Nutrient Source Identification and the BMAP

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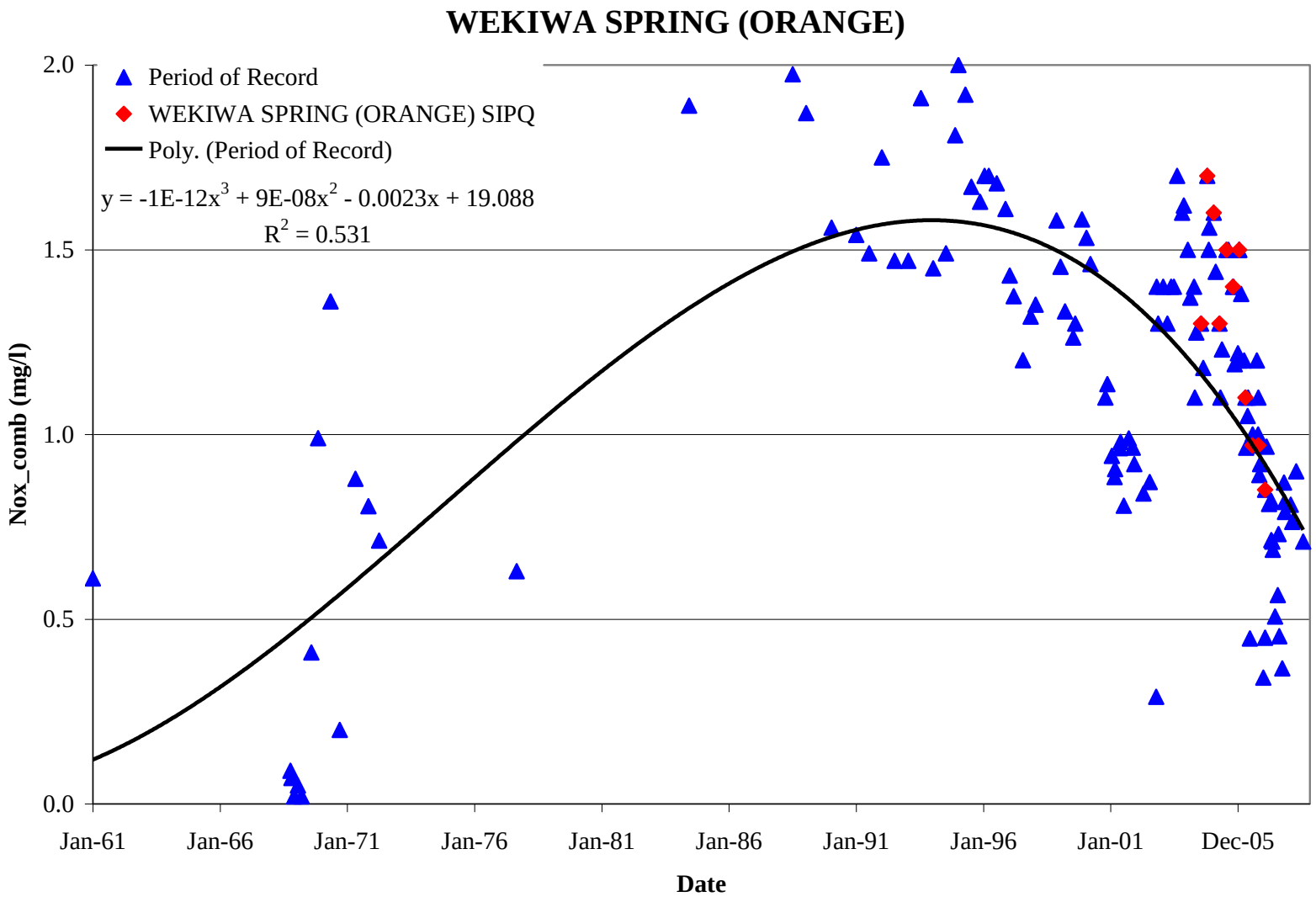
Topics to Discuss

- Source identification
  - Results from isotope studies
- Qualitative vs. quantitative
  - Are fertilizers or septic tanks or wastewater treatment plants sources of nitrogen?
    - Answerable
  - Is fertilizer or septic tanks or wastewater 15 or 25 or 35 percent of the load?
    - Not answerable

