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


THE TOURIST'S FAMOUS HEALTH RESORT.

"'Way down on the Suwanee Ribber."

Suwanee Springs,

SUWANEE, FLORIDA.

SITUATED ON THE MAIN LINE OF THE SAVANNAH, FLORIDA & WESTERN RAILWAY. 174 MILES FROM SAVANNAH, GA. 80 MILES FROM JACKSONVILLE, FLA.

Assured Cure for Kidney Troubles.

DAILY DEMONSTRATED TO BE

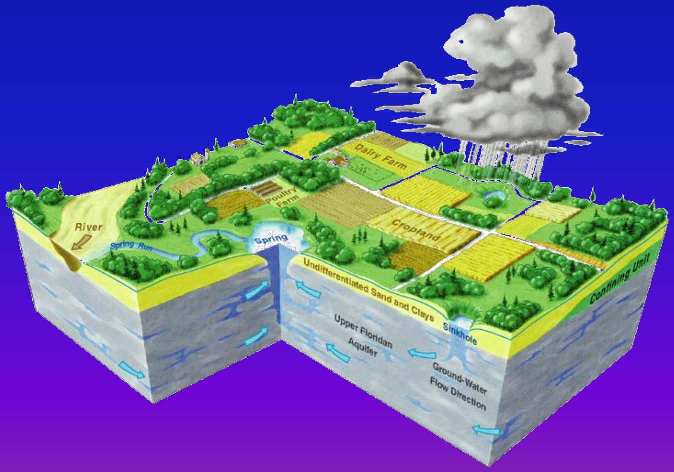
AN INFALLIBLE MINERAL WATER

In the CURE of Rheumatism, Gout, Malaria, Indigestion, Nervous Dyspepsia, Constipation, Loss of Appetite, Nervous Prostration, Skin Diseases, Liver Diseases, Jaundice, Female Troubles, Eczema, and all Blood Affections.

Hotel Accommodations Unsurpassed

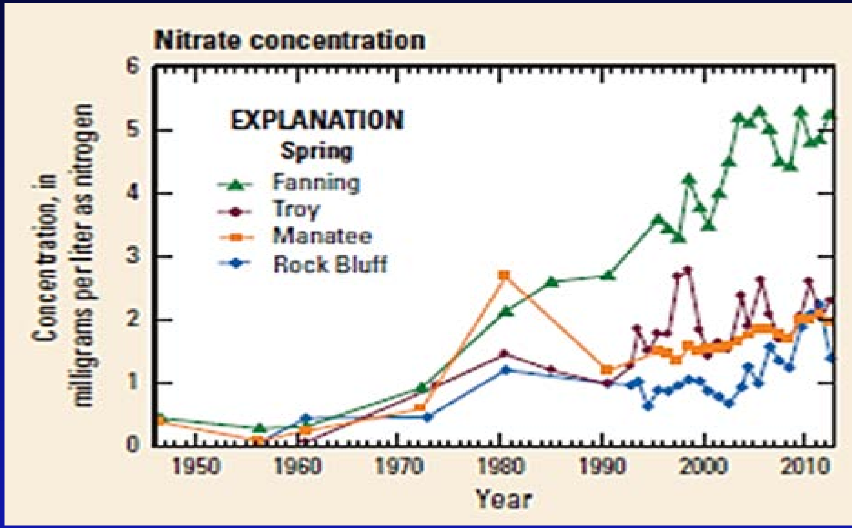
Provide unique opportunities to study hydrologic and geochemical processes in the Floridan aquifer system.

The challenge lies in deciphering the complex chemical signals that result from the temporal, spatial, and vertical integration of water from the aquifer system.



Conceptual Spring System

Elevated Nitrate-N in spring waters has resulted in widespread water-quality impairment

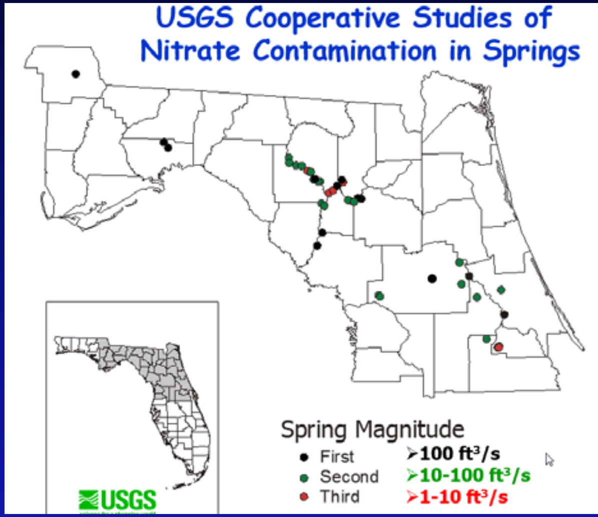


Photos: John Moran

Troy Spring (*Discover*, 2015)

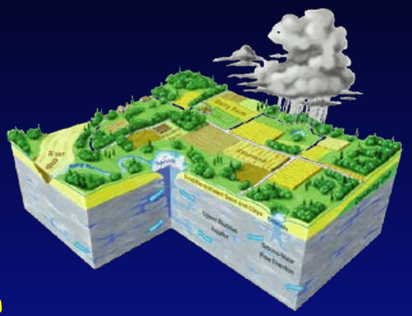
Studies of Sources and Timescales of Nitrate Contamination of Springs

- *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:

$\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$, major ions, nutrients, dissolved gases (N_2, Ar, Ne, He), DOC

Sources of Nitrate Contamination:

$^{15}N/^{14}N$ ($\delta^{15}N$-NO_3); $^{18}O/^{16}O$ ($\delta^{18}O$-NO_3)

Spring water age distribution:

CFC-11, CFC-12, CFC-113, $^{3}H/^{3}He$, SF_6

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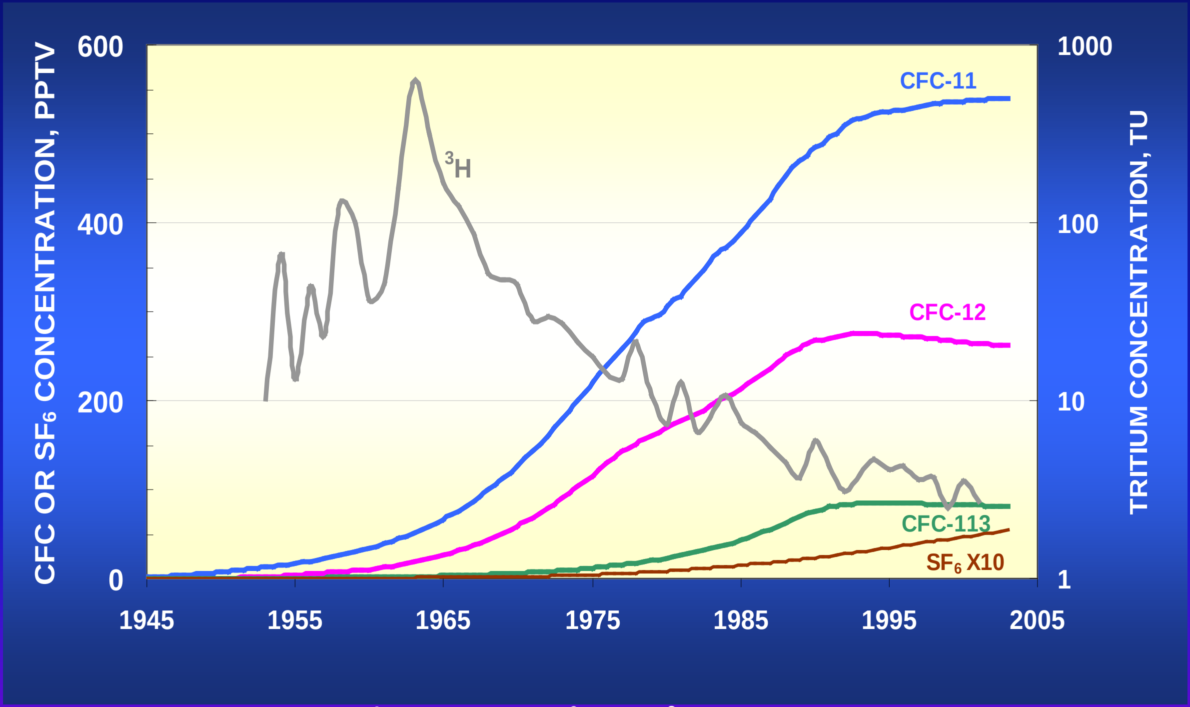
ATMOSPHERIC TRACERS USED FOR AGE DATING SPRING WATERS:

Chlorofluorocarbons (Freons):

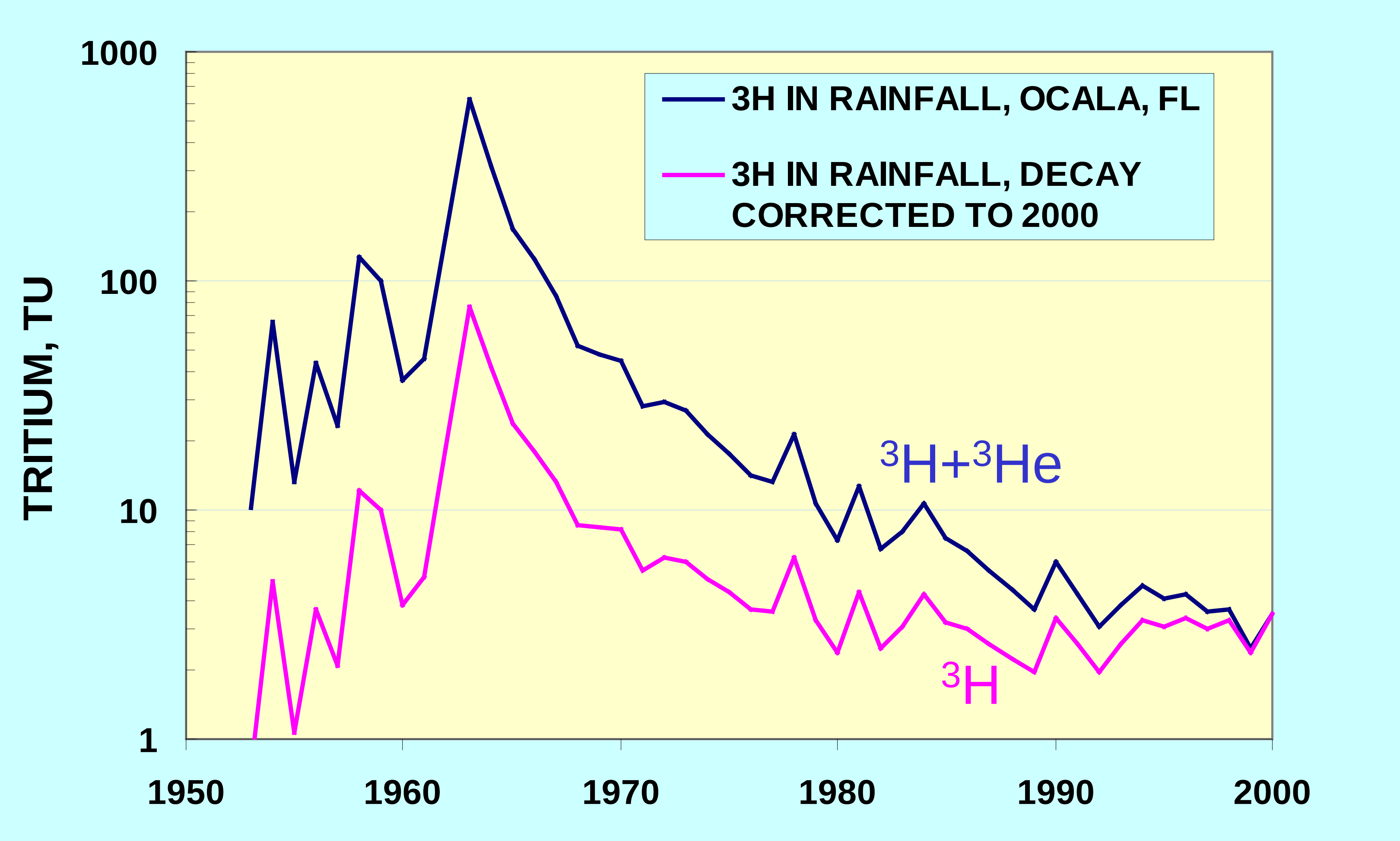
CFC-11 (CCl_3F)
CFC-12 (CCl_2F_2)
CFC-113 ($C_2Cl_3F_3$)



Sulfur Hexafluoride (SF_6)

Tritium and its decay product, helium-3:
^3H, $^3H/^3He_{trit}$

Tritium in Rainfall



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$^3H/^3He$ Dating Method

Schlosser et al. (1988, 1989)

- $T(\text{age}) = (t_{1/2}/\ln 2)\ \ln[1 + \mathbf{^3He_{trit}}/^3H]$
- $^3He_{tot} = \mathbf{^3He_{trit}} + {^3He_{eq}} + {^3He_{exc}} + {^3He_{nuc}}$
  - *Ne and ^4He used to calculate $^3He_{eq}$, $^3He_{exc}$, $^3He_{nuc}$*
  - *Crustal terrigenic $^3He/^4He$ ratio: 2×10^{-8}*

