Assessing Nitrate Leaching Hazard From Groundwater Recharge in Almonds

Project No.: **17-WATER7-Horwath**

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Objectives:

The overall objective of the project is to determine the risk of increased nitrate (NO_3^-) leaching into the underlying aquifers under winter groundwater recharge management in almond orchards on two contrasting soil sustainability classes determined by the Soil Agricultural Groundwater Banking Index (SAGBI).

1. Determine nitrogen cycling efficiency at two sites over one year (initially and subsequent years if support is available) - conduct soil coring to a depth of 30 feet to determine nitrate concentration in the deep vadose zone on two contrasting soil suitability classes, a moderately good and good/excellent soil suitability sites for recharge potential, before and after recharge events to assess leaching potential to contribute to a conceptual model of nitrate loading to groundwater (year 1).
2. Intensive core sampling on two large fields with contrasting soil types will give insights into the spatial variability of nitrate and solute transport of nitrate, as well as texture/stratigraphic controls on these flow patterns in two soil landscapes of different suitability for groundwater

recharge. This information can be used in future projects to inform model predictions on how vertical and horizontal soil and vadose zone heterogeneity affects the travel time, path, and biogeochemical transformations of nitrate as it moves below the rooting zone (year 1).

3. Data from intensive coring will be combined with extensive coring results from almond sites being examined in other ongoing projects (leverage results from Horwath, PI ($1.8M) NIFA# 2014-06565, providing economic evaluation of agricultural adaptation to climate and water constraints across CA. Horwath & Bachand (McMullin Project $5M and $2M from Terranova Ranch) will provide data on groundwater recharge (6K acres) used to restore Kings River flood flows. Bachand (NRCS Conservation Innovation No.68-9104-0-128 $75K; and Terranova Ranch, >$100K) will provide information on the technical feasibility of diverting storm flows to agricultural lands, Horwath CoPI CDFA California Specialty crops, potential for groundwater recharge in specialty crops).
4. Using stable isotopic profiles of nitrogen (N) and oxygen (O), determine the amount of nitrate attenuation by denitrification in the deep vadose zone (year 1-2).
5. The collected field data from intensive and extensive efforts will be used to parameterize a water flow and transport model, HYDRUS, that is currently being established with an extensive (less cores per field but multiple fields) field sampling effort on multiple cropping systems, including almonds to understand the nitrate leaching risk under groundwater recharge scenarios. (hypothetical year 2). Intensive data is required to build the 3-demensional capability of HYDRUS 3D.
6. Parameterize and validate a 3D model of the subsurface and nitrate distribution to constrain HYDRUS 3D with intensive and extensive data to construct a water flow and solute transport routine to determine nitrate loading to the groundwater table under varying almond cropping systems. We will use the model to extrapolate management practices and groundwater recharge scenarios based on soil properties and hypothetical water availability. This effort will answer questions as to which management practices mitigate nitrate contamination, the timing and concentration of nitrate transport to groundwater, whether groundwater recharge exacerbates or dilutes nitrate contamination over time, and how almond growers can participate in groundwater recharge activities without risk of liability (year 2 request).

Interpretive Summary:

In response to drought, farmers, out of necessity, turn to groundwater to meet their irrigation needs as surface water allocations are reduced. However, this has led to groundwater overdraft which threatens the long-term viability of California's production agriculture. Agricultural groundwater recharge presents an innovative climate change adaptation tool for farmers to secure a long-term water supply and buffer against surface water allotment reductions during future droughts, while mitigating potential damage from flood events. During times of excess water, such as in El Niño years, water can be diverted onto participating farmer's fields to recharge the underlying aquifers, which have the capacity to store three times the amount compared to surface reservoirs[1]. The potential benefits of groundwater recharge, in addition to a reliable future basin-wide water supply, include decreasing downstream flood risks by removing excess water from near flood stage rivers, reducing pumping costs by increasing groundwater levels, flushing salts from the rooting zone, increasing water storage in the root zone, and mitigating land subsidence.

However, of particular concern, is the potential to exacerbate nitrate (NO_3^-) contamination of at risk or already contaminated aquifers. We are examining the potential of groundwater banking in almond orchards to mobilize legacy nitrate in the soil. We did an extensive sampling across three cropping systems, grapes, tomatoes, and almonds in the Kings River Basin. We found that grape cropping systems had the lowest NO_3^- concentrations and posed the lowest threat to groundwater aquifers. However, nutrient management could make the difference in NO_3^- loading to groundwater. Nitrate levels differed by management with drip irrigation showing lower concentrations of NO_3^- below the rooting zone compared to sprinklers.