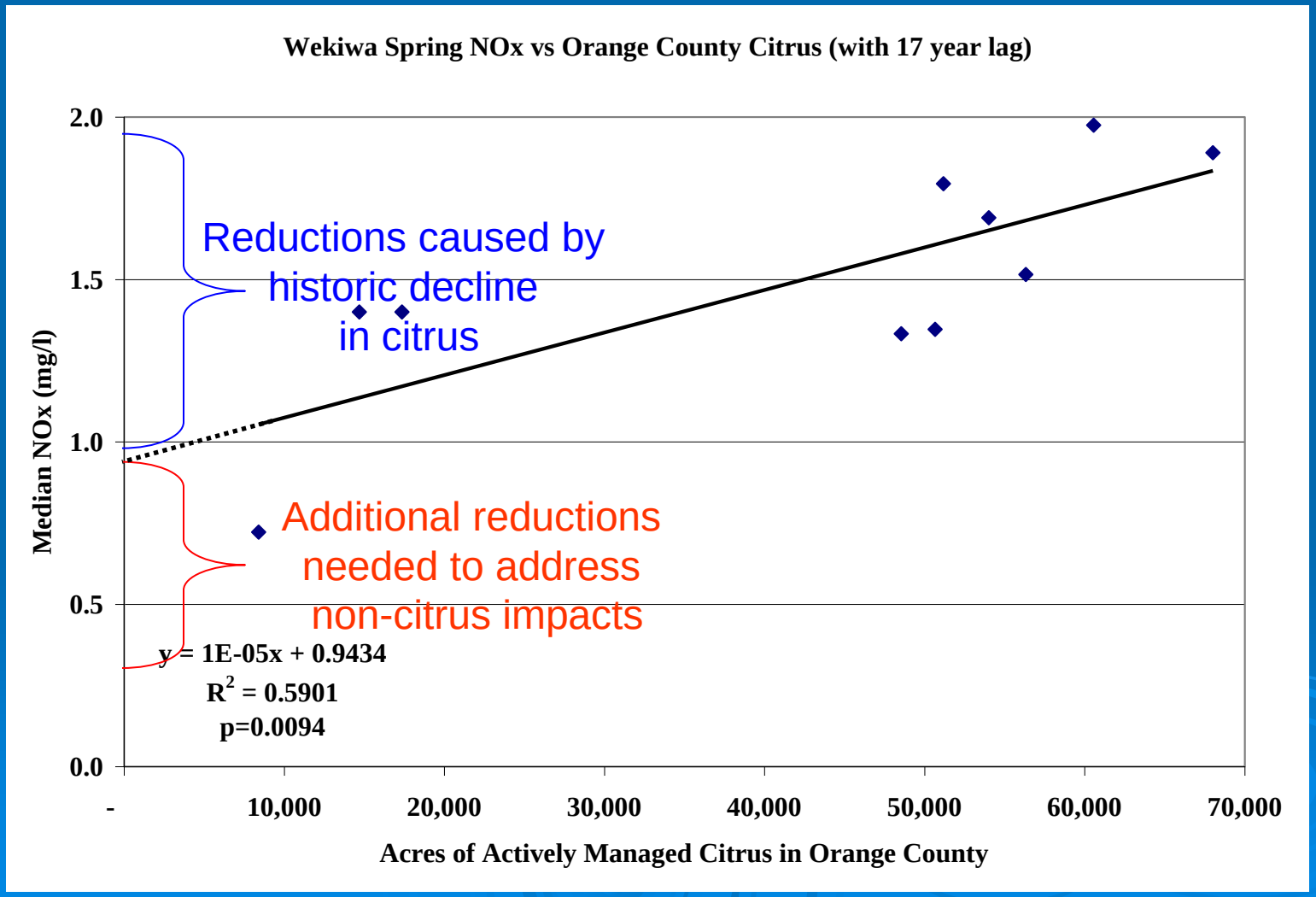
The majority of the nitrogen load comes from groundwater (FDEP 2008), and with groundwater, it is difficult to verify sources

Sources	Nitrate loads (pounds / yr)	Percent total load
Surface runoff from watershed	386,849	43 %
Spring contributions	511,433	57 %
TOTAL	898,282	100 %

