

Determining Groundwater Contamination Sources In Colorado Using $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ Isotopes

Ashton Dilka*, Troy Bauder*, Erik Wardle*, & Karl Mauch**

Colorado State University, Fort Collins, CO * and Colorado Department of Agriculture**

Introduction

Groundwater wells along the South Platte River alluvial aquifer in Colorado have median nitrate-nitrogen levels often exceeding the EPA drinking water quality standard of 10 milligrams per liter (mg L^{-1}). This area offers an interesting problem in identifying the source of this groundwater contamination because it is highly diverse. The area has large areas of irrigated cropland, large animal feeding operations and dairies, as well as an urban influence from the Denver metropolitan area. While these wells have been carefully monitored and documented since 1993, analysis has not been done to determine the sources of these high nitrate levels. Groundwater samples were taken 3 times from 22 wells along the South Platte in Weld County and analyzed for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotopic composition in order to attempt to better understand the sources of the high nitrate levels in the groundwater. Samples were sent to the UC Davis Stable Isotope Facility to be analyzed.

Background

Several stable isotopes can be used to distinguish sources of nitrate in groundwater. These include $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and $\delta^{87}\text{Sr}$ (Widory et al. 2003). The use of isotopes has been used extensively and dates back to the 1970s (Xue et al. 2009). Exner & Spalding used ^{15}N ratios to discover sources for 268 wells in southeast Nebraska in 1981 and 1982 (1984). Inorganic sources of nitrogen such as fertilizers have typical $\delta^{15}\text{N}$ values between -6‰ and $+6\text{‰}$ and $\delta^{15}\text{N}$ values for organic sources such as manure and sludge between $+4\text{‰}$ and $+25\text{‰}$ (Xue et al. 2009). $\delta^{18}\text{O}$ isotopes can be used to distinguish between atmospherically deposited NO_3^- and microbial-produced soil NO_3^- (Casciotti et al. 2002). This helps distinguish between synthetic fertilizers and other sources. Distinct values of $\delta^{18}\text{O}$ for synthetic fertilizers are between $+17\text{‰}$ and $+25\text{‰}$ (Xue et al. 2009).

Isotopic Analysis at UC Davis Stable Isotope Facility Denitrifier Method

- ✓ The UC Davis Stable Isotope Facility uses the Denitrifier Method to measure both nitrogen and oxygen isotopic composition of nitrate.
- ✓ Uses denitrifying bacteria to generate nitrous oxide gas from the nitrate (Sigman et al. 2001).
- ✓ Bacteria lack N_2O -reductase activity.
- ✓ Superior to other methods because of its high sensitivity (Casciotti et al. 2002).
- ✓ All nitrite must be removed from the samples because it interferes with the bacteria.



Field Sampling

Materials & Methods

Groundwater Sampling

- ✓ Collected 3 times in late June, late July into early August, and early October 2013
- ✓ 21-22 groundwater wells
- ✓ Recorded depth, dissolved oxygen, pH, specific conductivity, temperature, and TDS.
- ✓ Filtered in the field through a 0.2 micron filter nylon disk
- ✓ 60 mL samples were collected immediately placed in a 4°C cooler
- ✓ Samples were kept in a 4°C cooler until they were frozen.

Surface Water Sampling

- ✓ Samples were collected at the same three intervals as the groundwater samples
- ✓ 11 surface water sites
- ✓ Samples were taken from the thalweg of the rivers or as close as possible depending of flows and safety.
- ✓ 60 mL Nalgene bottle and immediately place in a 4°C cooler.
- ✓ Samples were filtered in the lab through a syringe and a 0.2 micron filter disk.
- ✓ Samples were kept in a 4°C cooler until they were frozen.

Removal of Nitrite

- ✓ Nitrite was removed by 5% Sulfamic acid method (Granger, J & D. Sigman, 2009)
- ✓ There was nitrite in most of the surface water samples but only one groundwater sample.
- ✓ Nitrite ranged from 0.017 ppm to 0.441 ppm.
- ✓ Sulfamic acid addition ranged between 150-250 μL .
- ✓ Reacted for a minimum of 30 minutes at a pH less than 2
- ✓ Samples were neutralized with 2 M NaOH to pH of 6-8.