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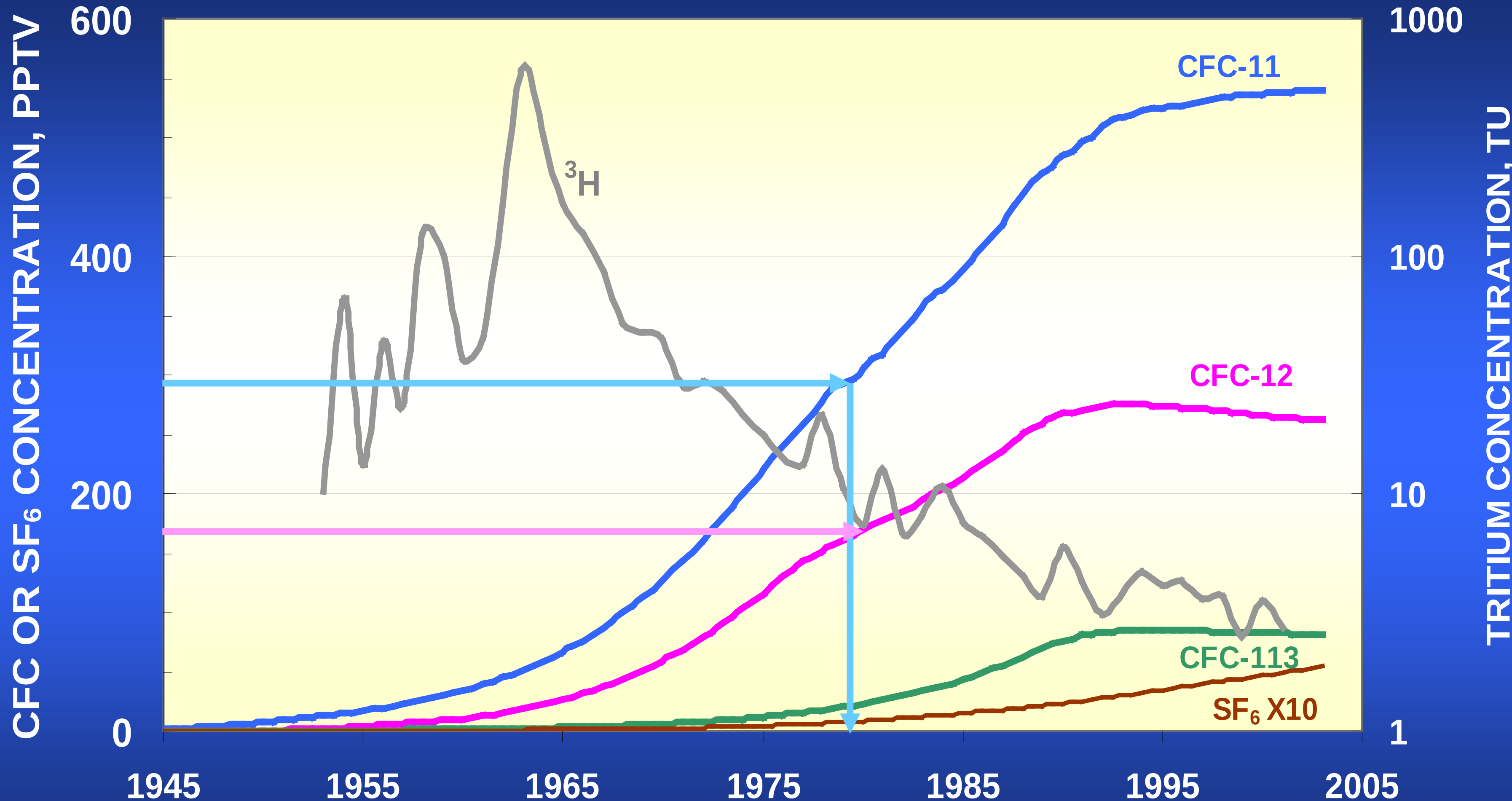
Determining Ground-Water Recharge Dates
Ideal situation



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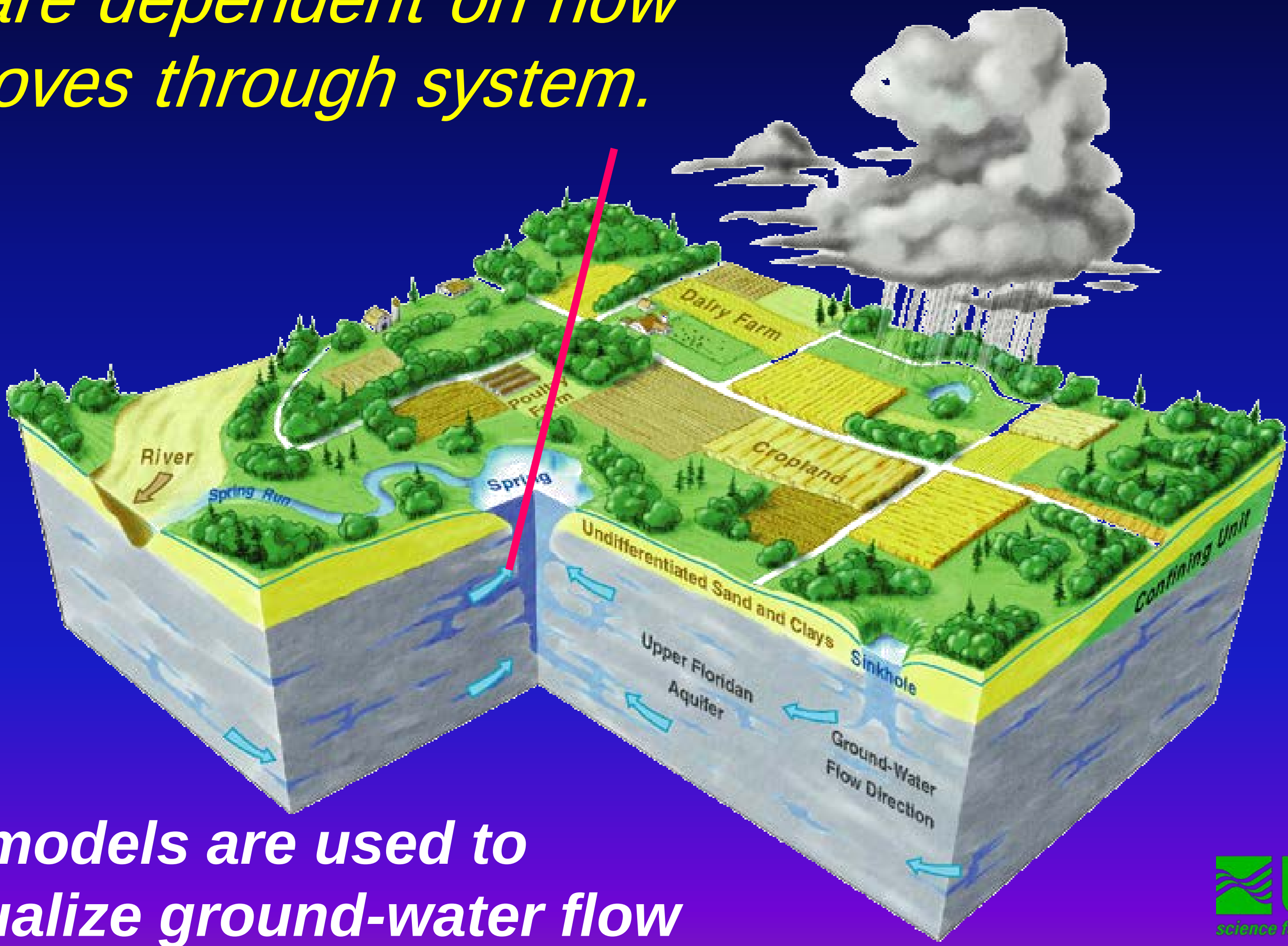
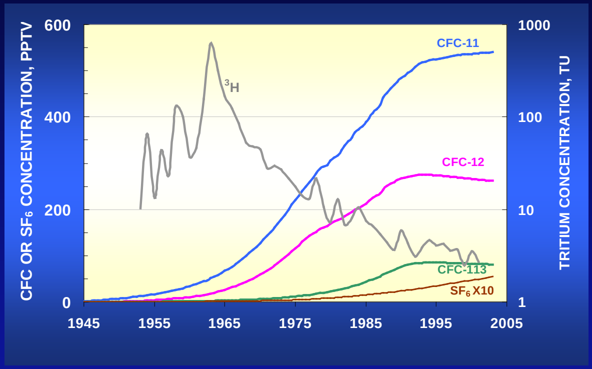
AGES OF SPRING WATERS—

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:



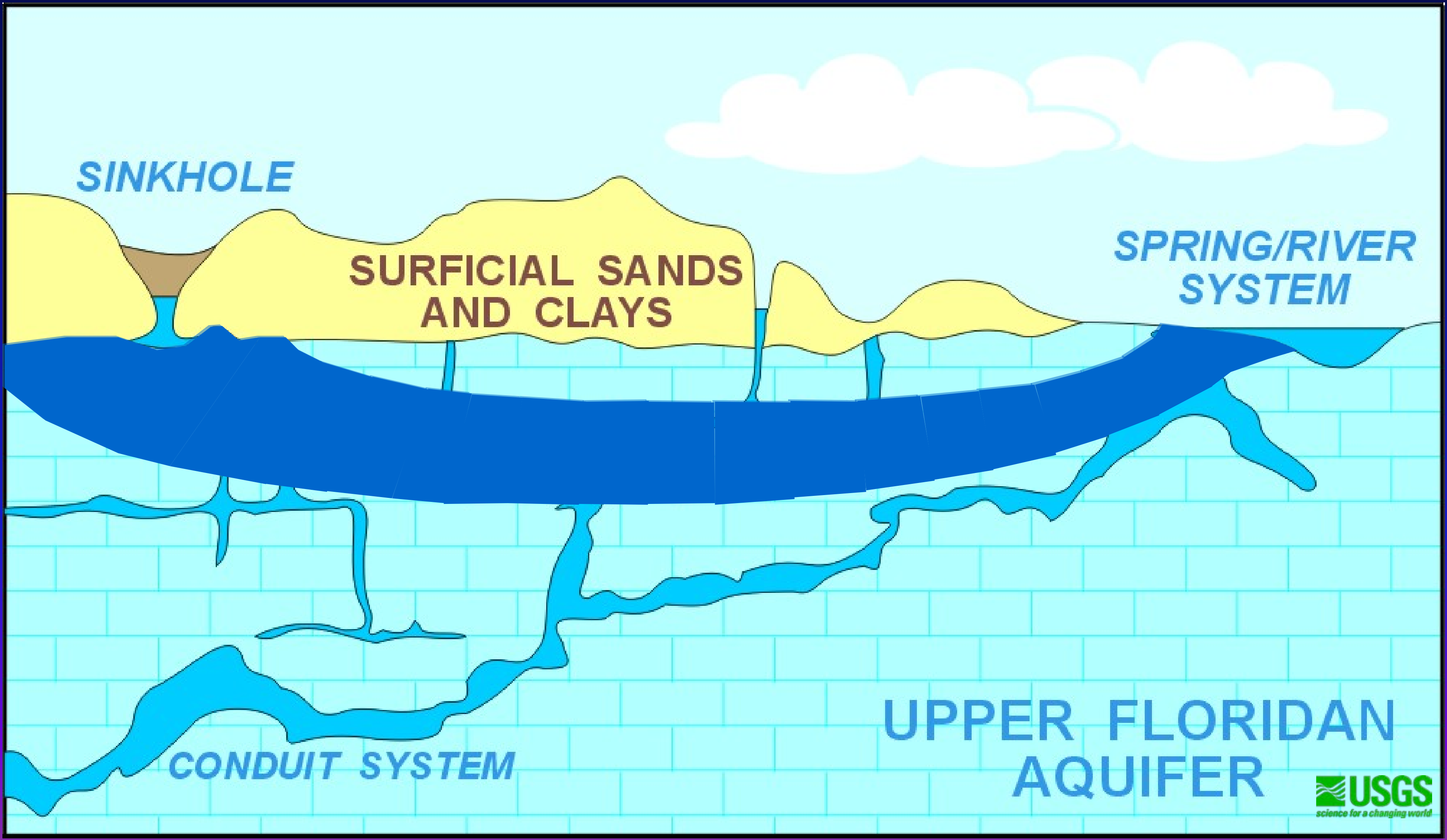
1. **Piston Flow**
2. **Exponential Mixing**
3. **Binary Mixing**

