Stable Isotope Compositions of Macroalgae, Sediment and Nitrate in Florida Springs

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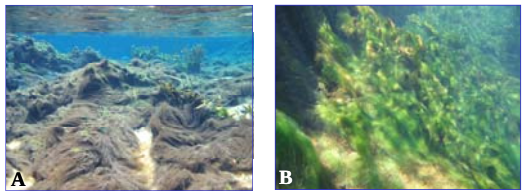
Introduction

The aquifers supplying water to Florida's more than 700 karst springs are susceptible to human activities and land use change. Nitrate levels have increased in most springs over the last 30 years and are often associated with nuisance macroalgal mats while phosphate levels have remained relatively stable. However, no quantitative relationship exists between nitrate concentrations and algal biomass with which to establish protective nutrient criteria. The stable isotope composition of algae and sediment ($\delta^{13}C$ and $\delta^{15}N$) as well as nitrate in spring water ($\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3) can provide valuable information about the sources of nitrogen and carbon to these algal mats.



Lyngbya wollei (A) and *Vaucheria* sp. (B) are the two most common mat-forming macroalgae found in springs throughout Florida. *L. wollei* can form mats up to 2.5 m thick. *Vaucheria* sp. mats can be 1 m thick.

Objectives

The main objectives of this study were to:

1. Assess nitrate sources to spring water using the dual-isotopic analysis of nitrate ($\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3) at a regional scale and along four spring river runs
2. Determine the $\delta^{15}N$ and $\delta^{13}C$ composition of macroalgae and spring sediments at a regional scale and along four spring river runs

Hypotheses

1. Nitrogen sources to spring water, algal mats and sediments will vary both at the regional scale as well as along spring river runs.
2. The $\delta^{13}C$ of algae and sediments will be relatively uniform at the regional scale and along spring runs, reflecting similar sources of dissolved inorganic carbon (CO_2 and HCO_3) in spring water throughout Florida.

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References: (1) Chang C. C. Y., J. Langston, M. Riggs, D. H. Campbell, S. R, Silva and C. Kendall. 1999. A method for nitrate collection for delta N-15 and delta O-18 analysis from waters with low nitrate concentrations. Canadian Journal of Fisheries and Aquatic Sciences 56: 1856-1864. (2) Sigman, D.M., K.L. Casciotti, M. Andreani, C. Barford, M. Galanter and J.K. Bohlke. 2001. A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater. Analytical Chemistry 73: 4145-4153.

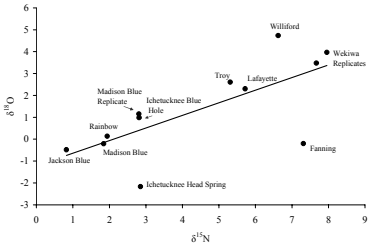
Methods

1. Dual-isotopic analysis of nitrate ($\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3) in spring water:
   - Water samples for isotopic analysis of nitrate were taken at 18 headwater spring boils throughout Florida and along four spring river runs, Weeki Wachee, Rainbow, Silver River and Wakulla, from the boil area to approximately 8 km downstream in Fall 2005 and Spring 2006.
   - A subset of samples were analyzed using the methods described by Chang et al. (1999) and the remainder will be analyzed using the denitrifying bacterial method developed by Sigman et al. (2001).

2. Stable isotope analysis of algal and sediment ($\delta^{13}C$ and $\delta^{15}N$):
   - Algal tissue samples (separated by species) and sediment samples were taken at 63 spring sites (boil areas as well as sites further downstream) throughout Florida in Fall 2005 and Spring 2006, including the sites mentioned above.
   - Carbonates were removed from sediment samples prior to analysis.
   - All samples were analyzed on a Delta-Plus XP isotope ratio mass spectrometer at the University of Florida.

At each site the following measurements were also taken:
- Water nutrient chemistry: TKN, NO_x, NH_4, TP, SRP
- Water physical-chemical parameters: temperature, pH, conductivity, dissolved oxygen
- Macroagal composition and % cover
- Mat and sediment % C, N and P

Results

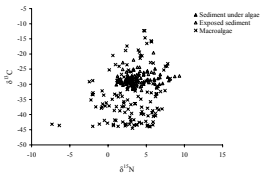


Stable isotopes of nitrate from 10 headwater springs. $R^2 = 0.5$. Slope of the line: 0.57.

- The springs with $\delta^{15}N$ values above 5‰ and $\delta^{18}O$ below 5‰ indicate soil nitrogen or human/animal wastes as likely sources.

- The springs with $\delta^{15}N$ values below 3‰ and $\delta^{18}O$ values below 1.5‰ indicate inorganic N-sources (NH_4 from fertilizer or rain and/or soil nitrogen).

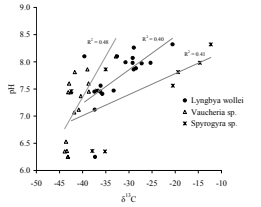
- Another possibility to consider is that denitrification could be occurring in matrix flows or at microsites within conduit flows. Progressive denitrification of a common source results in a slope of 0.5 and here the slope is 0.57. If the line is extrapolated to the x-axis ($\delta^{15}N$ intercept of -3‰), the common source indicated would be inorganic fertilizer.



Stable isotope composition of macroalgae and sediment from 63 spring sites (above).

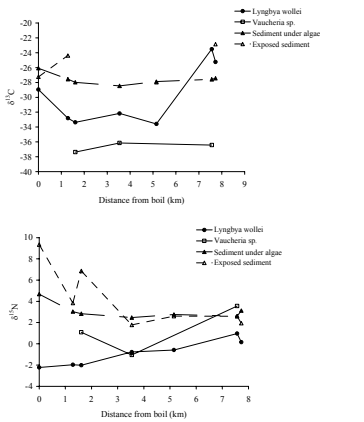
-A wide range of $\delta^{15}N$ values was found for both macroalgae and sediments (values <5‰ : inorganic N or soil N; values <5‰ : animal/human waste and/or soil N;

- The $\delta^{13}C$ range was narrow for sediments; recalcitrant terrestrial material may be the likely source (the $\delta^{13}C$ value of terrestrial C3 plants is approximately -28‰).



The relationship between the $\delta^{13}C$ of the three dominant algal species and spring water pH at 34 spring sites.

- Relatively distinct species specific $\delta^{13}C$ values found for algae and pH likely reflect the availability of CO_2 (more negative isotope values) vs. HCO_3 as a C source. At a pH of 8+, HCO_3 is the dominant form of DIC.



$\delta^{13}C$ values (top) and $\delta^{15}N$ values (bottom) measured in macroalgae and sediment along the Rainbow Springs river run.

- No clear overall trend was found for either $\delta^{13}C$ or $\delta^{15}N$ values of algae or sediment along the river run.

- Multiple inflows of water (both surface and subsurface flows) are likely complicating interpretation along the river run.