Recent improvements in groundwater

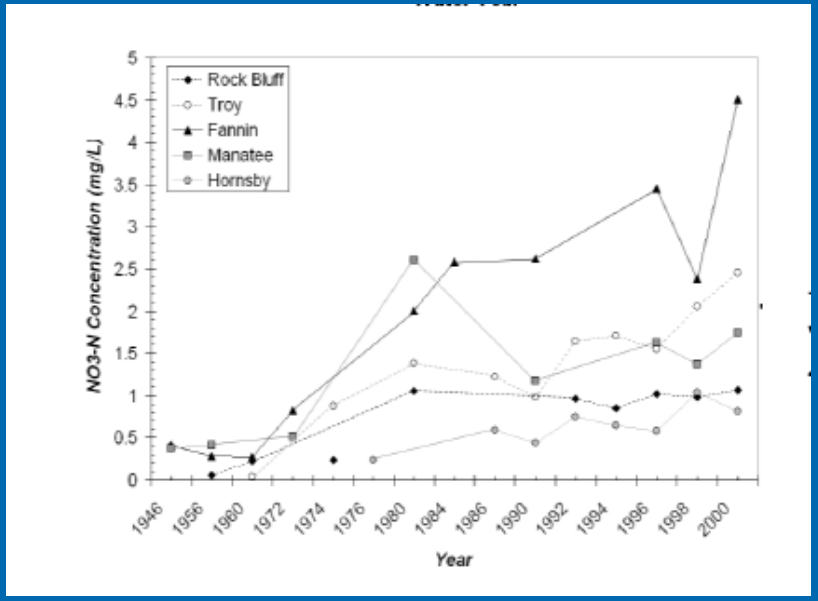


Reminder from prior meeting - nitrate levels at Wekiwa Spring are positively correlated with acreage of citrus 17 years earlier, with y-intercept higher than goal (0.286 mg NOx / liter)



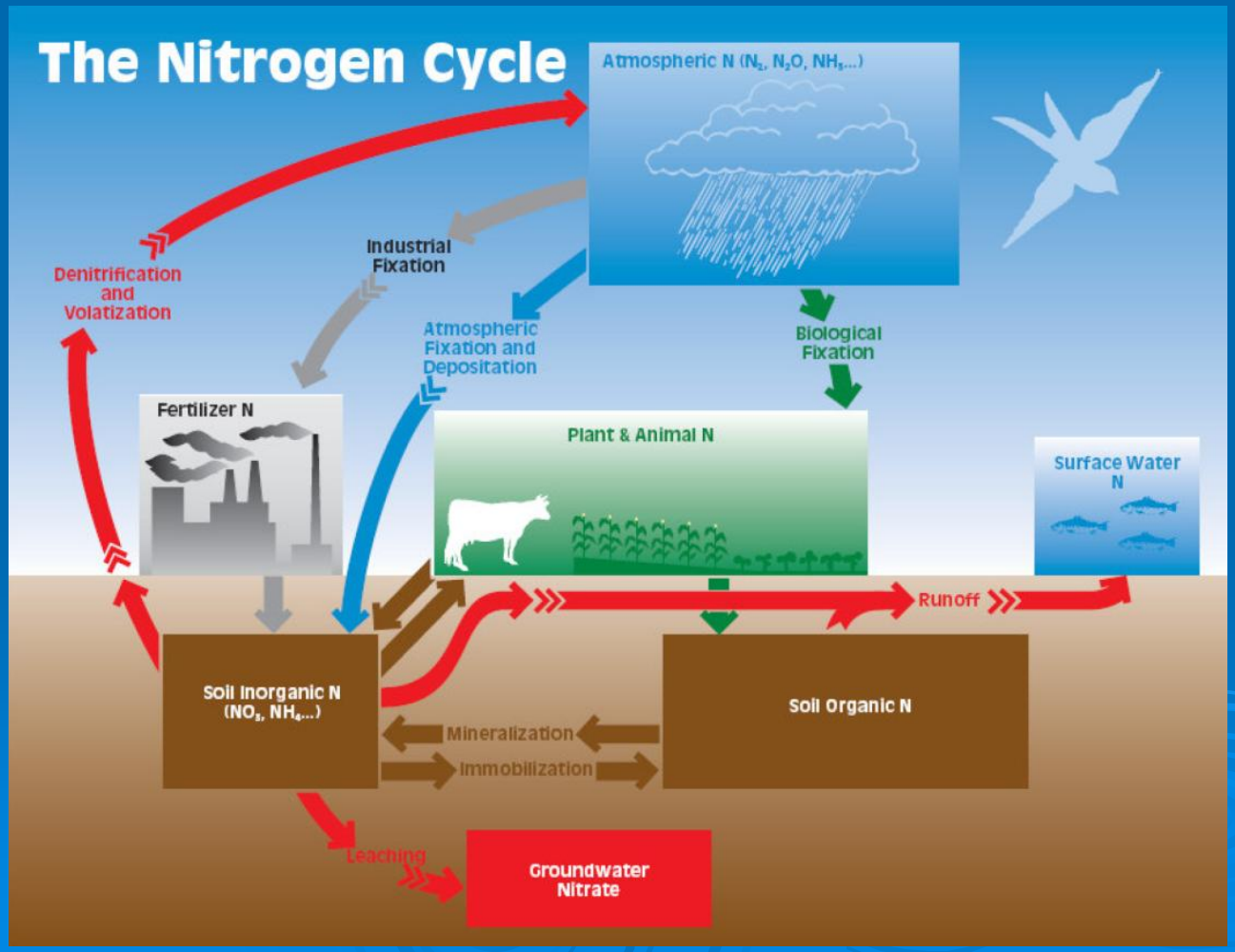
Good news on recently improving water quality, but will it continue to improve, or level off, or get worse again?