***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.**

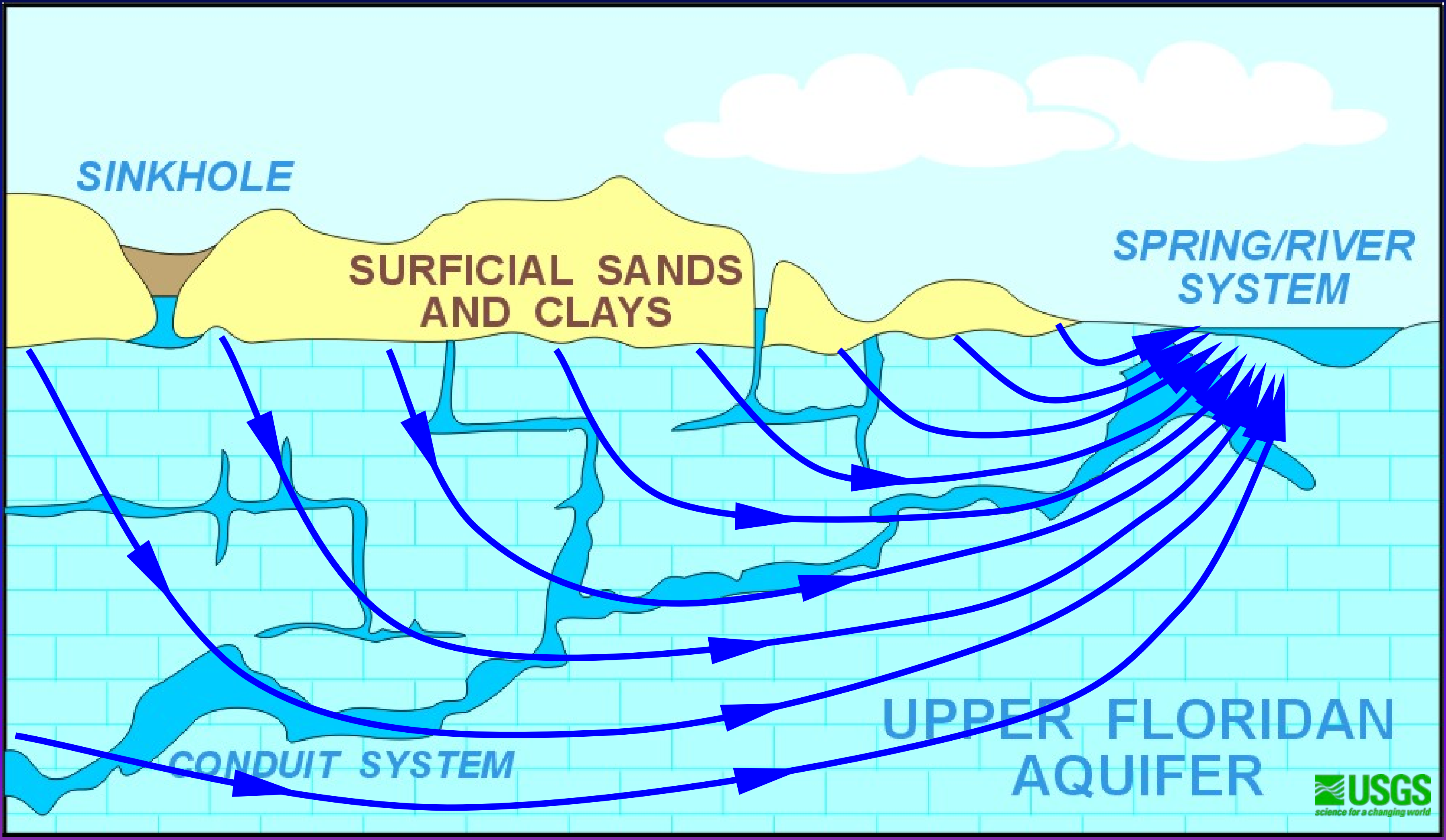
https://ca.water.usgs.gov/user_projects/TracerLPM/

Piston Flow Model

$$C_t = C_o e^{-\lambda t}$$

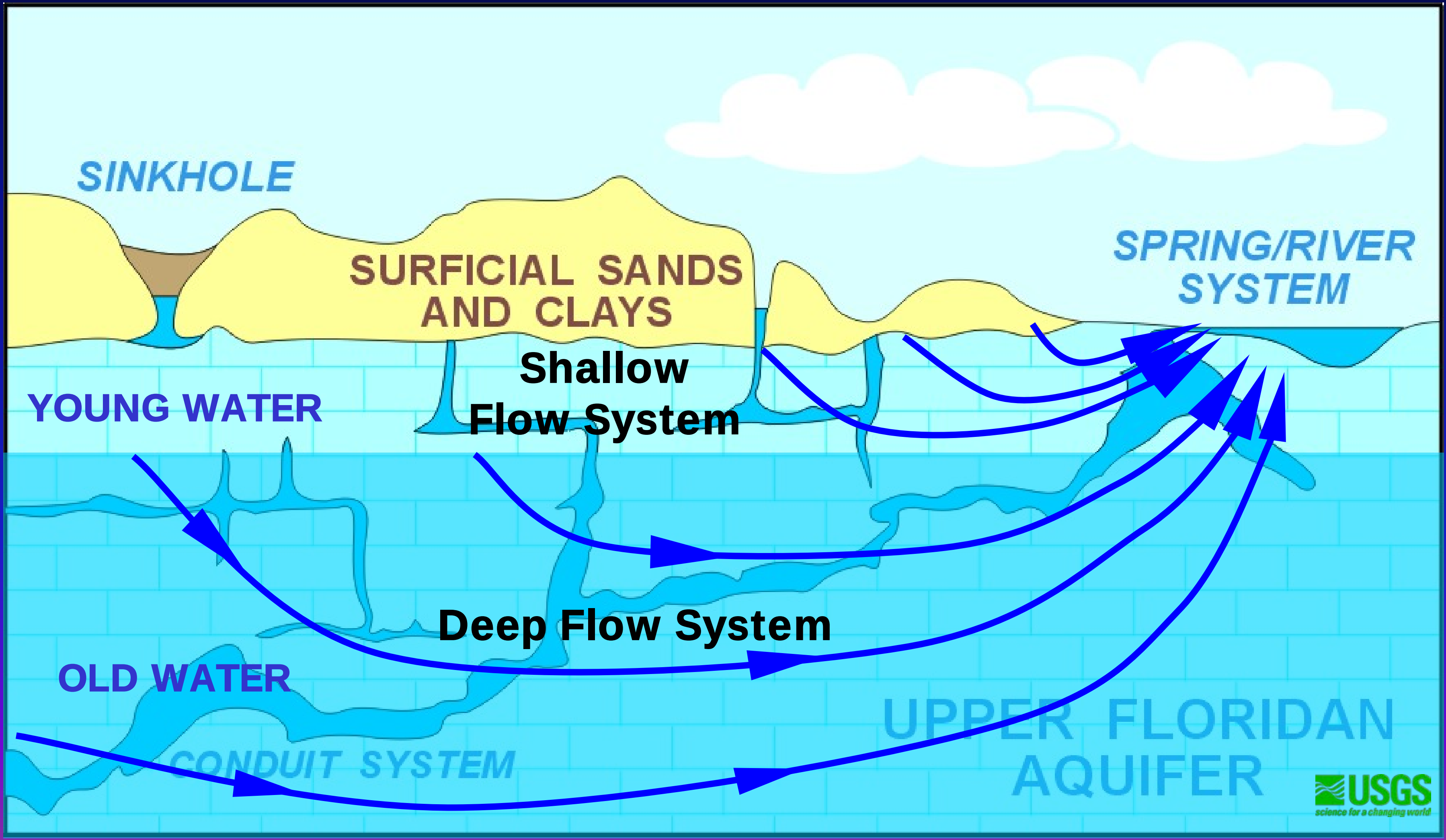


Exponential Mixing Model

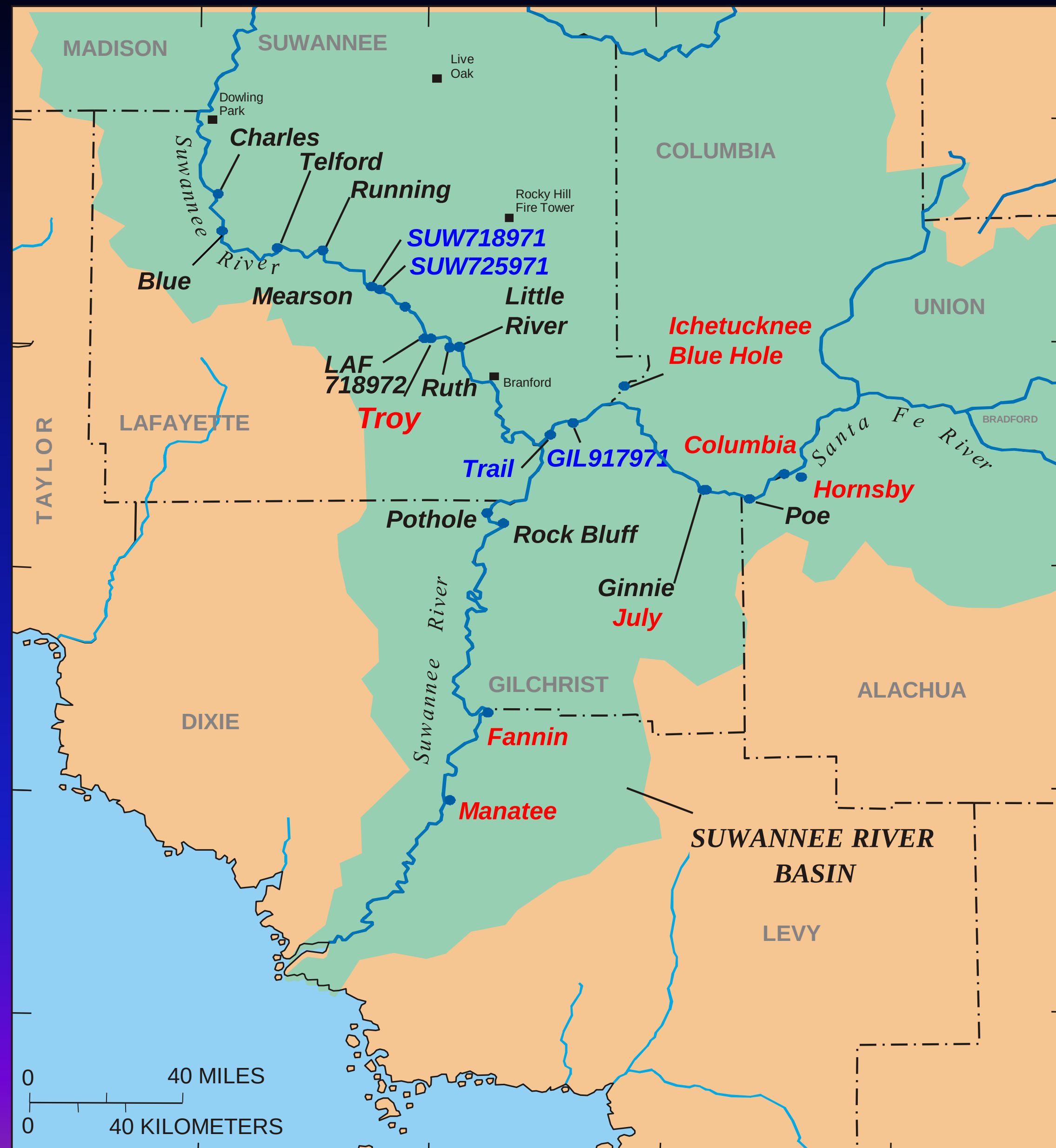


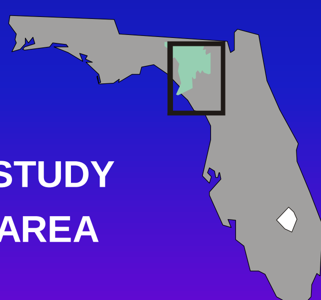
Binary-Mixing Model

$$f_{yw} = \frac{C_m - C_{ow}}{C_{yw} - C_{ow}}$$



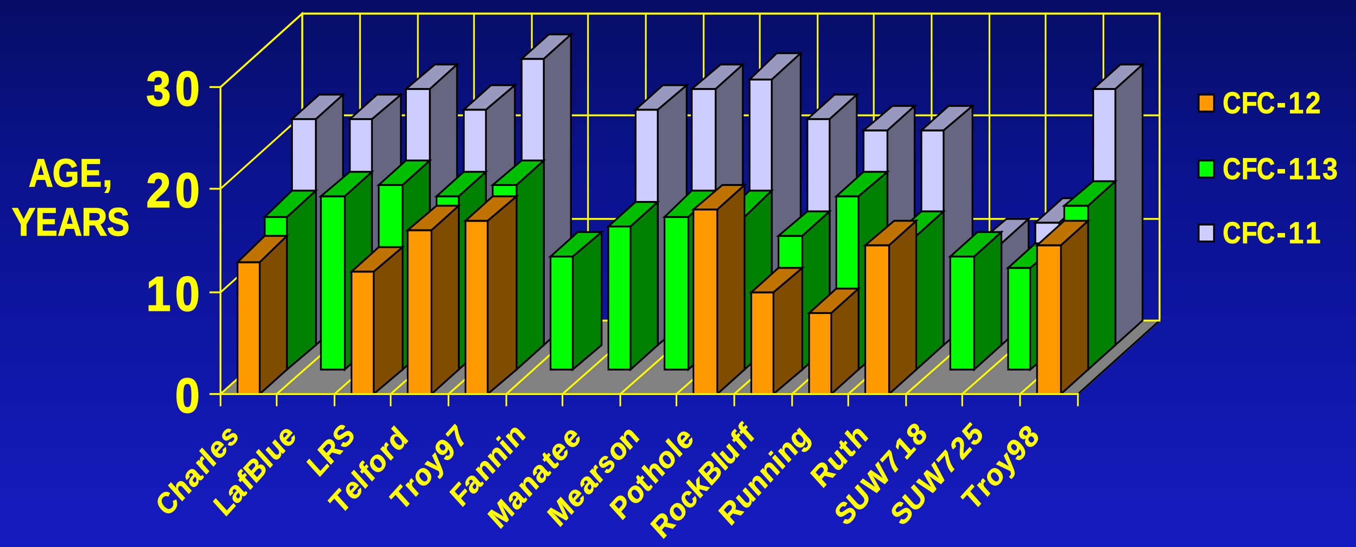
SPRINGS SAMPLED IN THE SUWANNEE RIVER BASIN





STUDY AREA

COMPARISON OF CFC-MODELED AGES FOR SPRINGS ALONG SUWANNEE RIVER



Discrepancy between ages and limitations associated with using CFCs demonstrates the need for comparing results from multiple age dating methods