We also examined the difference in NO_3^- concentrations in soils that are classified as soil hydrologic grouping A, more permeable soils, and soil hydrologic grouping C/D, less permeable soils. We found that group C/D soils had higher NO_3^- levels in the upper four meters but this pattern disappeared deeper in the soil, suggesting that the magnitude of leaching and crop N removal dictate NO_3^- levels in the subsurface.

After a recharge event we intensively cored down to 30 ft (nine meters) on one almond site in Modesto. We found very low levels of NO_3^- compared to the sampling done prior to the groundwater banking application. This could be due to leaching either via uniform flow or preferential flow paths. However, we also are examining the potential for this large amount of water application to allow for denitrification to occur in the deeper subsurface sediments. Denitrification represents a permanent sink for NO_3^- as it converts NO_3^- to dinitrogen gas which is not a threat to aquifers. The potential of groundwater banking on agricultural lands to benefit the health of the underlying aquifers in the Central Valley of California would provide strong incentives for this practice to be adopted. Isotopic signatures of ^{15}N and ^{18}O indicated that denitrification may be a significant process. We are verifying this on subsurface sediments using potential denitrification assays. We have found that there is potential to denitrify NO_3^- to less harmful dinitrogen gas below the rooting zone of cropping systems. After incubating subsurface sediments for 3 days we found that there is the potential to reduce up to 517 g NO_3^-- N/kg soil. These assays were carried out under ideal conditions for denitrification where plenty of NO_3^- and carbon were added to the system and anoxic conditions were allowed to develop. In the field, these ideal conditions would likely occur in “hotspots” and “hot moments”, if at all, under groundwater banking and only where the residence time of the water was such that anoxic conditions could develop.

The next steps include manipulating the environment of the incubations to see what factors are controlling or limiting denitrification from occurring in the deeper subsurface. Then a 2D TOUGHREACT water flow and solute transport model will be parameterized to understand if/when these conditions occur after a groundwater banking application and to see what the potential is to reduce NO_3^- loading to groundwater. Most water flow and solute transport models do not consider this reactive chemistry in their simulations, they could be significantly overestimating predictions of NO_3^- transport to groundwater.

Materials and Methods:

The first study area included an extensive survey of farms within the Kings River Basin in the San Joaquin Valley, CA. Using a Geoprobe (Geoprobe Systems, Salina, KS), cores down to 30 feet were taken across three different cropping systems, almonds, tomatoes, and grapes, and two different soil hydrologic groupings, class A or permeable soils, and class C/D soils or more impermeable soils. Three replicates per crop x soil hydrologic grouping were taken. Cores were then morphologically described, analyzed for texture, NO_3^- concentration, ^{15}N and ^{18}O isotopes, and dissolved organic carbon.

Class A soils are defined as soils with low runoff potential, with saturated hydraulic conductivity greater than 5.67 inches/hour (NRCS Part 630 Hydrology National Engineering Handbook), Class C soils are defined as having moderately high runoff potential and saturated hydraulic conductivity 0.14 inches/hour to 1.42 inches/hour and Class D soils have high runoff potential with saturated conductivity less than 0.14 inches/hour. Class C and Class D soils on farmland were considered in this study as many of these soils are deep tilled to remove restrictive soil horizons and to increase infiltration rates especially in orchard and vineyard systems (O'Geen et al. 2015). R studio was used for statistical analysis on the entire profile (entire nine-meter depth), top four meters and below four meters. These depths were chosen as a sudden decrease in the variability of nitrate occurred at four meters depth.

Table 1. Summary of sampling sites for first study.

Crops	Soil Hydrologic Class	Location Replicate	Replicate within Farm	Total Nuber of Cores	Site Code
3	2	2	3	36	
Almonds	A	1			Alm-A-1
Almonds	A	2			Alm-A-2
Almonds	C/D	1			Alm-CD-1
Almonds	C/D	2			Alm-CD-2
Tomatoes	A	1			Tom-A-1
Tomatoes	A	2			Tom-A-2
Tomatoes	C/D	1			Tom-CD-1
Tomatoes	C/D	2			Tom-CD-2
Wine Grapes	A	1			WGr-A-1
Wine Grapes	A	2			WGr-A-2
Wine Grapes	C/D	1			WGr-CD-1
Wine Grapes	C/D	2			WGr-CD-2

Cores from the first study were analyzed in the lab for NO_3^- , texture, moisture and electrical conductivity. For the first meter subsamples were taken every 25cm. Below the first meter samples were taken based on morphological changes within the core where distinct layers were identified. Where a lighter textured soil overlay a heavier texture layer, a sample was taken in the middle of the sandy layer, at the top of the heavier texture layer, and in the middle of the heavier texture layer to capture any NO_3^- that may have accumulated at the top of the heavier texture layer (**Figure** 1).