Likely it will get worse



- More development
  - More stormwater
  - More sewage
  - More residential fertilizer
- Acceptable to wait 17 years to find out it DID get worse?
- While not likely for nitrate to reach 2.0 mg / liter when citrus dominated, just as unlikely that doing nothing will allow reaching the TMDL goal of 0.286 mg / liter

Understanding the nitrogen cycle is key to understanding nitrogen "behavior" and the relative impact of different sources



Main concepts

- N_2 gas is biologically inert
  - 78 % of atmosphere, yet we buy fertilizer
- Some processes convert N_2 gas into forms that make your lawn, your citrus trees (or your water) greener
- Some processes convert biologically available forms back into inert forms
- Understanding those processes is key to understanding the importance of various sources

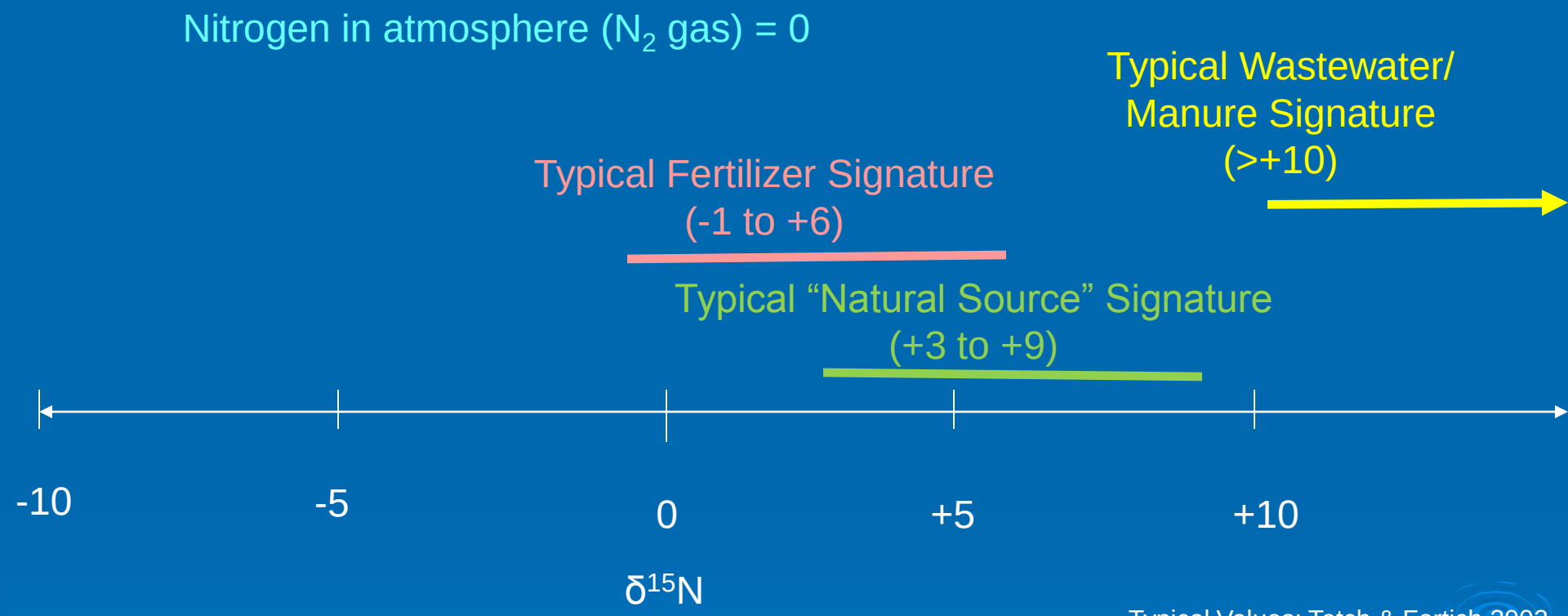
What's the big deal with denitrification?