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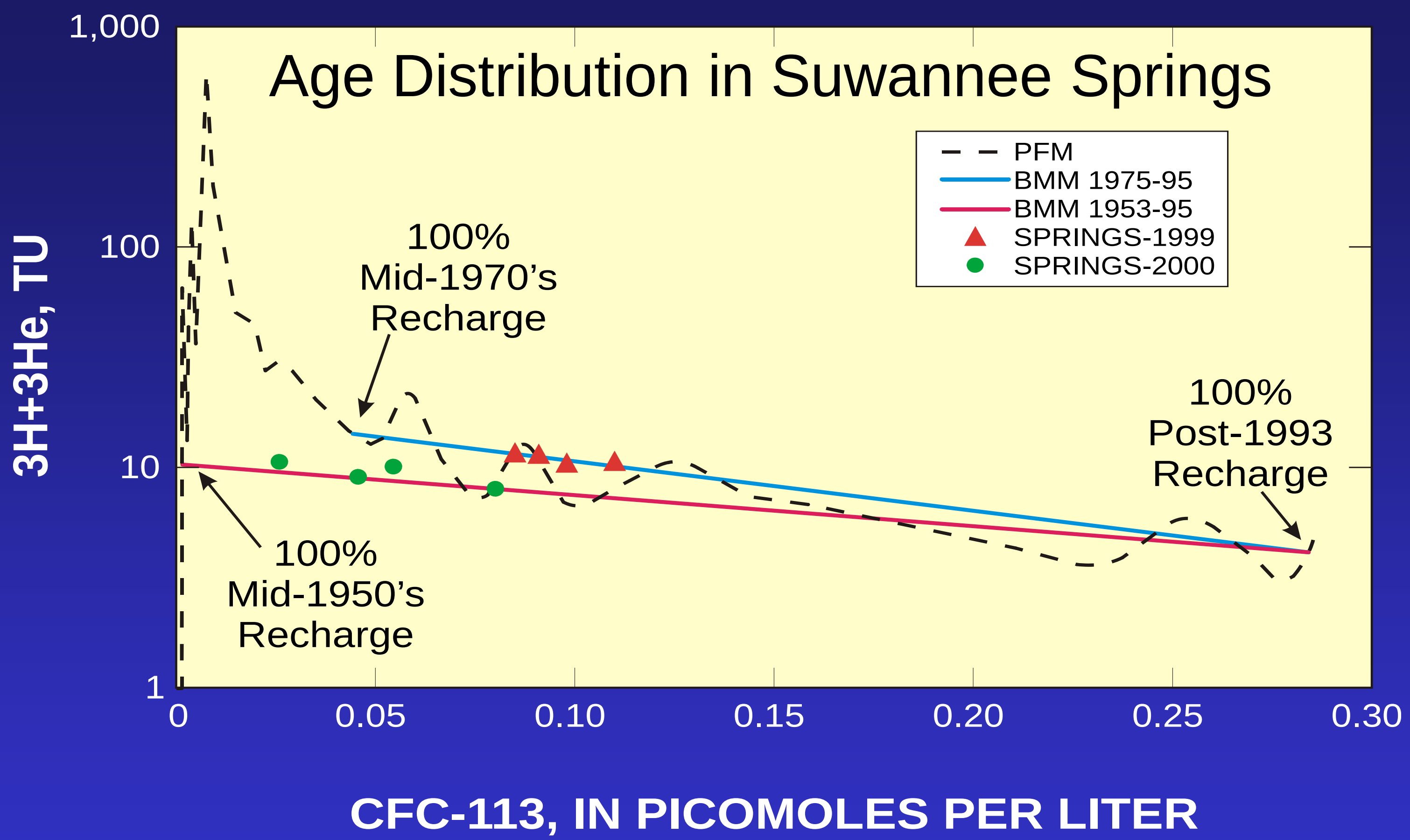
^3H / ^3He and CFC-113 in SPRING WATERS



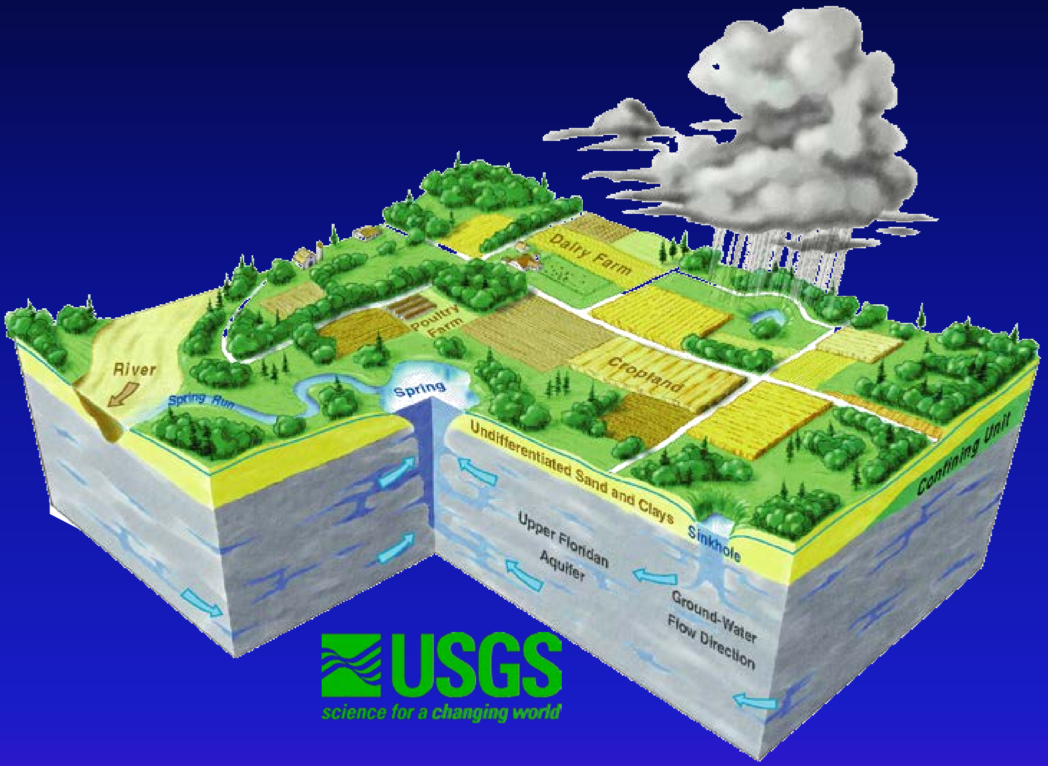
References:

Katz et al, 1999; 2001; 2005; Katz, 2004

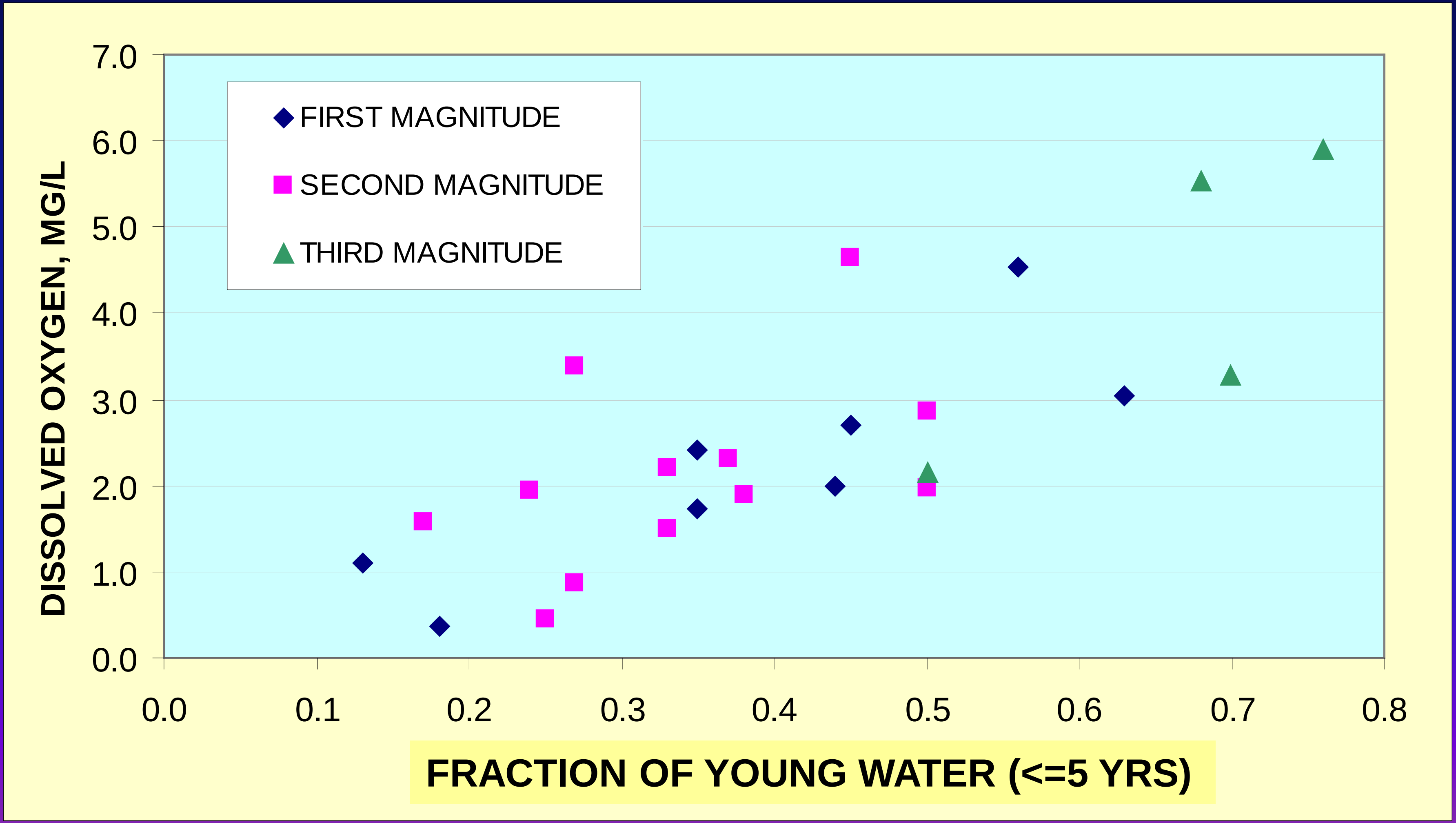
Comparison of fraction of young water in first, second, and third magnitude springs with:

Dissolved oxygen,

Nitrate-N



DISSOLVED OXYGEN AND YOUNG FRACTION OF SPRING WATER



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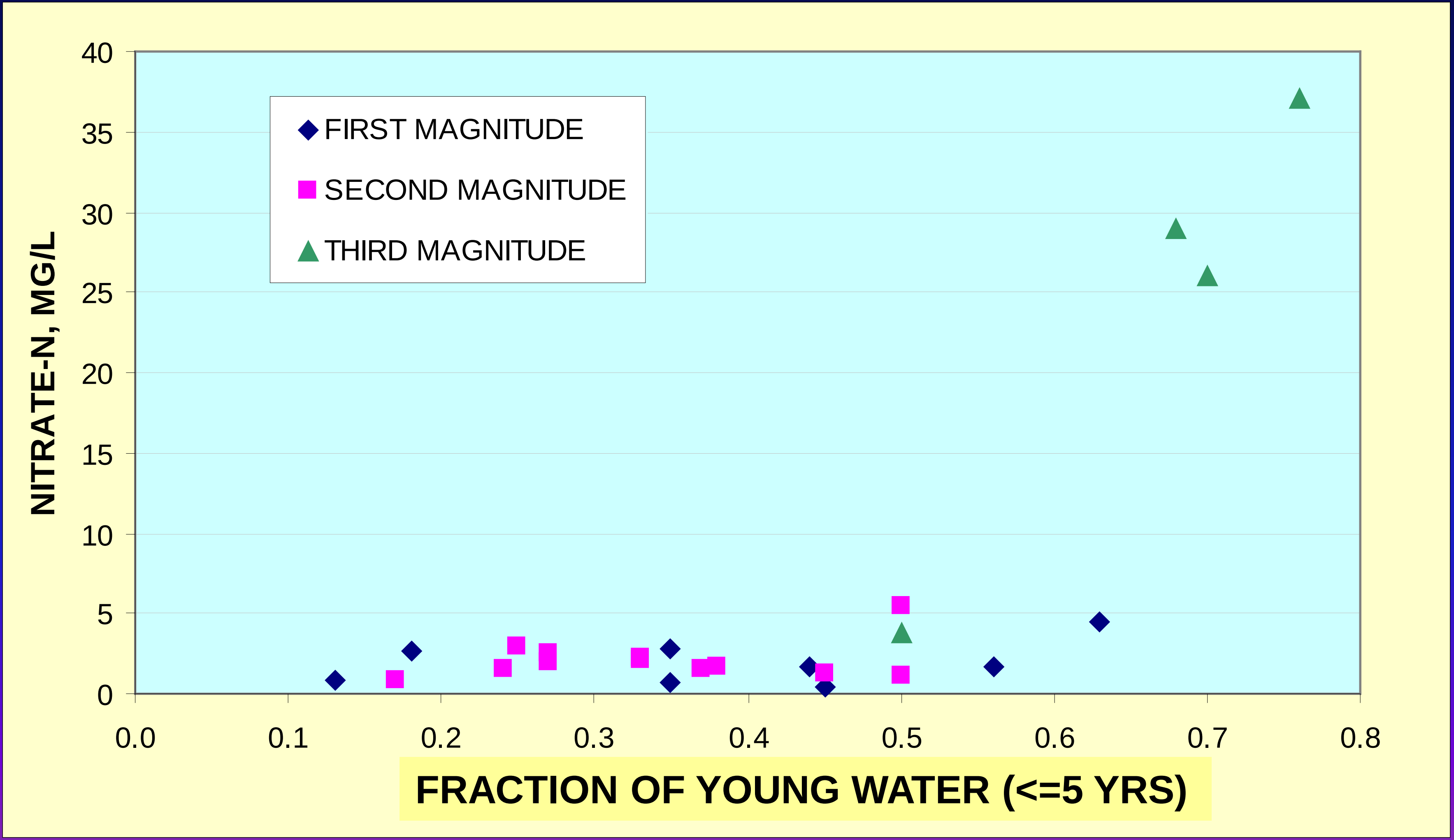
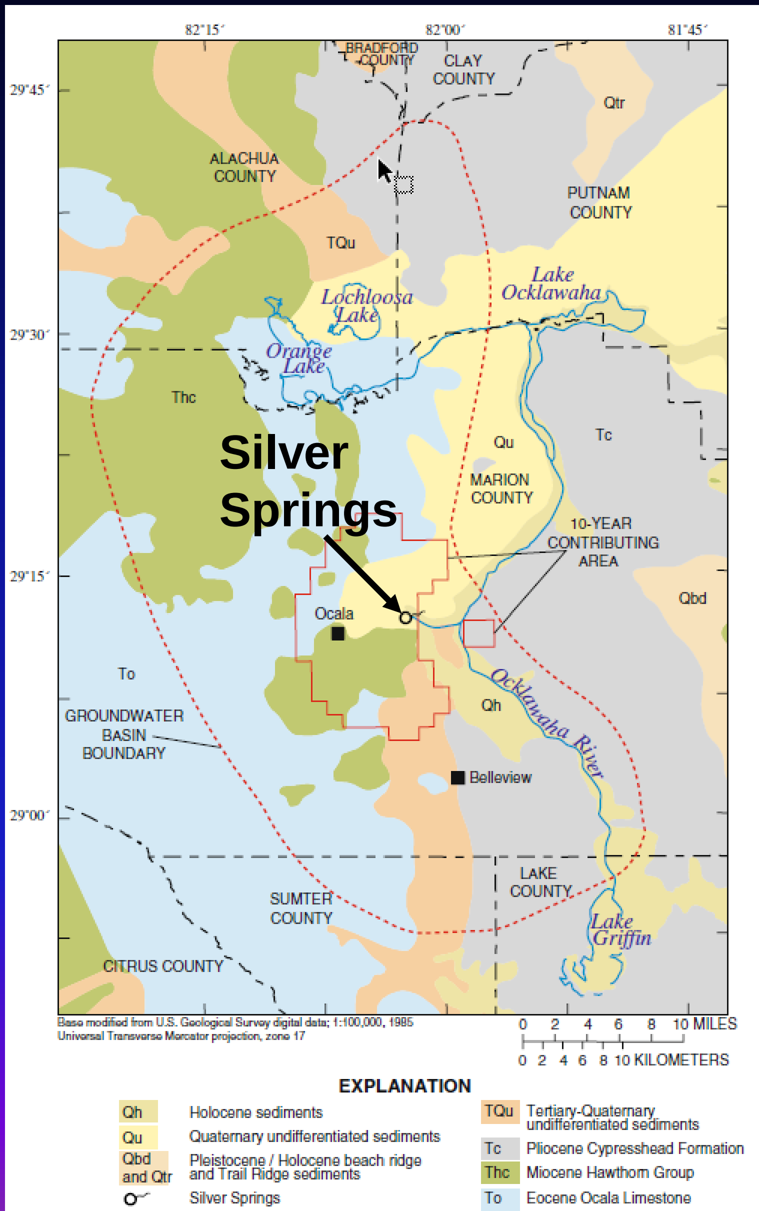
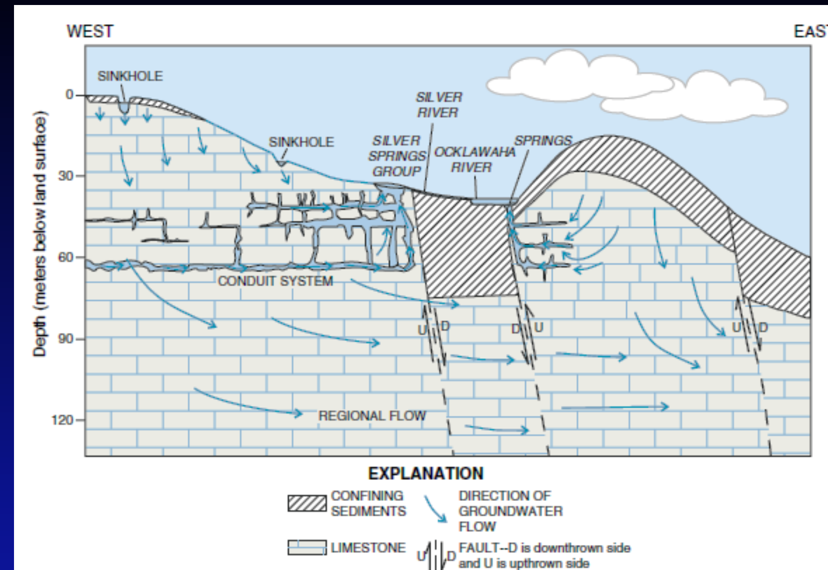
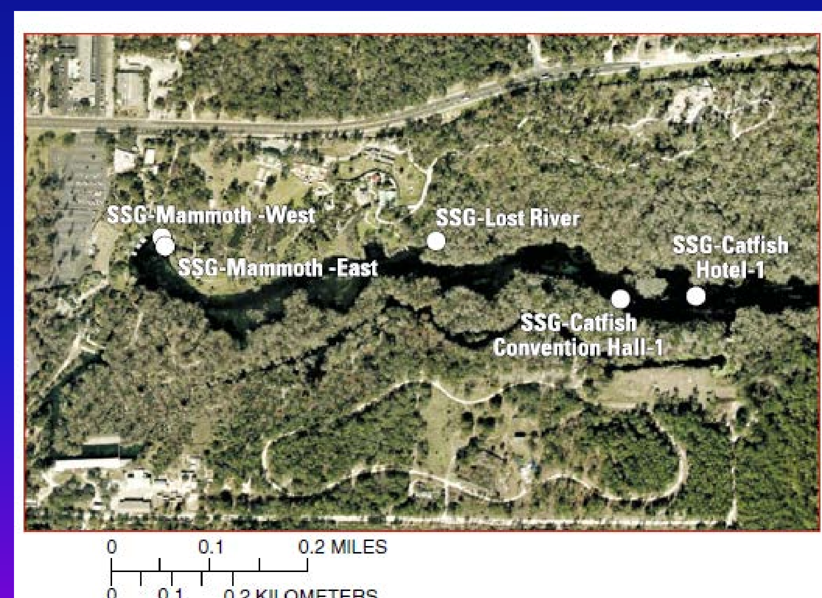
NITRATE AND YOUNG FRACTION OF SPRING WATER



Silver Springs Study

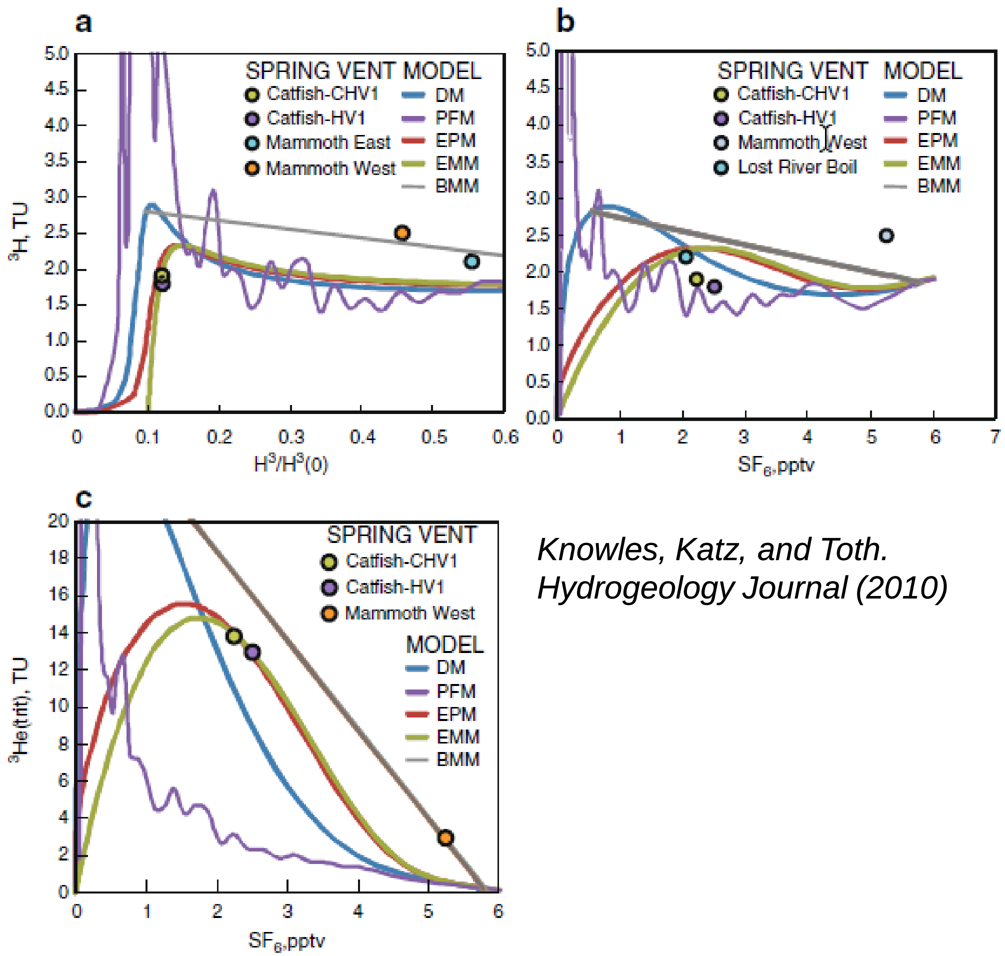






Knowles et al., 2010

Age Mixtures of Silver Springs Vents and water quality

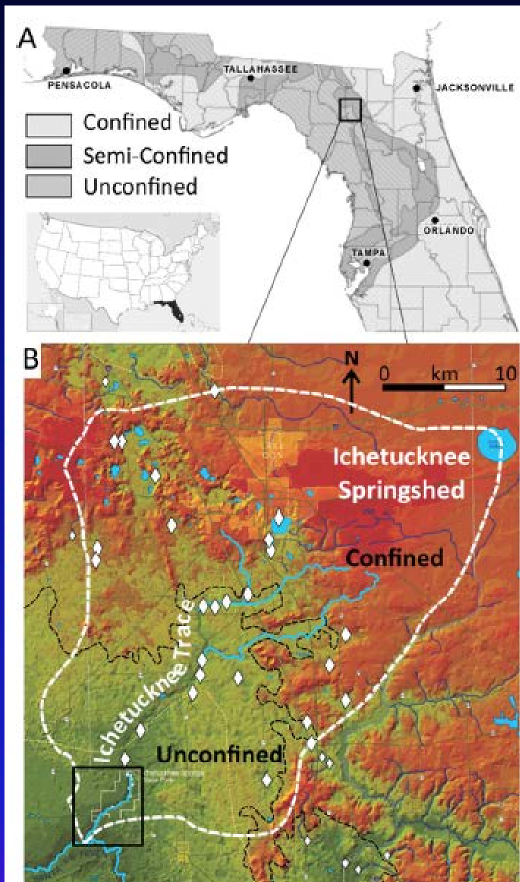


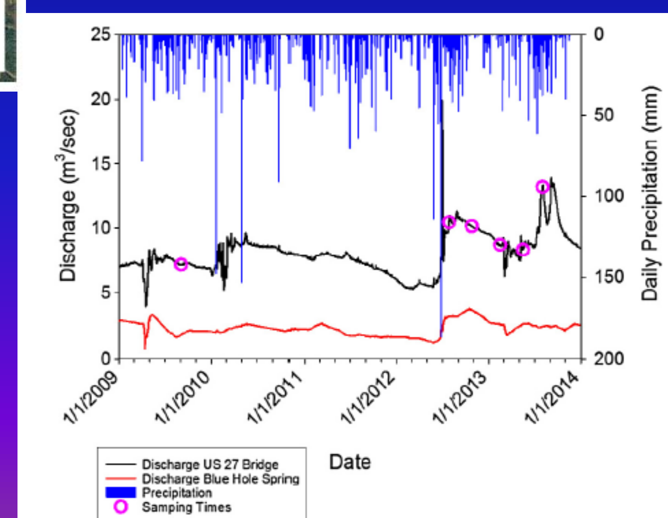
Knowles, Katz, and Toth. Hydrogeology Journal (2010)

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 NO_3-N, dissolved O_2, and Ca/Mg ratio

