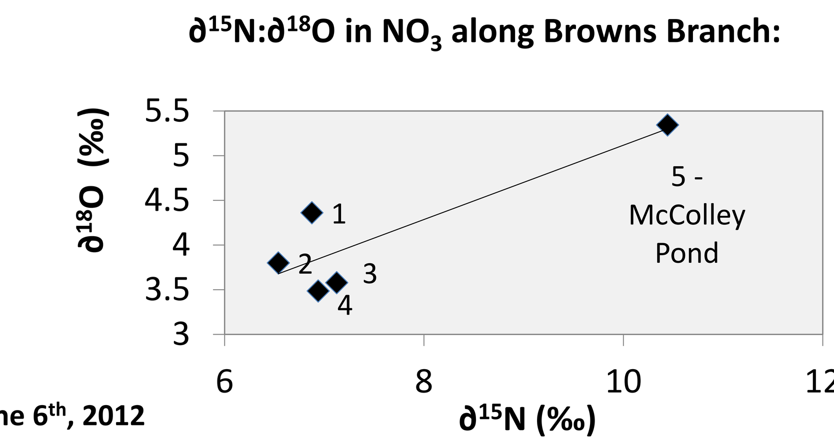
Isotope source ranges: Kendall (1998)

- KCWTF effluent had a significantly enriched isotopic signature consistent with the facility's biological nitrate and nitrogen removal systems that couple nitrification and denitrification.
- In June, isotopic ratios increased along the watershed to estuary transition, consistent with the vector established for denitrification.
- In July, the isotopic ratios of NO_3^- did not increase according to the denitrification vector from the freshwater reaches to the estuary. This could indicate contrasting degrees of N cycling in the watershed and estuary during July.

Results: signs of natural nitrogen attenuation

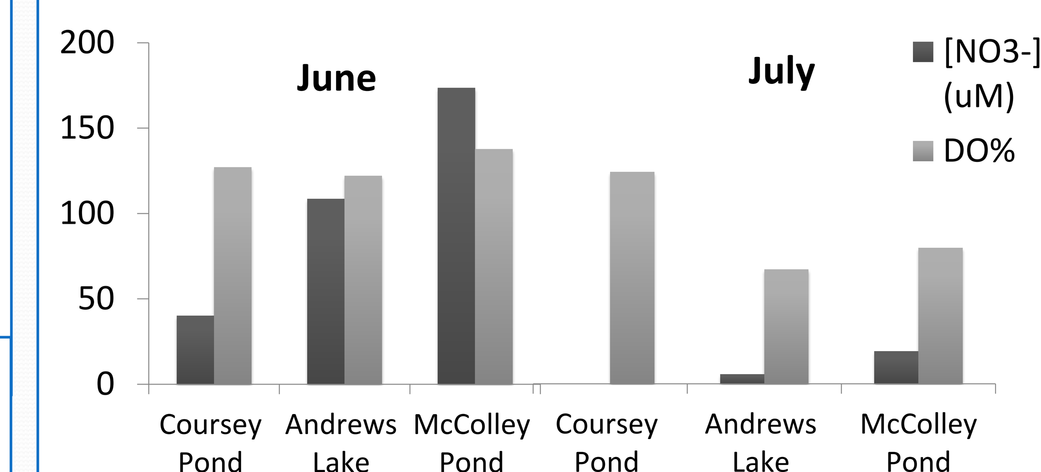
Watershed





June 6th, 2012

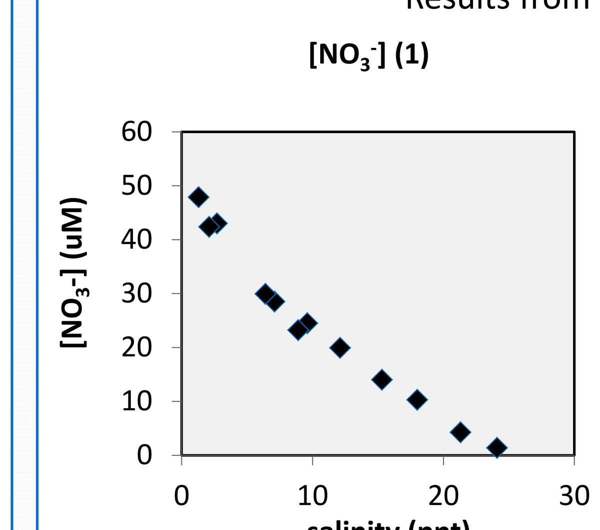
- Increases in ∂^{15}N and ∂^{18}O in NO_3^- from tributaries to ponds suggest significant nitrogen processing occurred.

