Using Isotopes and Other Chemical Indicators to Gain Insights into Spring Water Age and Timescales of Nitrate Contamination in Florida Karst Systems

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Outline of Presentation

Brief description of environmental tracers for estimating the “springwater age” and sources of nitrate contamination.

Results from previous studies of Suwannee River springs and Silver Springs

Convey a better understanding of groundwater residence time, springwater age, and most importantly the age distribution in springwaters
Springs in Florida

Provide unique opportunities to study hydrologic and geochemical processes in the Floridan aquifer system.

The challenge lies in deciphering the complex chemical signals that result from the temporal, spatial, and vertical integration of water from the aquifer system.
Elevated Nitrate-N in spring waters has resulted in widespread water-quality impairment

Photos: John Moran

Ichetucknee Springs State Park, 1995
Ichetucknee Springs State Park, 2012

THEN & NOW

Photos: John Moran

Troy Spring (Discover, 2015)
Studies of Sources and Timescales of Nitrate Contamination of Springs

In 1997, USGS, in cooperation with other State agencies, collected more than 70 samples from 44 springs during various flow conditions for environmental isotopes and other chemical indicators.

More recently, UF researchers have conducted studies in the Ichetucknee Springs basin to look at decadal-scale changes in ages of spring water, and information about denitrification.
Chemical Tracers Used in Studies:

Geochemical Process Identification:
\[ \delta^{18}O, \delta^2H, \delta^{13}C, \text{major ions, nutrients, dissolved gases (N}_2, \text{Ar, Ne, He), DOC} \]

Sources of Nitrate Contamination:
\[ ^{15}N/^{14}N (\delta^{15}N-\text{NO}_3); \quad ^{18}O/^{16}O (\delta^{18}O-\text{NO}_3) \]

Spring water age distribution:
\[ \text{CFC-11, CFC-12, CFC-113, } ^3\text{H}/^3\text{He, SF}_6 \]
ATMOSPHERIC TRACERS USED FOR AGE DATING SPRING WATERS:

Chlorofluorocarbons (Freons):
CFC-11 \( (\text{CCl}_3\text{F}) \)
CFC-12 \( (\text{CCl}_2\text{F}_2) \)
CFC-113 \( (\text{C}_2\text{Cl}_3\text{F}_3) \)

Sulfur Hexafluoride \( (\text{SF}_6) \)

Tritium and its decay product, helium-3:
\( ^3\text{H}, \frac{^3\text{H}}{^3\text{He}}_{\text{trit}} \)
Tritium in Rainfall

TRITIUM, TU

3H IN RAINFALL, OCALA, FL

3H IN RAINFALL, DECAY CORRECTED TO 2000


3H+3He

3H
\( ^3H/\overline{3}He \) Dating Method
Schlosser et al. (1988, 1989)

- \( T(\text{age}) = \left( \frac{t_{1/2}}{\ln 2} \right) \ln [1 + \frac{\overline{3}He_{\text{trit}}}{\overline{3}H}] \)

- \( \overline{3}He_{\text{tot}} = \overline{3}He_{\text{trit}} + \overline{3}He_{\text{eq}} + \overline{3}He_{\text{exc}} + \overline{3}He_{\text{nucl}} \)

- \( Ne \) and \( ^4\text{He} \) used to calculate \( \overline{3}He_{\text{eq}}, \overline{3}He_{\text{exc}}, \overline{3}He_{\text{nucl}} \)

- Crustal terrigenic \( ^3\text{He}/^4\text{He} \) ratio: \( 2 \times 10^{-8} \)
Determining Ground-Water Recharge Dates

Ideal situation
AGES OF SPRING WATERS—

Tracer concentrations measured in springs are dependent on how water moves through system.

Various models are used to conceptualize ground-water flow patterns
Evaluating Groundwater Age Distributions using Lumped Parameter Models:

1. Piston Flow
2. Exponential Mixing
3. Binary Mixing

TracerLPM (Jurgens et al., 2012) Interactive Excel workbook program using lumped parameter models, which are mathematical models of transport based on simplified aquifer geometry and flow configurations.

https://ca.water.usgs.gov/user_projects/TracerLPM/
Piston Flow Model

\[ C_t = C_0 e^{-\lambda t} \]
Exponential Mixing Model
Binary-Mixing Model

\[ f_{yw} = \frac{C_m - C_{ow}}{C_{yw} - C_{ow}} \]

- **Shallow Flow System**
- **Deep Flow System**
- **Young Water**
- **Old Water**
- **Surficial Sands and Clays**
- **Sinkhole**
- **Spring/River System**
- **Upper Floridan Aquifer**
SPRINGS SAMPLED IN THE SUWANNEE RIVER BASIN
Discrepancy between ages and limitations associated with using CFCs demonstrates the need for comparing results from multiple age dating methods.
$^{3}H / ^{3}He$ and CFC-113 in SPRING WATERS

Age Distribution in Suwannee Springs

- PFM
- BMM 1975-95
- BMM 1953-95
- SPRINGS-1999
- SPRINGS-2000

References:
Comparison of fraction of young water in first, second, and third magnitude springs with:

- Dissolved oxygen,
- Nitrate-N
DISSOLVED OXYGEN AND YOUNG FRACTION OF SPRING WATER

FRACTION OF YOUNG WATER (<=5 YRS)
NI TRATE AND YOUNG FRACTION OF SPRING WATER

Y = 40.7x - 10.9
R² = 0.51

NITRATE-N, MG/L

FIRST MAGNITUDE
SECOND MAGNITUDE
THIRD MAGNITUDE

FRACTION OF YOUNG WATER (<=5 YRS)
Silver Springs Study

Knowles et al., 2010
Multiple age-tracer data are consistent with a binary mixtures that are dominated by recently recharged water (6-7 years; 87-97% young water).

Inverse relation btw mean apparent ages and NO₃-N, dissolved O₂, and Ca/Mg ratio.
Climate Control of Decadal-Scale Increases in Apparent Ages of Eogenetic Karst Spring Water, Ichetucknee Springs

Martin et al., 2016, Journal of Hydrology
Climate Control of Decadal-Scale Increases in Apparent Ages in Ichetucknee Springs

Higher NO3, DO, concentrations in young water (data from Katz (2004) and Martin et al (2016)).

Longer time-scale changes of apparent age (decades) may include variations in recharge from ENSO or AMO climate cycles, or from increased pumping.

Martin et al., 2016, Journal of Hydrology
Denitrification in UFA— (Heffernan et al 2012)

Importance of measuring $N_2$, Ar, Ne, $O_2$ along with $\delta^{15}N$ and $\delta^{18}O$

Denitrification removed >75% of N inputs in 8 of 61 springs, and >50% in 20 of 61 springs
**Denitrification in UFA–**  (Heffernan et al 2012)

Positive correlation btw \(\delta^{15}\text{N}_{\text{NO}_3}\) and \(\delta^{18}\text{O}_{\text{NO}_3}\) is consistent with denitrification rather than variation in source as driver of \(\delta^{15}\text{N}_{\text{NO}_3}\).

A, C, and E springs: contribution from organic N sources (0.33 to 0.5)

However, when correcting for denitrification, in high DO springs (B, D, F): inorganic fertilizers and soil N are the predominant N sources
CONCLUSIONS

- Naturally occurring isotopic and other chemical tracers are effective tools for assessing sources and chronology of nitrate contamination and for developing conceptual and quantitative models of groundwater flow systems.

- Information on excess \( N_2 \) and other dissolved gases (Ar, Ne, He, \( O_2 \)) should be used to assess denitrification in the aquifer and provide detailed information on \( N \) sources.
Other Potential Chemical Indicators

- Other contaminants, such as pharmaceutical compounds, sucralose, and pesticides and their degradates can be used to assess groundwater residence times and anthropogenic impacts on the aquatic ecosystem.
Selected References:


SOURCES OF NITRATE IN SPRING WATERS
\[ \delta^{15}N-NO_3 \text{ vs. } NO_3-N \]

NITRATE ASSOCIATED WITH MANURE SPREADING OR WASTE DISPOSAL

NITRATE ASSOCIATED WITH ARTIFICIAL FERTILIZER USE

N in atmospheric deposition

NITRATE-N CONCENTRATION, MILLIGRAMS PER LITER

SANTA FE RIVER SPRINGS
SUWANNEE RIVER SPRINGS IN LAFAYETTE COUNTY
LOWER SUWANNEE RIVER SPRINGS
SUWANNEE RIVER SPRINGS IN SUWANNEE COUNTY
Springs in Suwannee River Basin—

1. Groundwater flow system to springs is dominated by mixtures of water recharged during past 10-30 years.

2. Young fraction of spring water (sampled during baseflow conditions) is related to spring magnitude, nitrate, and dissolved oxygen concentrations.
Springs Sampled Multiple Times In the Suwannee River Basin
RAINFALL DEPARTURES FROM NORMAL

RAINFALL DEPARTURE FROM NORMAL, IN CENTIMETERS

Mayo, FL

DATES OF SAMPLING

1997 1998 1999 2000

-20 -10 0 10 20 30 40

USGS
USGS'S DEDICATED WORKERS
Troy Spring—
Age and Discharge

[Graph showing changes in age and discharge over time]

Sampling Date

AGE, YEARS

DISCHARGE, CFS

CFC-113 AGE

DISCHARGE
Troy Spring—
Age and Nitrate-N
Springs in Suwannee River Basin—

3. Denitrification unlikely due to low DOC, oxygenated waters (DO> 3 mg/L, little or no excess N₂, little or no increase in δ¹⁵N-NO₃.

4. Lower nitrate concentrations in older waters may be related to lower amounts and type of N applied in 1950’s and 1960’s.
Scenarios for Low NO$_3$-N in older waters

- **Denitrification** - microbially mediated, low O$_2$; carbon source

- **Historic changes in agricultural practices** – (N source type)
$\delta^{15}\text{N-NO}_3$ and DISSOLVED $O_2$ in SPRING WATERS

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