Sampling Locations

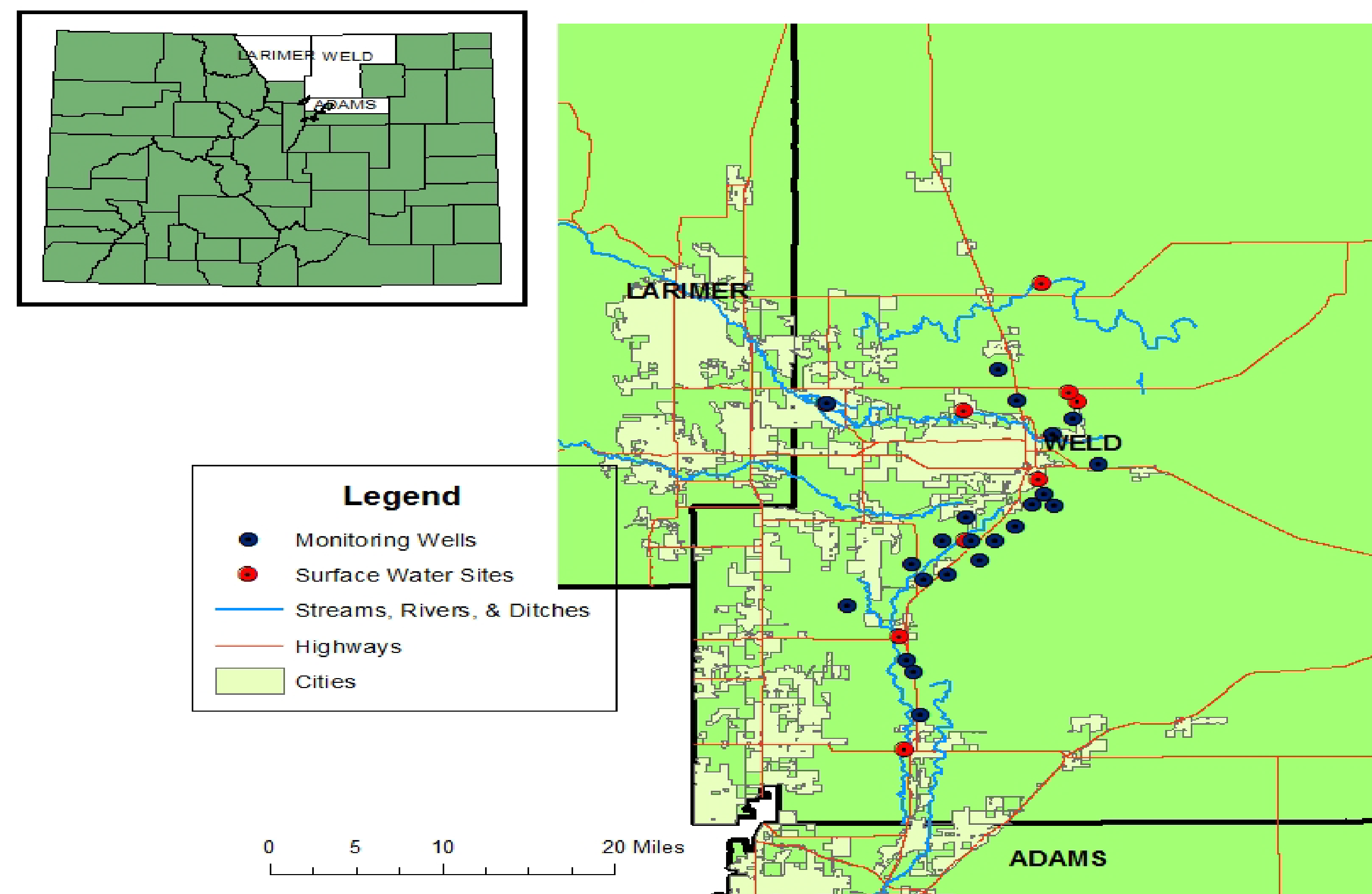