- Not all nitrogen loaded to groundwater is transported to the springs
- Some of it becomes "inert" N_2 gas
- That portion is no longer of concern
- Also, as denitrification occurs, it can change the nitrogen isotope signature of that portion not converted back to N_2 gas
- Nitrogen isotope signatures have been used as "tracers" of nitrogen sources

Isotope Results

- Single sample from springs by SJRWMD
- Two more recent studies
  - MACTECH – nitrogen chemistry and nitrogen isotopes
  - FDEP / USGS – nitrogen chemistry, nitrogen isotopes, and oxygen isotopes
- Recent studies did well / spigot samples, as well as both Rock and Wekiwa Springs

Two forms of stable isotopes for nitrogen ^{14}N and ^{15}N. Ratio = $\delta^{15}N$ value



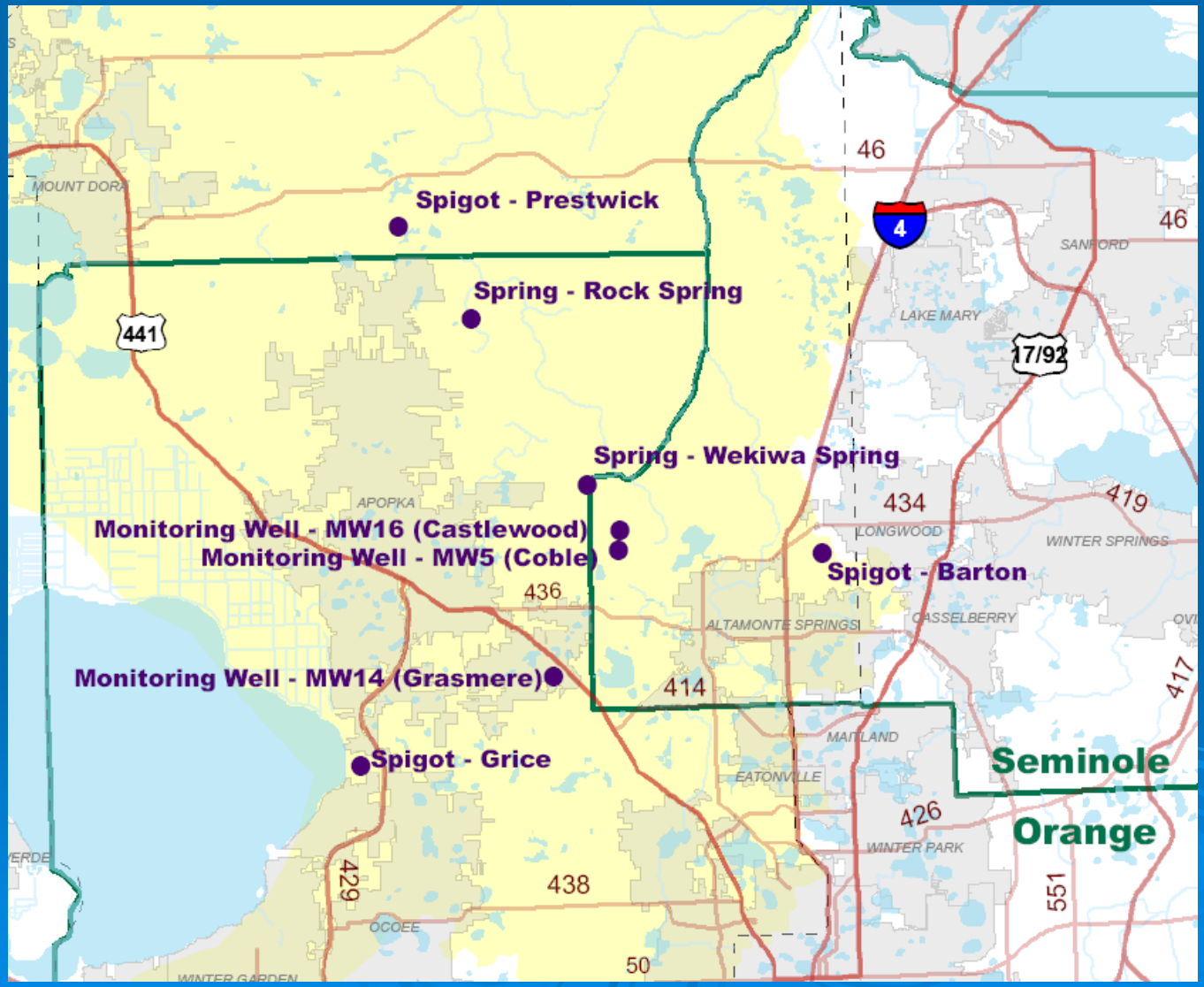
Typical Values: Totch & Fortich 2002

- **What about + 8.6?**
  - Prior value from Wekiwa Springs
    - single sample in 1999 from USGS (for SJRWMD)
  - Interpreted as a mixture of sewage/manure and fertilizer
  - Need nitrate concentration as well – as it also fits within range of "natural"