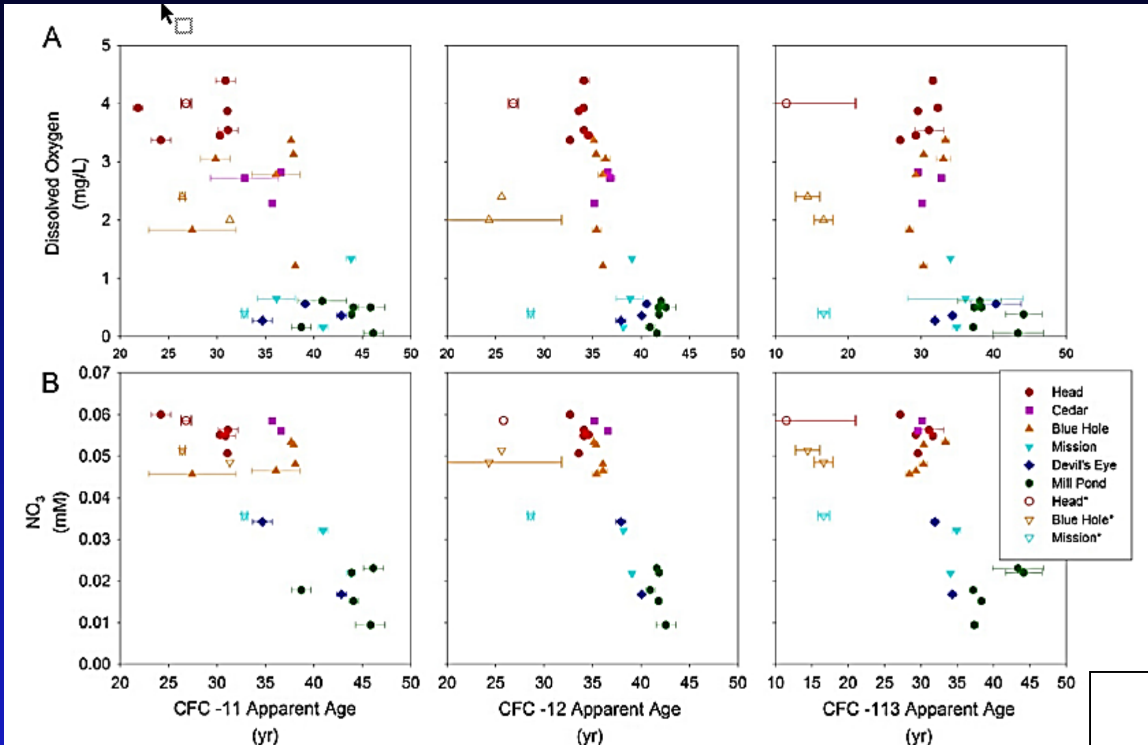
Climate Control of Decadal-Scale Increases in Apparent Ages of Eogenetic Karst Spring Water, Ichetucknee Springs





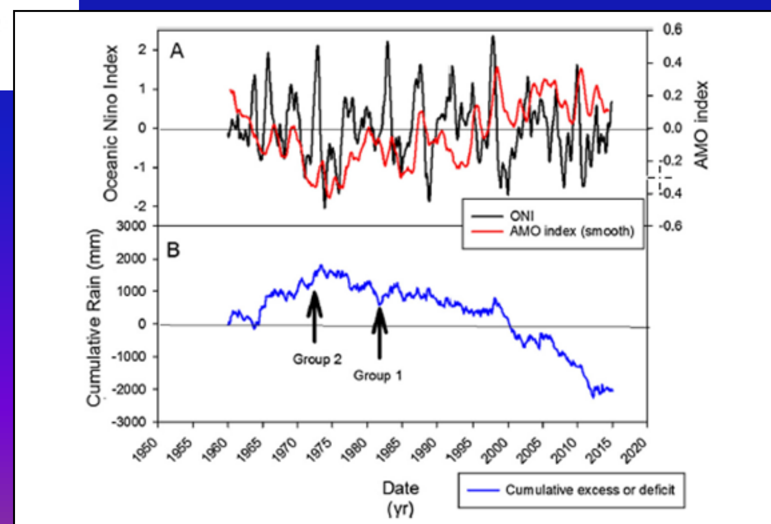
Martin et al., 2016, Journal of Hydrology

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).

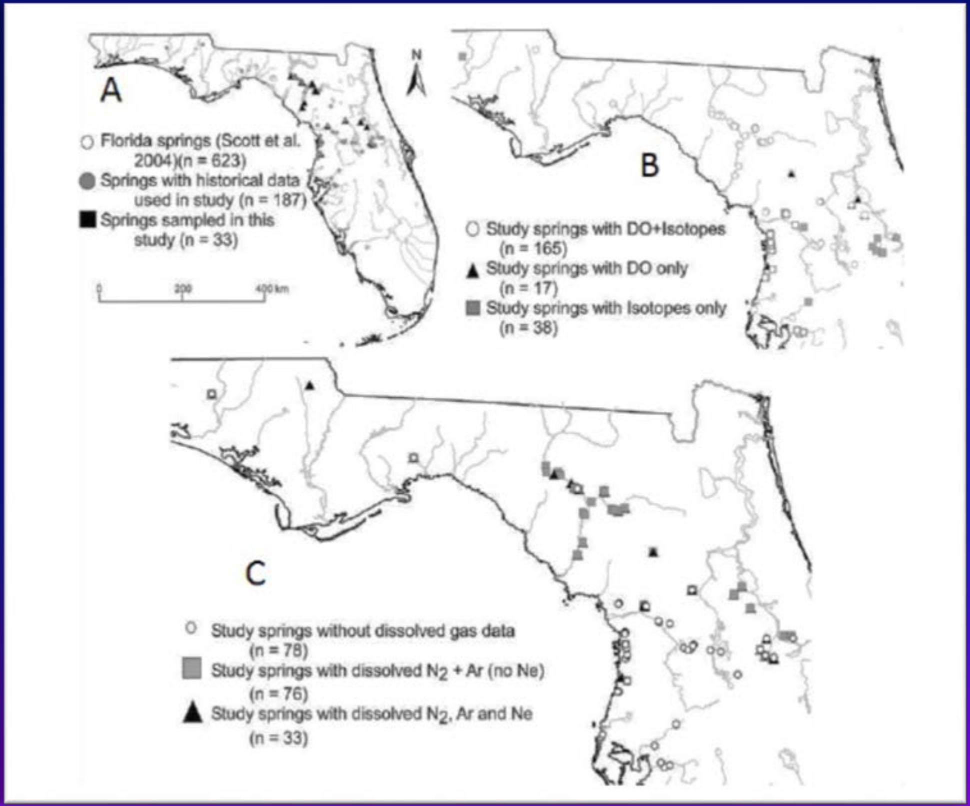
Longer time-scale changes of apparent age (decades) may include variations in recharge from ENSO or AMO climate cycles, or from increased pumping

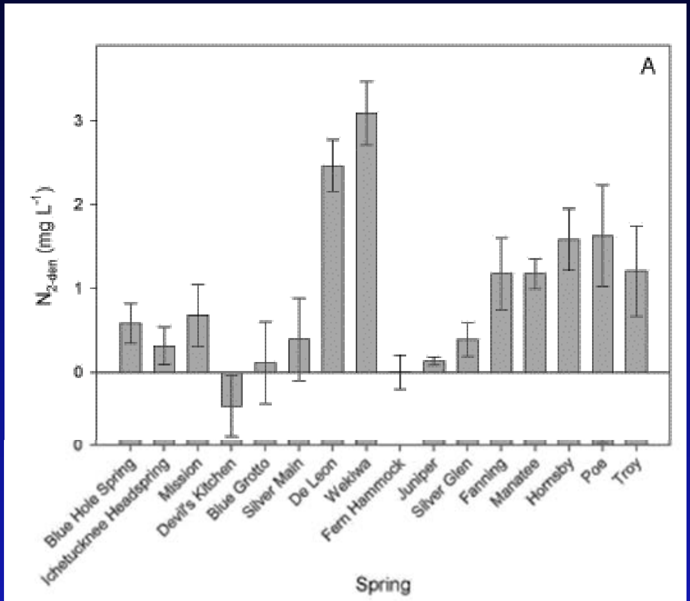


Martin et al., 2016, Journal of Hydrology

Denitrification in UFA– (Heffernan et al 2012)

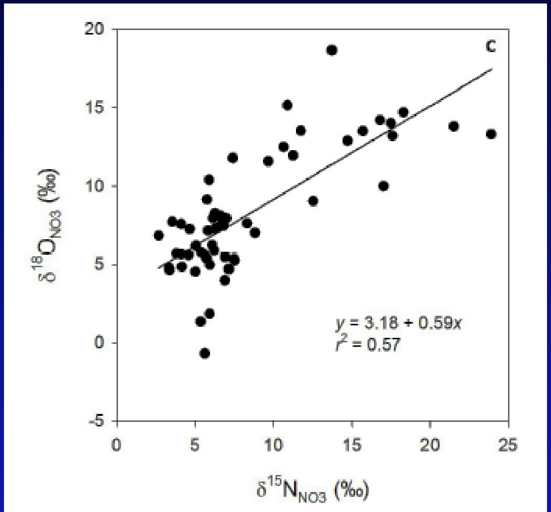
Importance of measuring
N_2 , Ar, Ne, O_2
along with $\delta^{15}N$ and $\delta^{18}O$

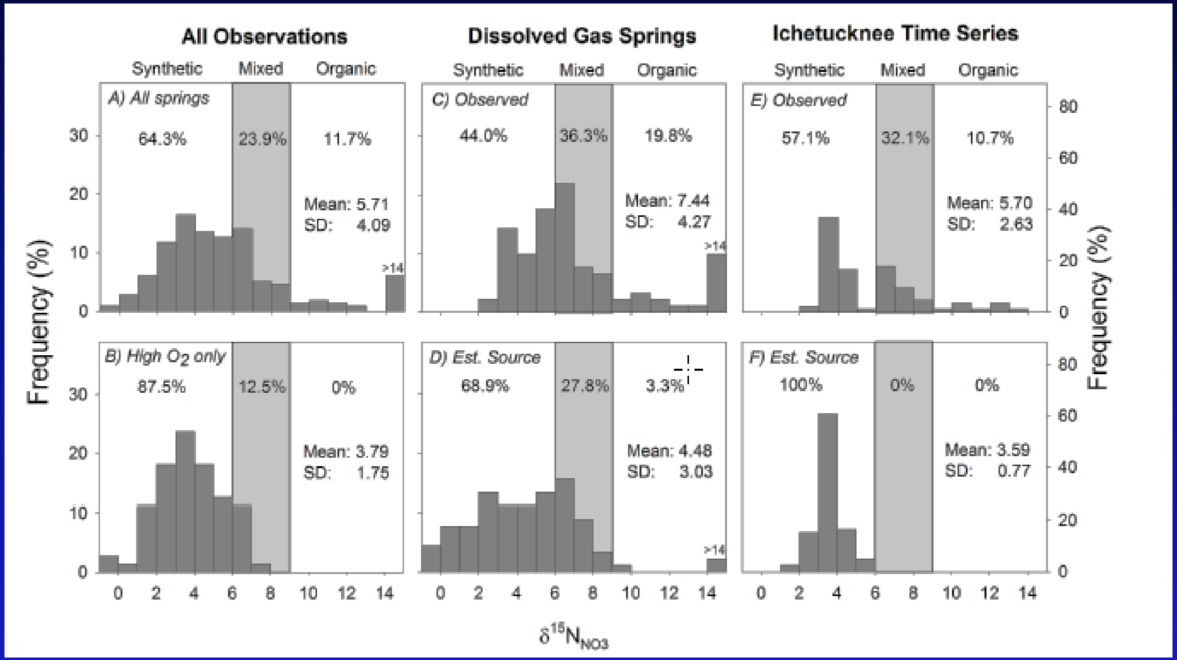




Denitrification removed >75% of N inputs in 8 of 61 springs, and >50% in 20 of 61 springs

Denitrification in UFA– (Heffernan et al 2012)





Positive correlation btw $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ is consistent with denitrification rather than variation in source as driver of $\delta^{15}N_{NO3}$.

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.*

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Selected References:

Heffernan, J. B., Albertin, A.R., Fork, M. L., Katz, B.G., and Cohen, M. J., 2012. Denitrification and inference of nitrogen sources in the karstic Floridan Aquifer, *Biogeosciences* 9: 1671-1690.

Katz, B.G., Berndt, M.P., Crandall, C.A., 2014. Factors affecting the movement and persistence of nitrate and pesticides in the surficial and upper Floridan aquifers in two agricultural areas in the southeastern United States. *Environmental Earth Sciences* 71: 2779-2795.

Katz, B.G., Sepulveda, A.A., and Verdi, R.J., 2009. Estimating nitrogen loading to ground water and assessing vulnerability to nitrate contamination in a large karstic spring basin, *Journal of the American Water Resources Association* 45: 607-627.

Katz, B.G., Copeland, R., Greenhalgh, T., Ceryak, R., and Zwanka, W., 2005. Using multiple tracers to assess sources of nitrate contamination and age of ground water in a karstic spring basin. *Environmental and Engineering Geoscience* XI: 333-346.

Katz, B.G., 2004. Sources of nitrate contamination and age of water in large karstic springs of Florida, *Environmental Geology* 46: 689-706.

Katz, B.G., Chelette, A.R., and Pratt, T.R., 2004. Use of chemical and isotopic tracers to assess sources of nitrate and age of ground water, Woodville Karst Plain, USA, *Journal of Hydrology* 289: 36-61.

Katz, B.G., Bohlke, J.K, and Hornsby, H.D., 2001. Timescales for nitrate contamination of spring waters, northern Florida: *Chemical Geology* 179: 167-186.

Knowles, L., Jr., Katz, B.G., and Toth, D.J., 2010. Using multiple chemical indicators to characterize and determine the age of groundwater from selected vents of the Silver Springs Group, central Florida, USA. *Hydrogeology Journal* 18:1825-1838.

Martin, J.B., Kurz, M.J., Khadka, M.B. 2016. Climate control of decadal-scale increases in apparent ages of eogenetic karst spring water. Journal of Hydrology 540: 988-1001.

Toth, D.J., and Katz, B.G., 2006. Mixing of shallow and deep ground water as indicated by the chemistry and age of karstic springs. *Hydrogeology Journal* 14: 1060-1080.