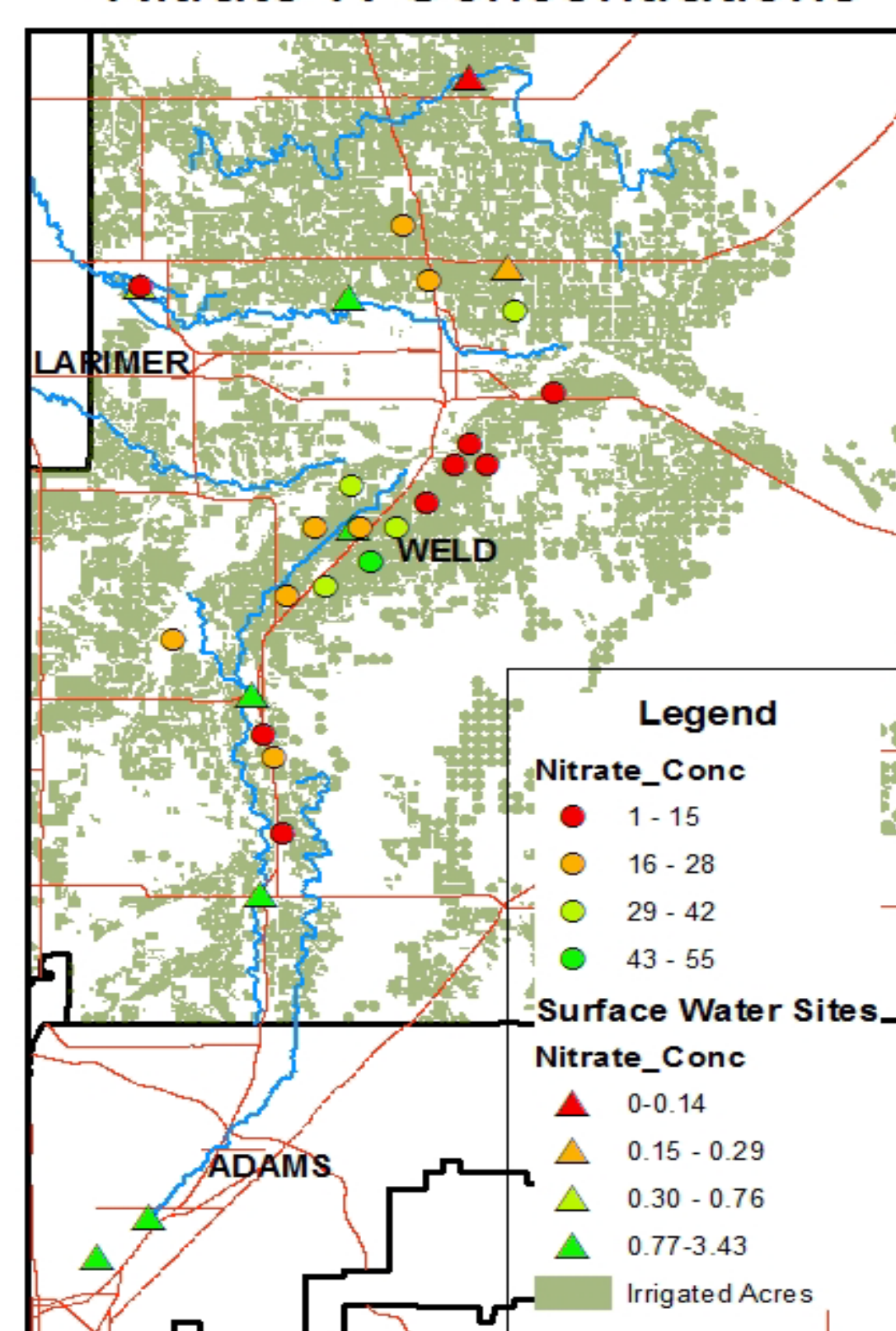