Recently completed studies

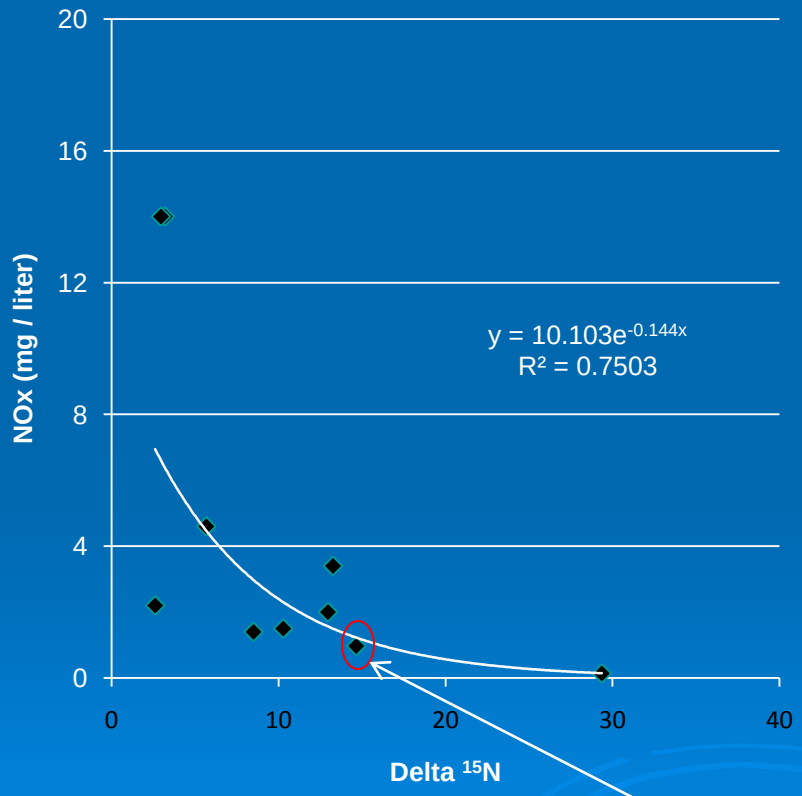
- MACTECH study
  - Nitrogen chemistry and nitrogen isotopes
  - 2008 and 2009
  - More than 20 sites, plus Wekiwa Spring vent
- FDEP / USGS study
  - Nitrogen chemistry and nitrogen and oxygen isotopes
  - 2009
  - 3 wells, 3 spigots, Rock and Wekiwa Springs vents

Sampling Sites for FDEP / USGS Study (2009)

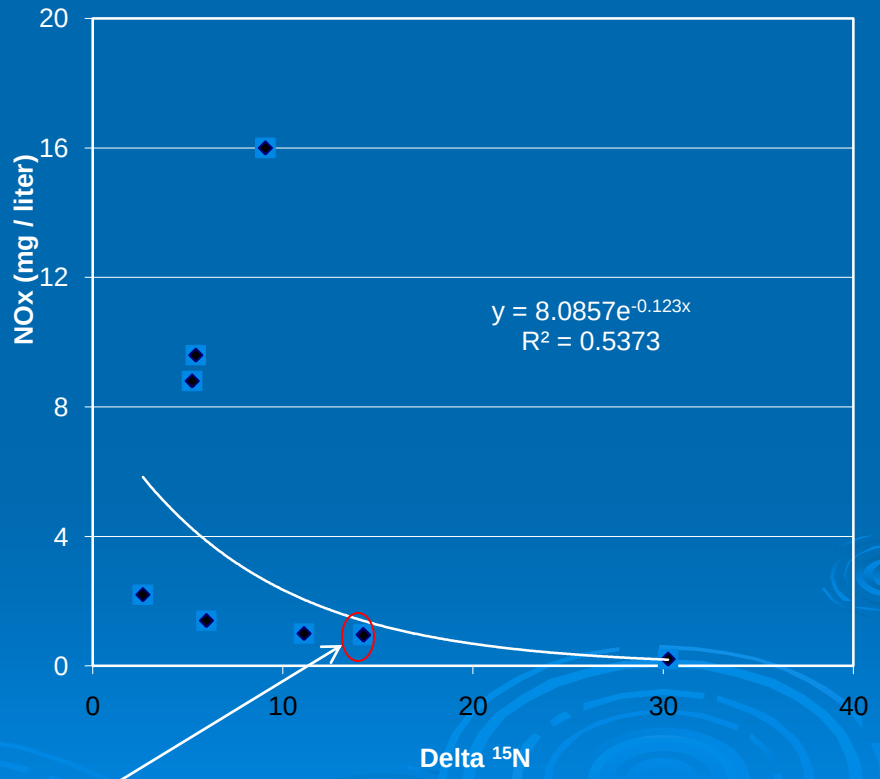


Similar results from two additional yet separate efforts

Data from MACTEC (2009)



Data from FDEP / USGS (2009)



Values from Wekiwa Spring Vent

Interpretation of isotope data

- Overall pattern of decreasing nitrate concentrations with increased $\delta^{15}N$ values
- Generally speaking, highest nitrate concentrations within the recharge area are not due to sewage/manure
- Fertilizer application seems to be the basis for most of the highest nitrate levels
- However, water samples from Wekiwa Spring vent had $\delta^{15}N$ values of 14.6 and 14.2, indicating sewage/manure at that location

So, while fertilizer is the basis for high nitrate in the watershed, most of the nitrate exiting the vent is due to sewage, right?