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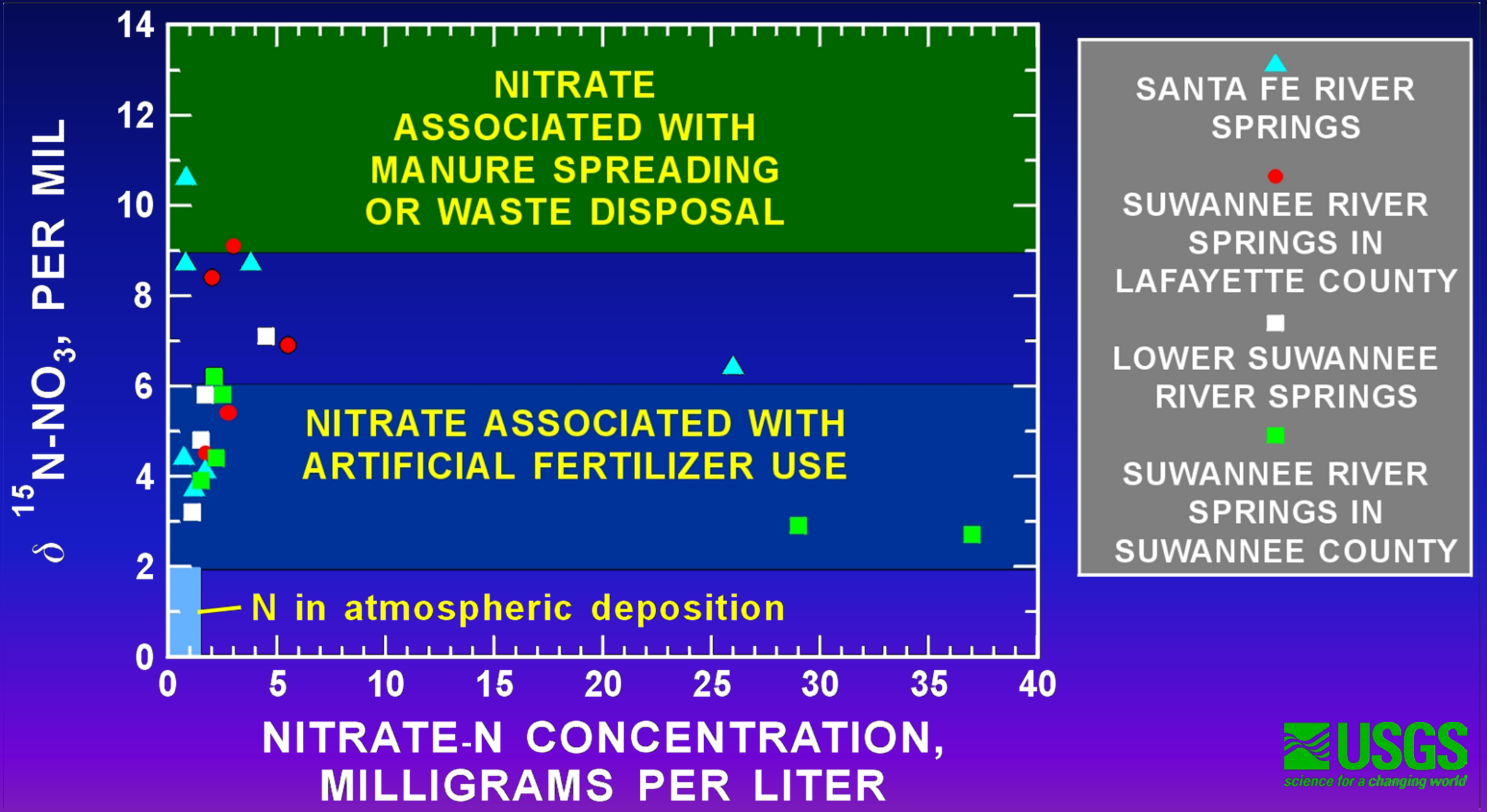
SOURCES OF NITRATE IN SPRING WATERS

$\delta^{15}N\text{-}NO_3$ vs. $NO_3\text{-}N$



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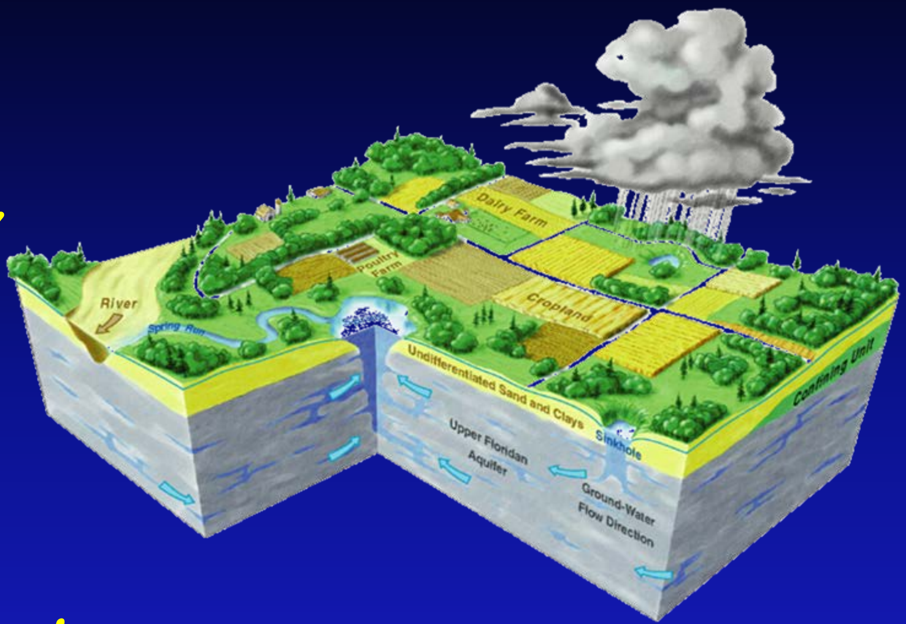
Springs in Suwannee River Basin—



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.

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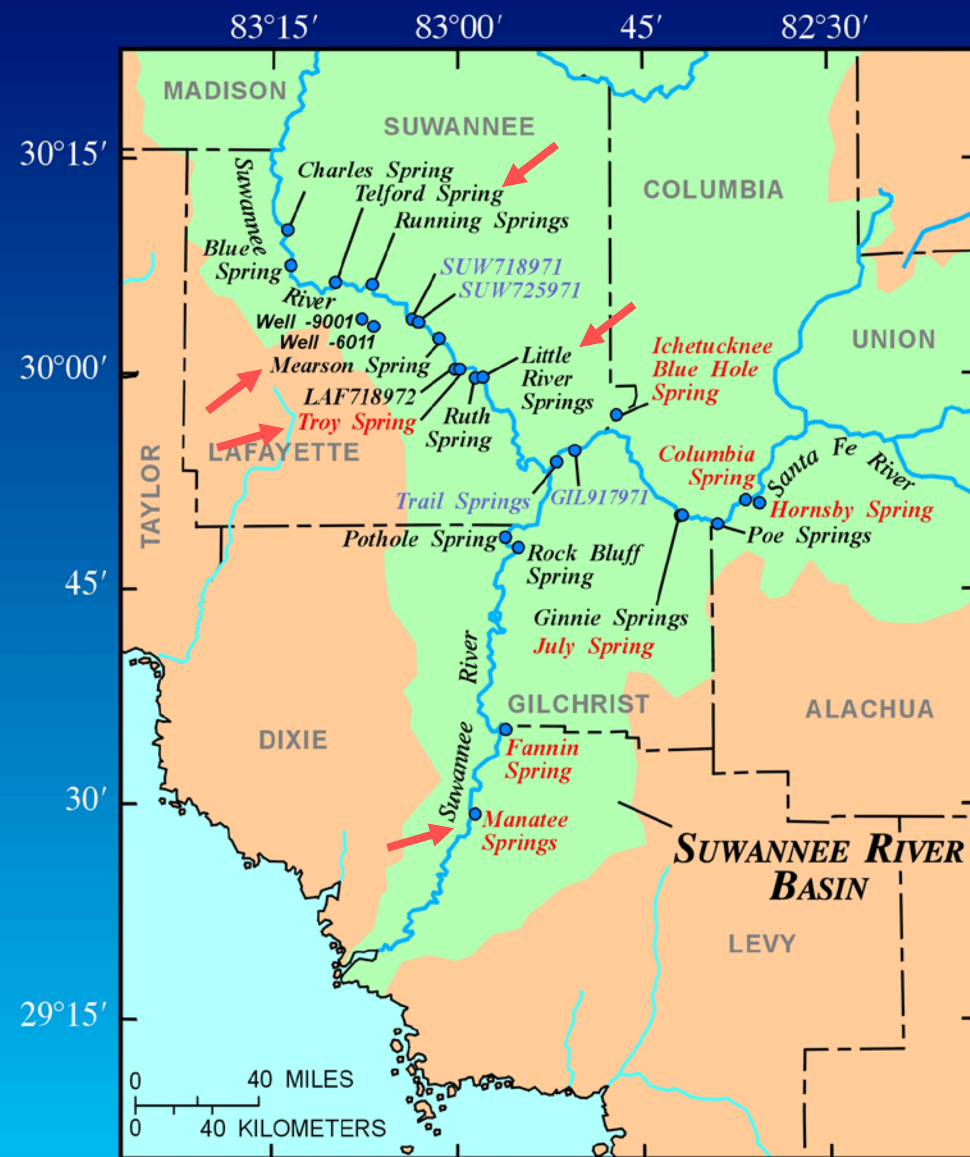
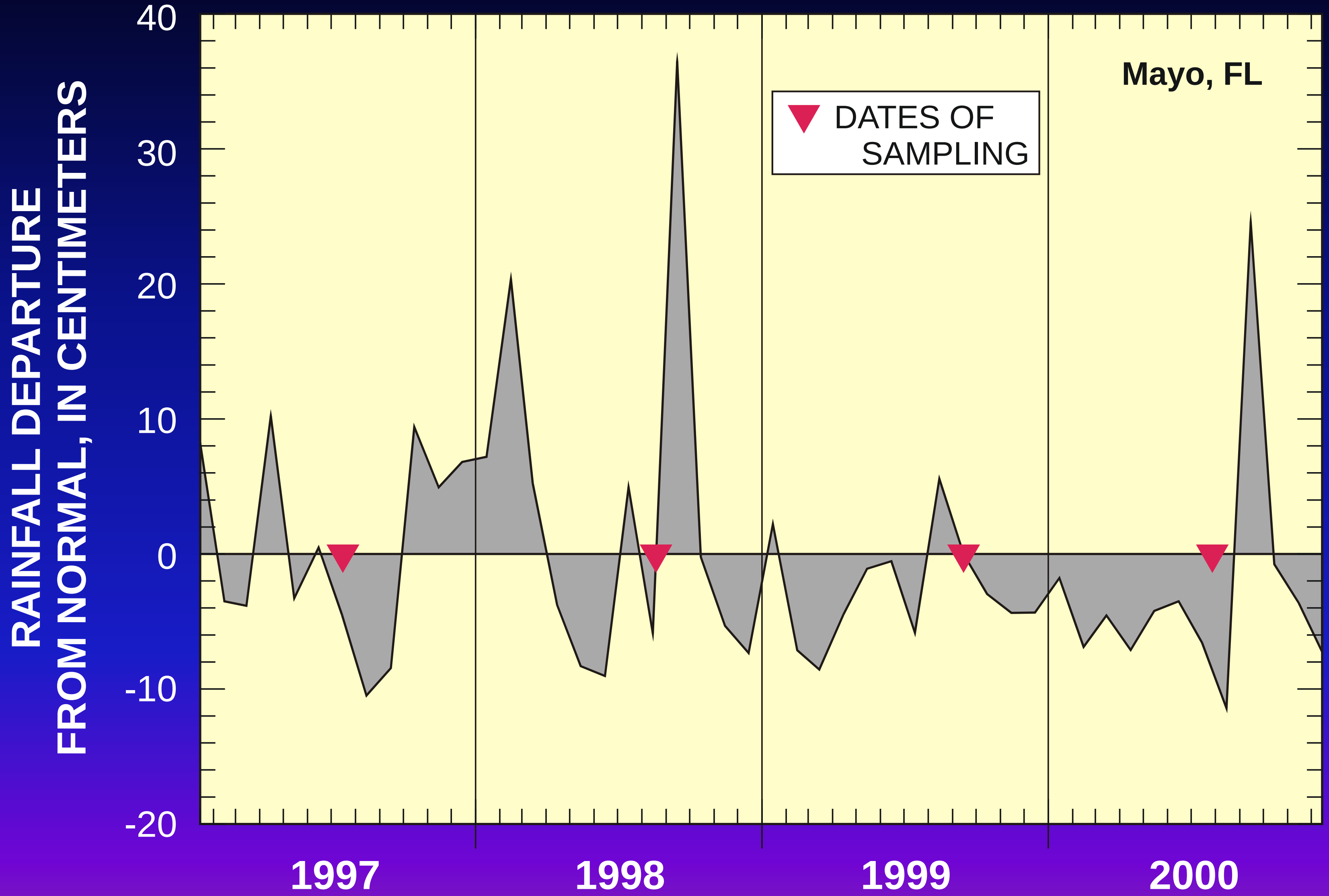
Springs Sampled Multiple Times In the Suwannee River Basin