Figure 1. Map of Sample Locations

Nitrate-N Concentrations



$\delta^{15}\text{N}$ Isotopic Ratio

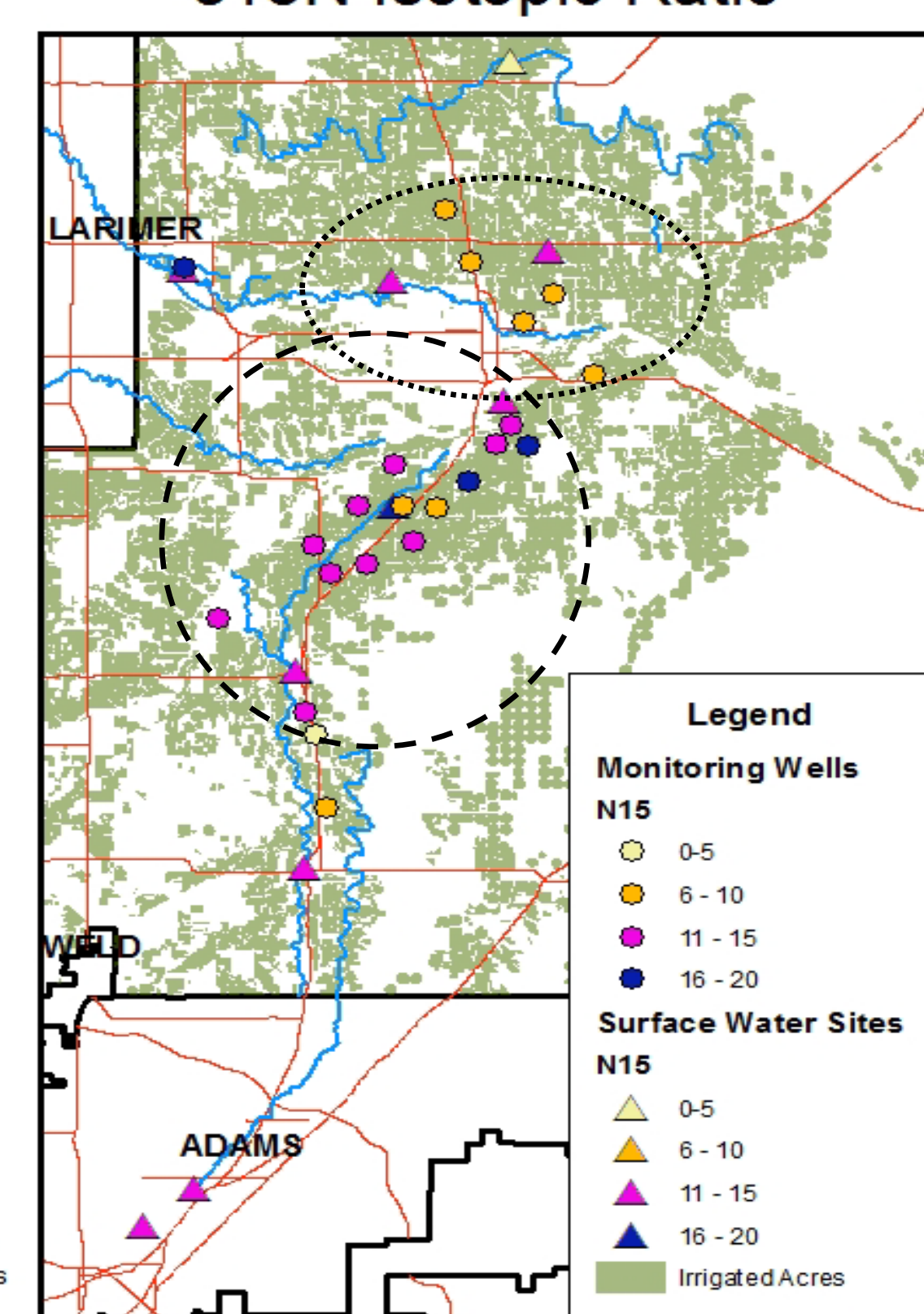


Figure 2. Maps of NO₃-N concentration and $\delta^{15}\text{N}$ gradients across sample area.

Preliminary Results

- ✓ $\delta^{15}\text{N}$ isotopic ratios from groundwater and surface water samples are statistically different ($p=0.03$), but $\delta^{18}\text{O}$ isotopic ratios ($p=0.80$) are not (Figure 3)
- ✓ The relationship between $\delta^{15}\text{N}$ and nitrate concentration is not well explained by linear regression. (Figure 4)
- ✓ Samples with similar $\delta^{15}\text{N}$ signatures appear to be grouped geographically. (Figure 2)
- ✓ First sample set isotopic signatures suggest organic source of nitrate in area. (Figure 5)