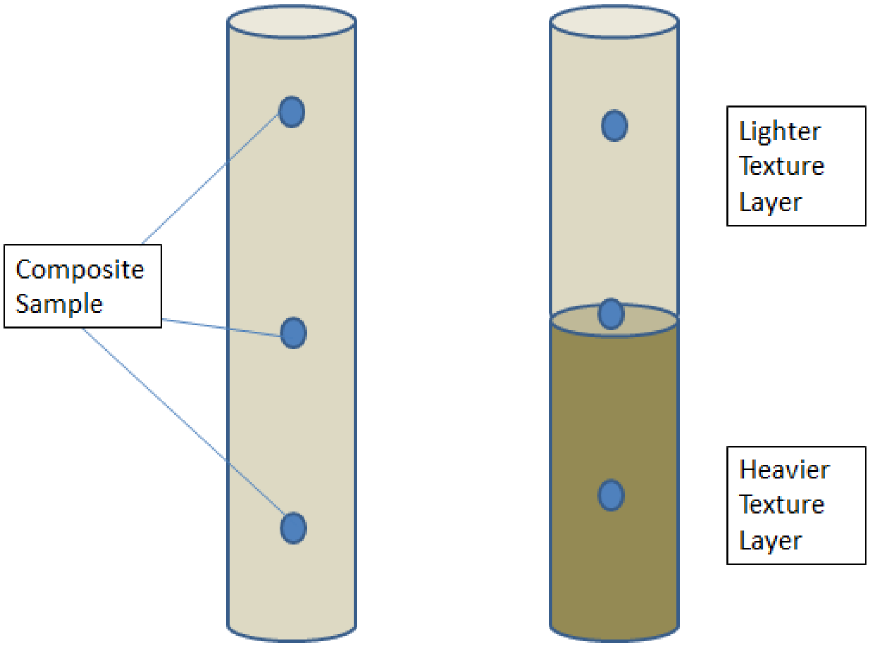


Figure 1. Core sample collection**.**

A modified pipette method was used to analyze texture whereby 5 g of soil were placed in 50 mL centrifuge tubes with 40 mL of 0.5% sodium phosphate and shaken overnight (Soil Survey Laboratory Methods Manual, 1992). After shaking samples were sampled hand shaken right before sampling and a 2.5 mL aliquot was taken and placed in a pre-weighed tin at 11 seconds and at one hour and 51 minutes for the sand and clay fractions, respectively. Tins were oven dried 105°C overnight and reweighed the next day.

Nitrate was analyzed by weighing 8-10 g into a 50-mL centrifuge tube and extracted with 2M KCl. Samples were centrifuge and supernatant were analyzed colorimetrically using a UV mini 1240, Shimadzu spectrophotometer as per the methods described in Doane and Horwath (2003) for nitrate. Nitrate is reported in ug NO_3^--N/g soil and then was normalized by water content by dividing the per mass soil by water content to get estimated pore water NO_3^- (mg NO_3^--N/L water). Moisture was determined gravimetrically in 105° C oven. Electrical conductivity(EC) was measured by creating a 2:1 deionized water to soil slurry and inserting a conductivity electrode (Rhoades et al. 1999). Total dissolved solid (TDS, mg/L) levels were calculated by multiplying EC (us/cm) by 0.64 (Iyasele and Idiata 2015)

The second study included an intensive 3D grid sampling effort on one almond orchard in Modesto, CA using the same Geoprobe machine as listed above (see sampling design below). Sixteen cores were taken down to 30 feet spaced evenly in a 36 sq ft area. The Modesto site soil is listed as hydrologic group A. Cores have been morphologically described, analyzed for texture, NO_3^- concentration, ^{15}N and ^{18}O isotopes, microbially reducible iron, dissolved organic carbon, and denitrification potential assays have been conducted. DNA analysis is pending due to complications in extracting and amplifying the DNA. Results will be analyzed using the R studio statistical package.