Not necessarily.

Potential effect of denitrification

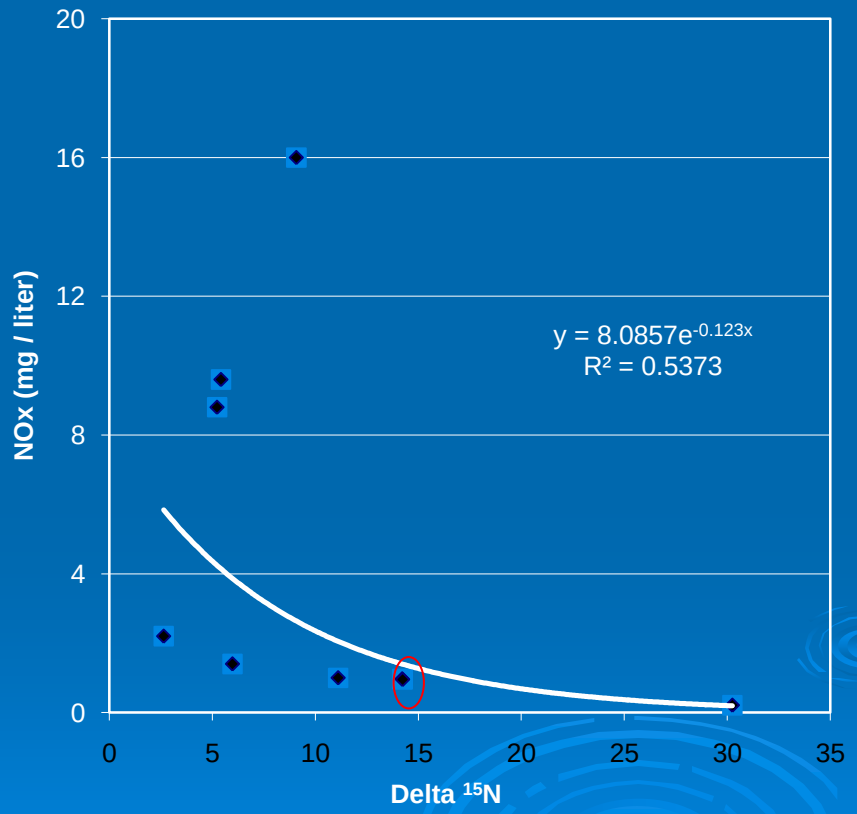
High levels of nitrate from far away have a fertilizer signature.

But as they travel to the spring vent (15 to 20 years?) nitrate levels could decrease via denitrification and partial fractionation.

This would result in both lower nitrate levels, and higher $\delta^{15}N$ values as you get farther from sources

This also could explain the pattern.

Need to understand if this process is occurring.



Additional data collected (2009)

- Oxygen isotopes (^{16}O and ^{18}O) of the oxygen within NOx molecules
  - Oxygen from fertilizer formation will have atmospheric signature ca. 18 to 25*
  - Oxygen from waste / sewage will have signature ca. -5 to +10*
  - Oxygen isotope values will increase with denitrification (as does nitrogen) but if values are below 18, not likely due to fertilizer alone
  - Additional N_2 in groundwater would suggest denitrification is occurring and producing this inert gas

* Says who? Aravena et al. (1993), Kendall et al. (1995), Kendall (1998), Panno et al. (2001), Silva et al. (2002)

What was found?