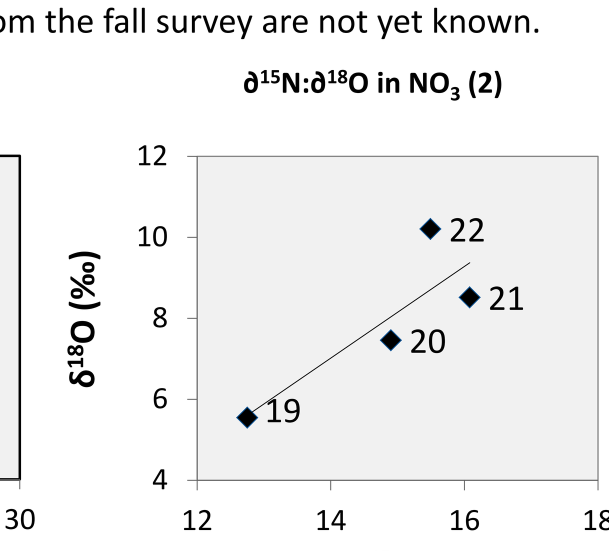


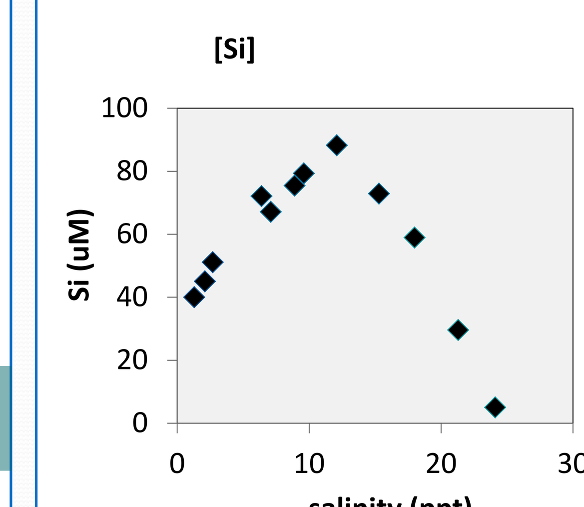
- Decreases in [NO_3^-] and DO from June to the end of July suggest significant N attenuation in ponds.
- Hydrological data suggests June and July differences could be due to low freshwater flow and long pond residence times in July.

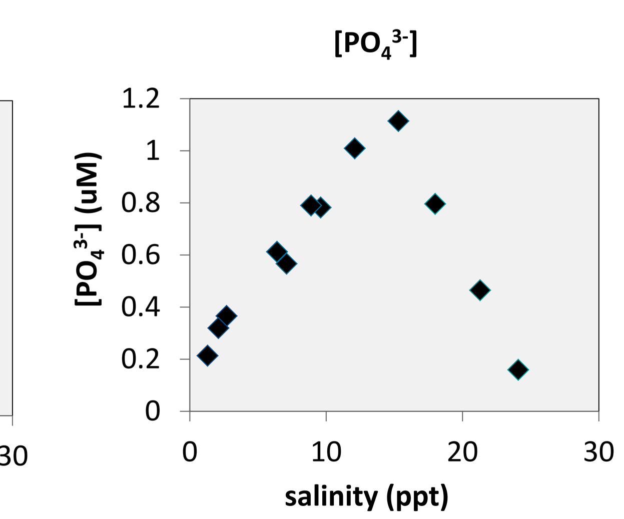
Estuary

June 6th, 2012 results shown. Similar patterns were seen in July. Results from the fall survey are not yet known.









- In the estuary, conservative mixing appears to control decreasing [NO_3^-], particularly at higher salinities where mixing of estuarine waters and Delaware Bay waters is rapid (1)
- The isotopic enrichment of NO_3^- might be controlled by physical mixing with higher signature waters or uptake/denitrification (2)
- Peaks in [PO_4^{3-}] and [Si] are consistent with KCWTF effluent discharge mid-estuary. [Si] might serve as a conservative tracer of the plume in future work.

Conclusions and Future Work

During summer 2012, the distributions of NO_3^- δ^{15}N and δ^{18}O are consistent with denitrification in the watershed ponds and KCWTF effluent. KCWTF effluent appears to alter PO_4^{3-} and Si, but not NO_3^- input to the estuary. Additional work will be done to deconvolve the impact of physical mixing of KCWTF effluent and Delaware Bay waters from indications of biogeochemical processes occurring in the estuary. Data on NH_4^+, DON, Chl-a and δ^{15}N:δ^{18}O of NO_3^- from other seasons could establish this distinction.

Acknowledgements: John Biddle (Marine Operations), and Peggy Conlon (U.D.). Financial support from: The Kent County Levy Court and Department of Public Works (Hans Medlarz, Director) Delaware Department of Natural Resources and Environmental Control (DNREC), Delaware Sea Grant College Program, and the Du Pont Clear Into the Future Fellowship.