RAINFALL DEPARTURES FROM NORMAL



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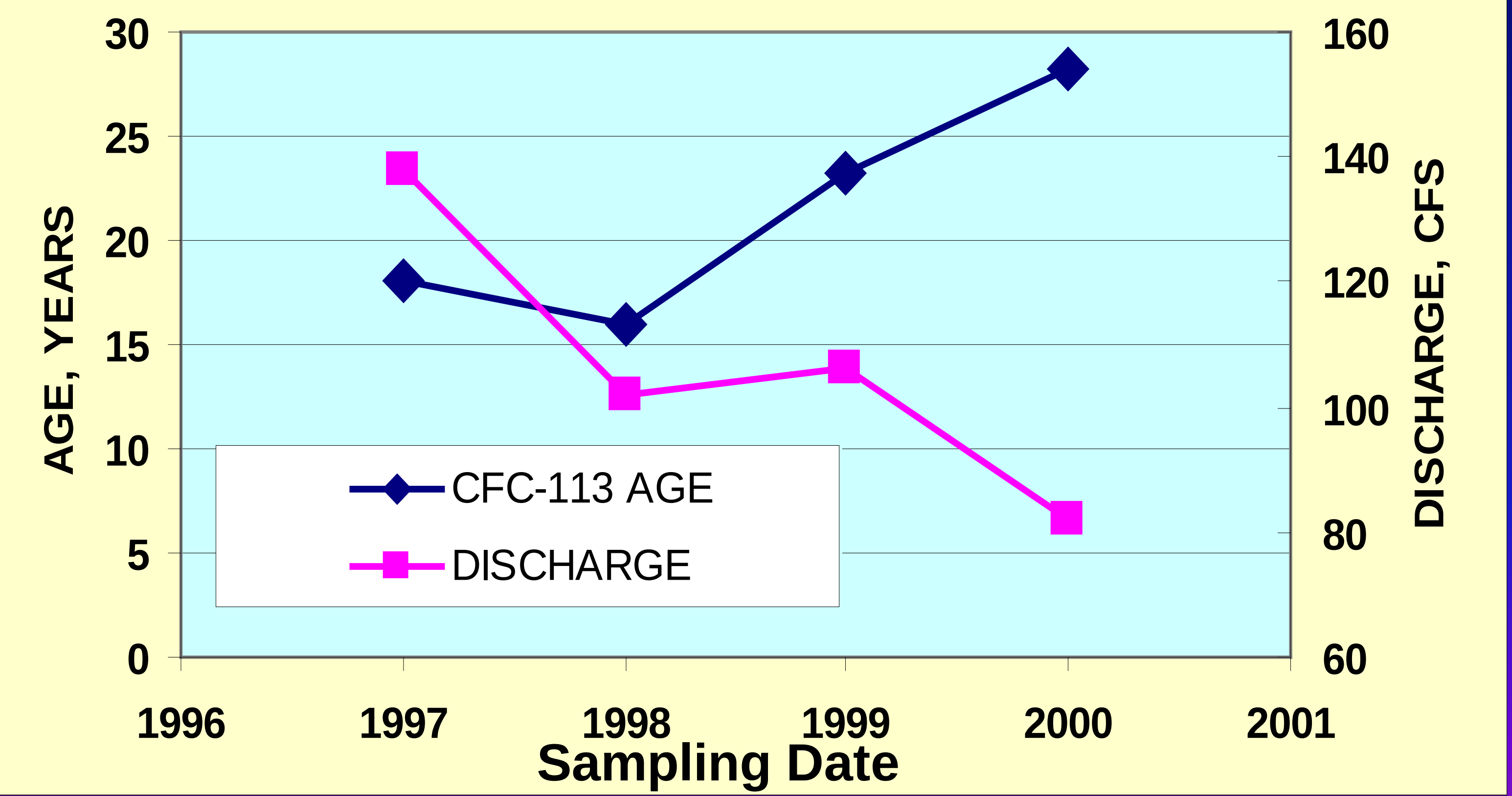
Troy Spring— Age and Discharge



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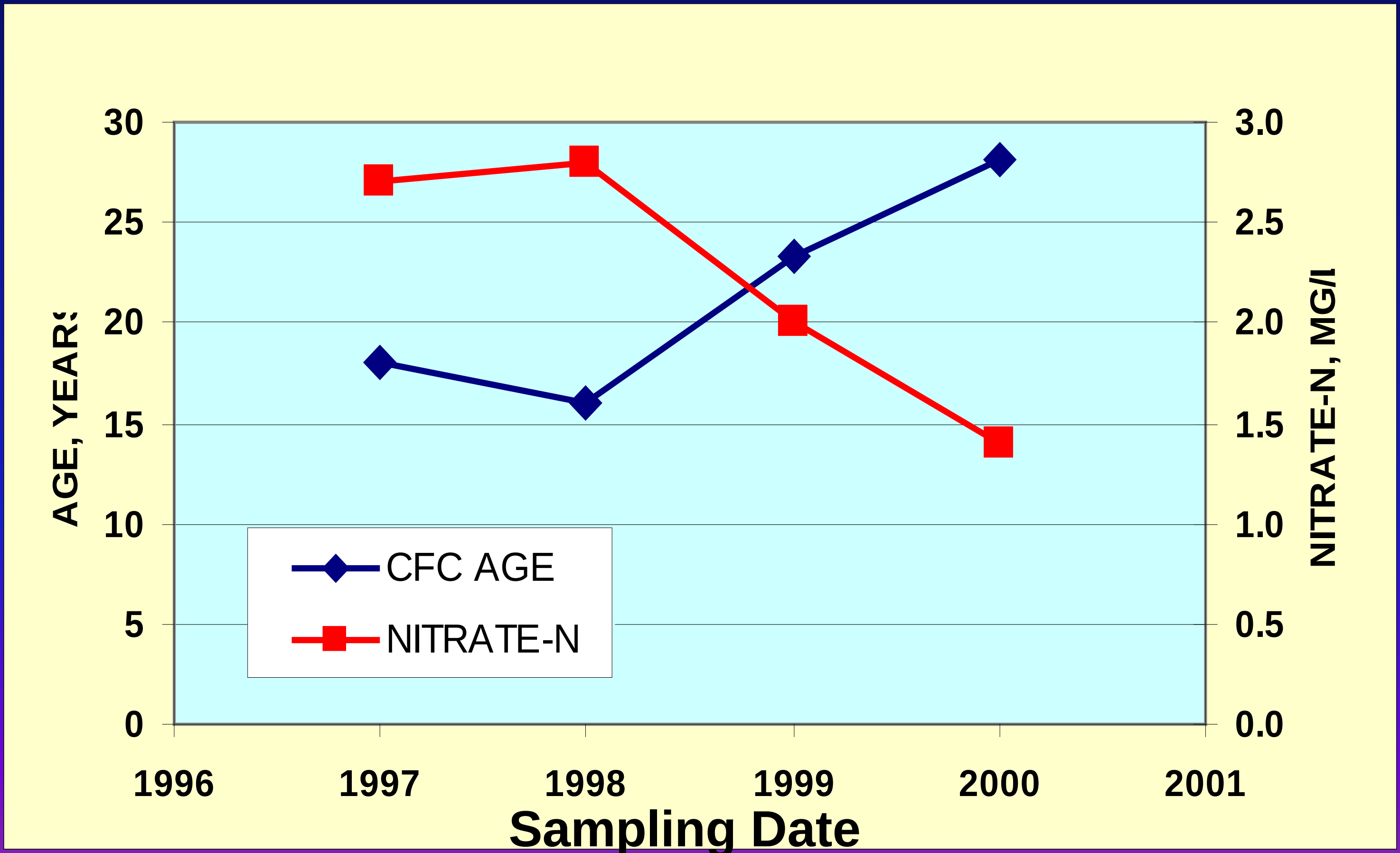
Troy Spring— Age and Nitrate-N



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Springs in Suwannee River Basin—

3. Denitrification unlikely due to low DOC, oxygenated waters (DO>3 mg/L, little or no excess N_2, little or no increase in $\delta^{15}N$-NO_3.

4. Lower nitrate concentrations in older waters may be related to lower amounts and type of N applied in 1950's and 1960's.

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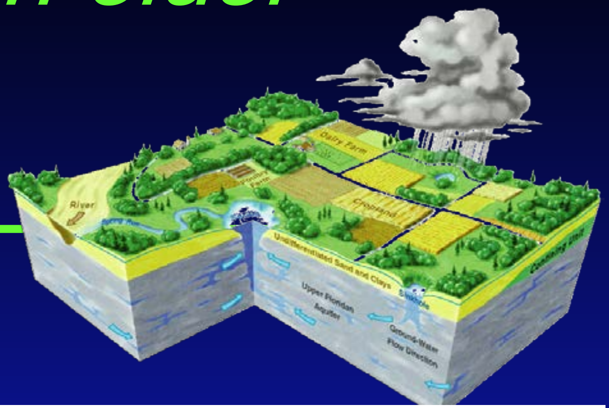
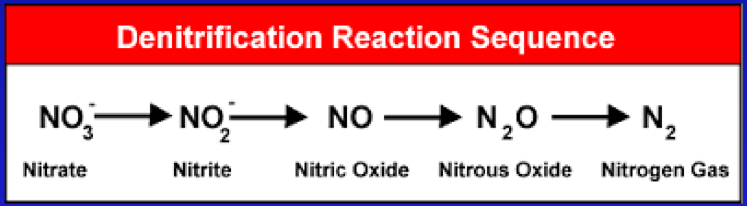
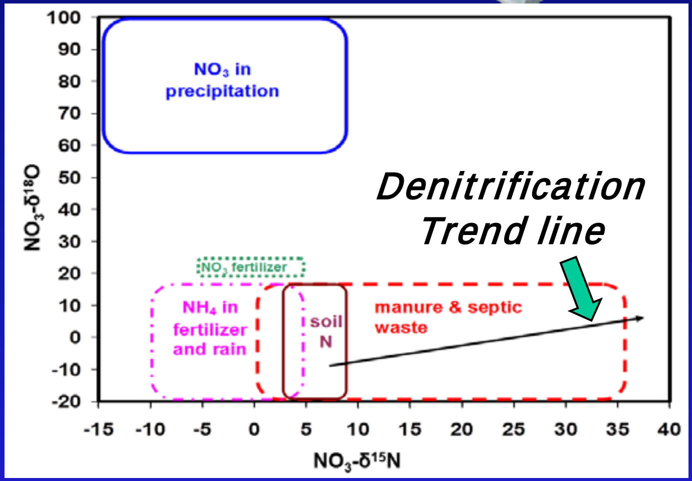
Scenarios for Low NO_3-N in older waters



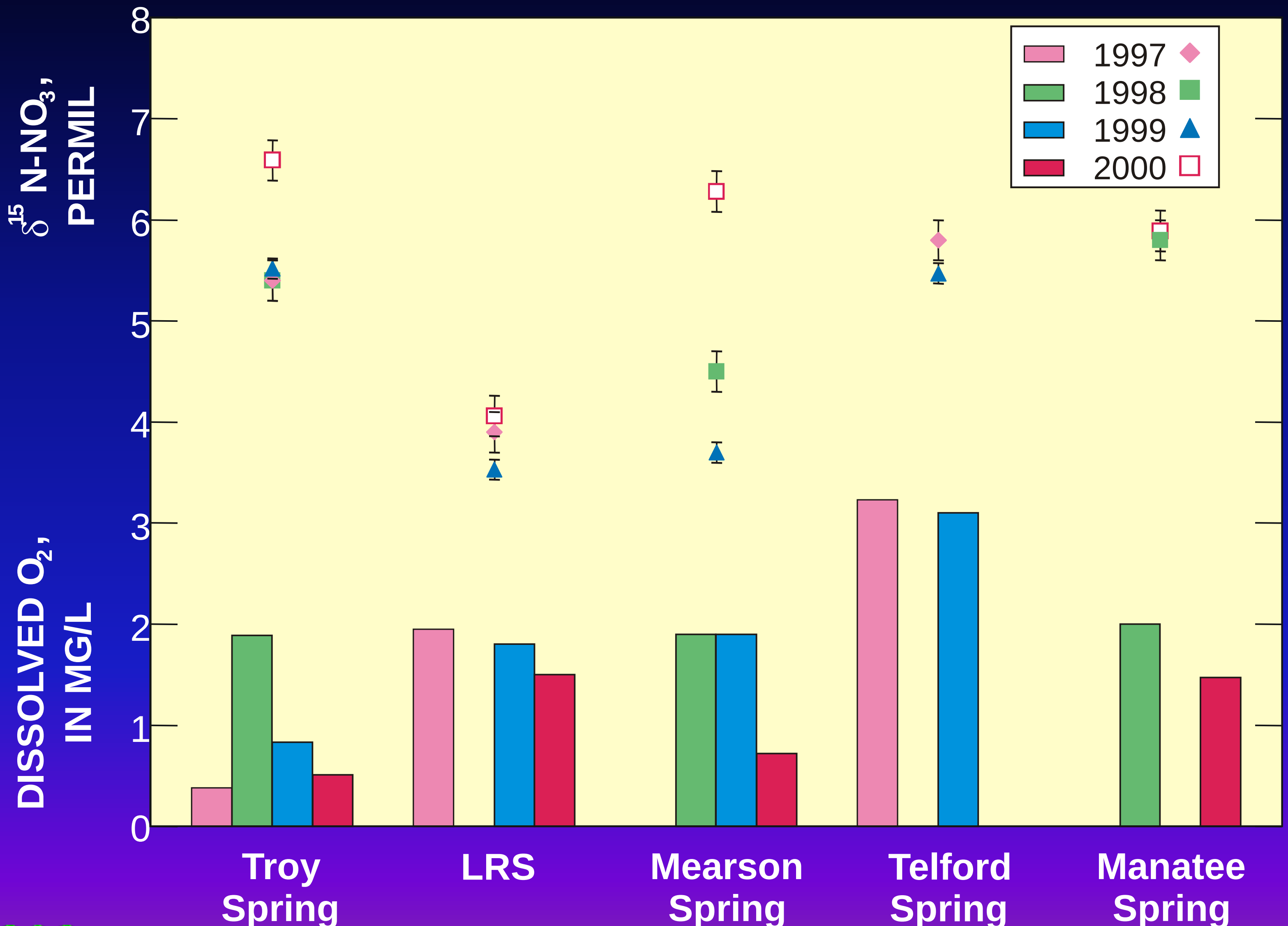
- *Denitrification- microbially mediated, low O_2; carbon source*





- *Historic changes in agricultural practices – (N source type)*

$\delta^{15}N\text{-}NO_3$ and DISSOLVED O_2 in SPRING WATERS



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Estimated N Inputs, Lafayette Co.