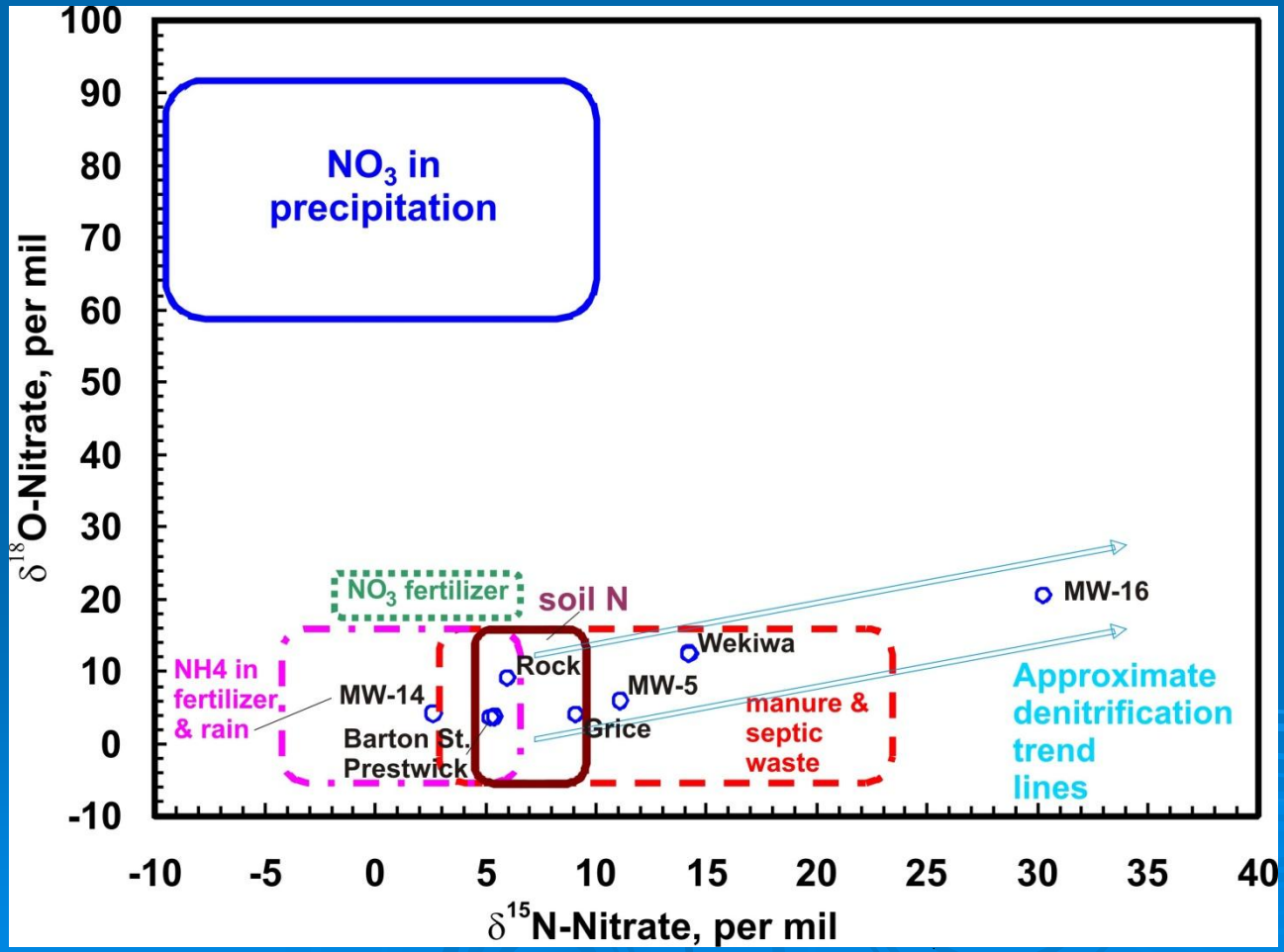
- Rock Spring
  - Nitrate value of 1.4 mg / liter
  - $\delta^{15}N$ value of 6.0
  - $\delta^{18}O$ value of 9.1
  - Excess N_2 gas of 1 mg / liter
- Wekiwa Spring
  - Nitrate value of 1.0 mg / liter
  - $\delta^{15}N$ value of 14.2
  - $\delta^{18}O$ value of 12.5
  - Excess N_2 gas of 2 mg / liter

Overall conclusion from USGS –

Wekiwa: influence from manure / sewage

Rock: manure / sewage influence not as strong, but still clear

Both: additional influences from fertilizers and natural sources



But “sewage” could come from wildlife, right?

- Possible, but likely more wildlife in the past, when nitrate levels were lower
- More wildlife in Ocala National Forest, where large mammals are more common
- Yet “reference” springs in Ocala National Forest (e.g., Juniper and Alexander Springs) have levels of nitrate of ca. 0.02 mg / liter
  - TMDL target for nitrate is about 10 times higher than “reference” spring nitrate
  - TMDL not aiming for pristine or pre-development conditions

Results from previous studies suggest following sources of nitrogen. Independently derived results from isotope studies support that conclusion.

Source Type	MACTEC	DOH	Isotope Studies
Residential fertilizer	Y	Y	Y
Agricultural fertilizer	Y	Y	
Golf course fertilizer	Y	Y	
Other fertilizer	Y	Y	Y
Livestock	Y	Y	Y
Human Wastewater	Y	Y	
Natural Background/ Atmospheric	Y	Y	Y

Additional studies

- Early August – additional sites sampled
  - Address issue of OSTDS vs. reclaimed water
  - Use of additional tracers of sewage treatment vs. disposal
  - Results not yet available