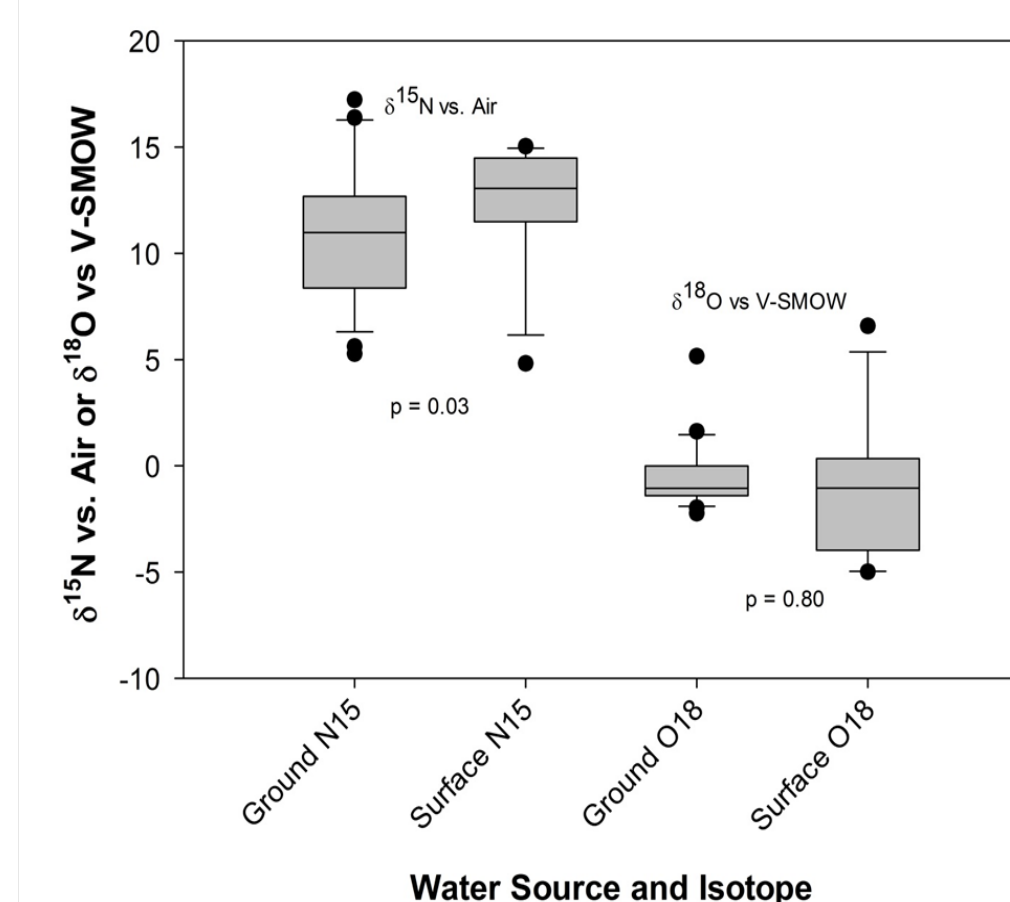


Figure 3. Median, 25th, 75th (box) and 10th and 90th percentiles (whiskers) of $\delta^{15}\text{N}$ and $\text{O}18$ isotopic ratios.