Combining both physical samples and electrical resistivity tomography samples, we are creating a 2D permeability field in TOUGH REACT, in which we will impose multiple management scenarios to see the effects of timing and quantity of nitrate to groundwater.

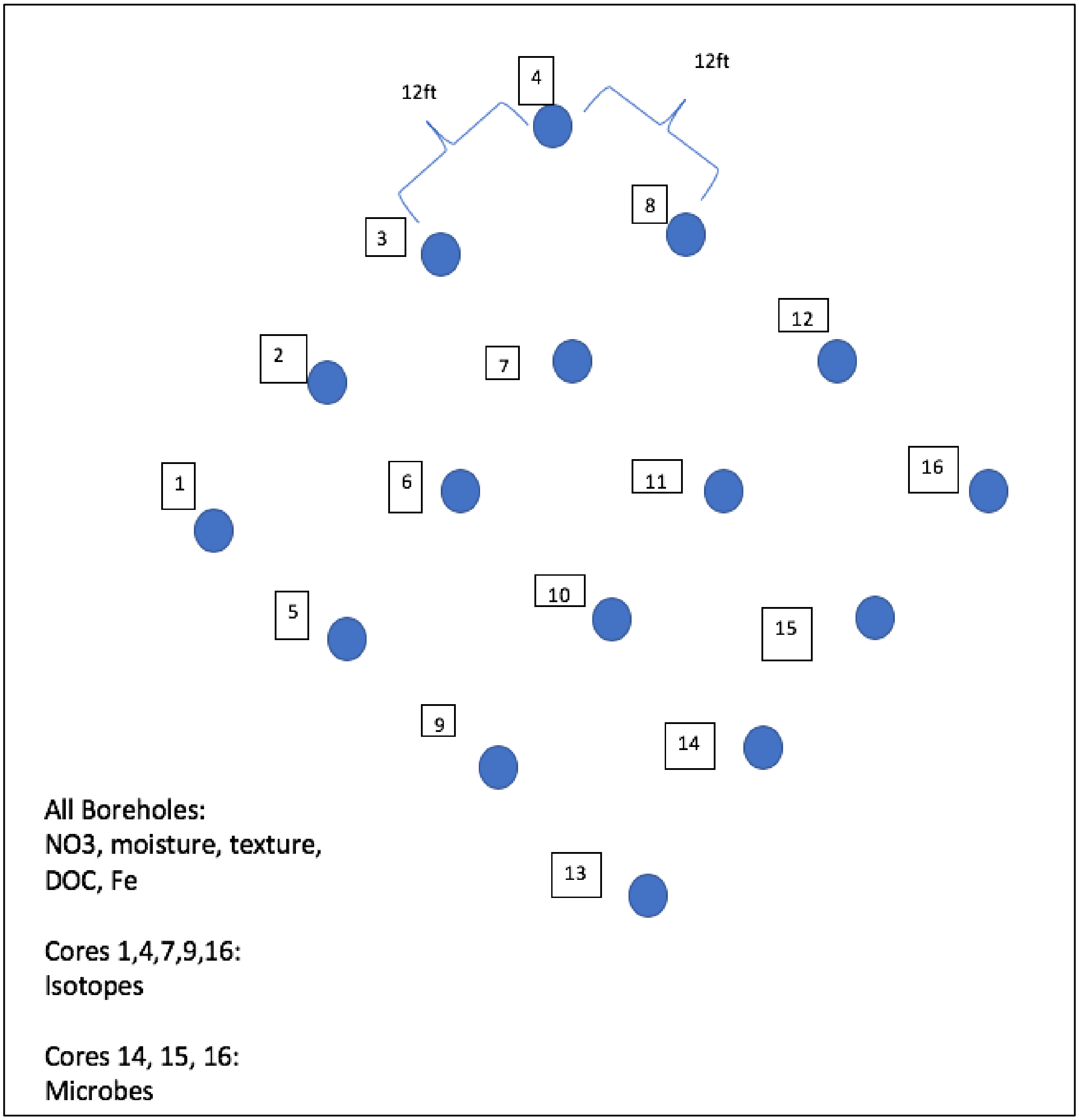


Figure 2: 3D intensive sampling design

Results and Discussion:

Crop, Farm, and Depth Effects

From the extensive sampling, we found that 79% of nitrate concentrations were above the 10ppm limit set by the EPA drinking water quality standard (**Figure 2**). Nitrate levels were higher in the rooting zone and decreased with depth, with the variance in nitrate concentration decreasing with depth as well.