NO₃-N Concentration vs $\delta^{15}\text{N}$

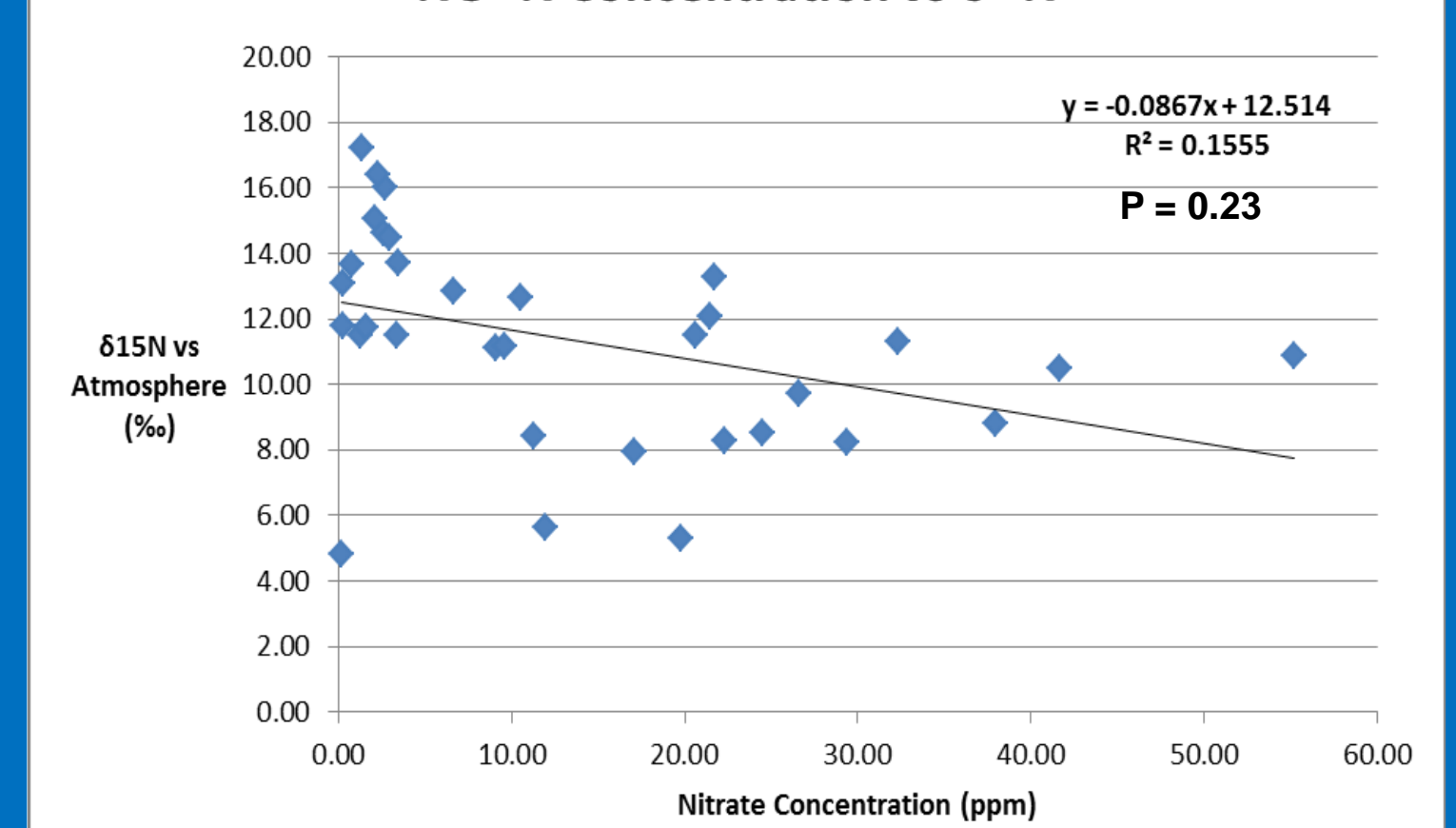


Figure 4. NO₃-N Concentration vs. $\delta^{15}\text{N}$ regression

$\delta^{15}\text{N}$ vs. $\delta^{18}\text{O}$

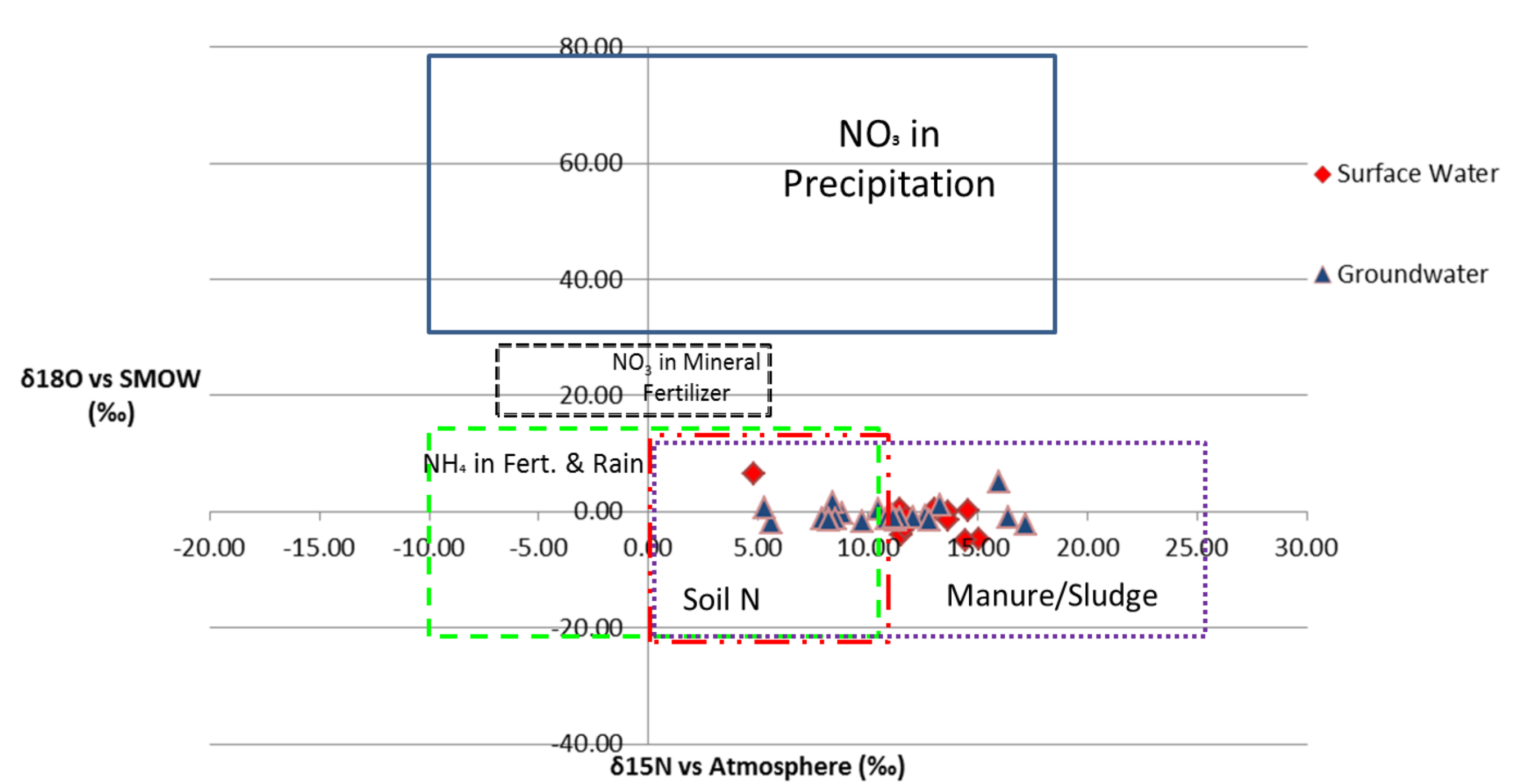


Figure 5. Samples plotted as $\delta^{15}\text{N}$ vs $\delta^{18}\text{O}$. Source boxes recreated from Widory et al. 2004

Future Work

- ✓ Process and analyze isotopic data from last 2 sampling sets
- ✓ Boron isotopic analysis will be used to better differentiate between animal and human sources
- ✓ Perform spatial analysis regarding CAFOs, irrigated agriculture, and waste water treatment plants in sample area
- ✓ Utilize results to make recommendations as to education and policy in the area

References

- Casciotti, K. L., et al. "Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method." *Analytical Chemistry* 74.19 (2002): 4905-4912.
- Exner, Mary E., and Roy F. Spalding. "Ground-Water Contamination and Well Construction in Southeast Nebraska." *Ground Water* 23.1 (1985): 26-34.
- Granger, Julie, and Daniel M. Sigman. "Removal of nitrite with sulfamic acid for nitrate N and O isotope analysis with the denitrifier method." *Rapid Communications in Mass Spectrometry* 23.23 (2009): 3753-3762.
- Sigman, D. M., et al. "A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater." *Analytical chemistry* 73.17 (2001): 4145-4153.
- Widory, David, et al. "Nitrate in groundwater: an isotopic multi-tracer approach." *Journal of Contaminant Hydrology* 72.1 (2004): 165-188.
- Xue, Dongmei, et al. "Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater." *Water Research* 43.5 (2009): 1159-1170.

Acknowledgements

This work was funded by the Agriculture Chemicals and Groundwater Protection Program at the Colorado Department of Agriculture.