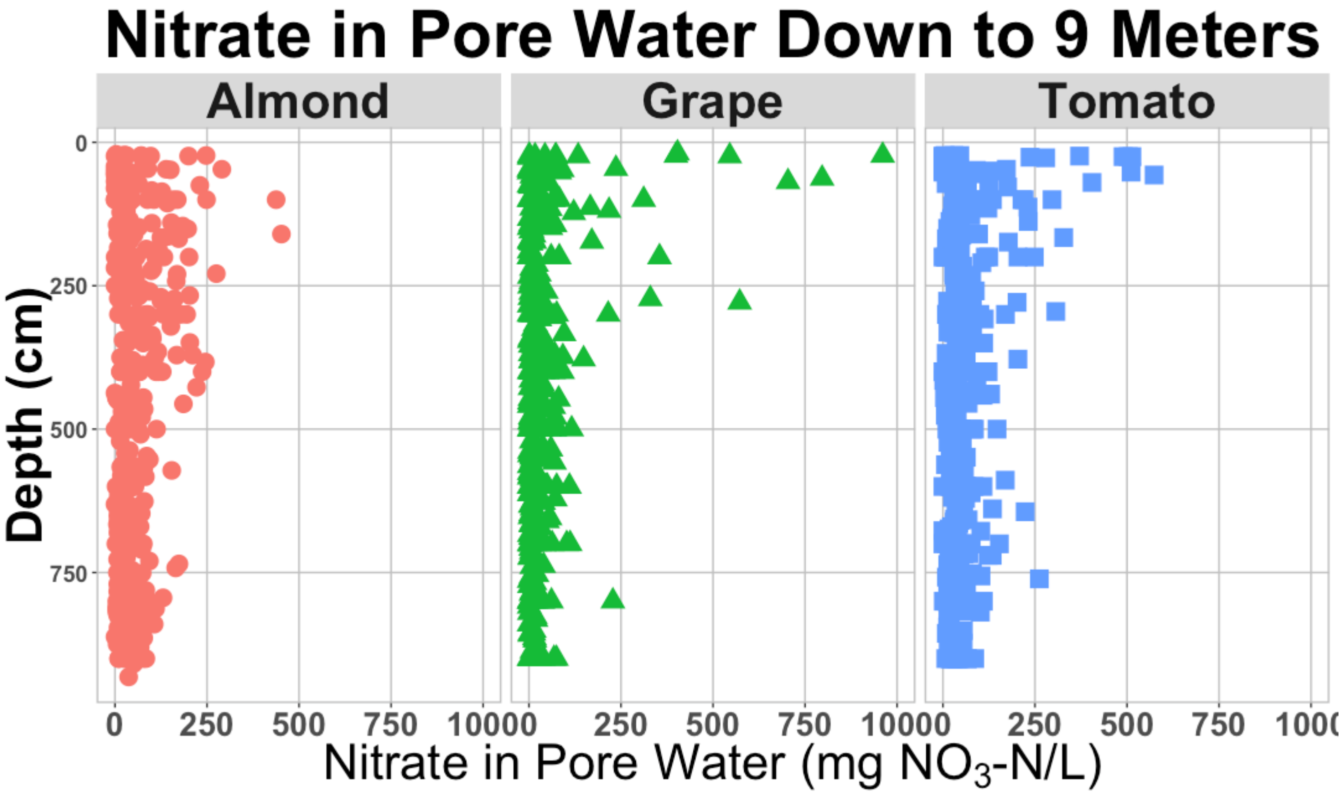


Figure 3. Pore water nitrate (mg N/L) down to 9 meters across almonds, grapes, and tomatoes.

Almonds and tomatoes had the highest soil nitrate concentrations (ug N/g soil) compared to grapes across the entire nine meter profile and in the top four meters(**Figure 2**). This pattern changed below four meters with tomatoes having the highest concentrations, followed by almonds and then grapes (**Figure 3**). This could be due to annual cropping systems having lower water use efficiency and higher N loading per year compared to perennial systems due to the more extensive root systems of perennial crops providing for more water and N recovery. Annual systems also are more intensive in terms of N and water management compared to perennial as these systems can have multiple crop harvest per year.

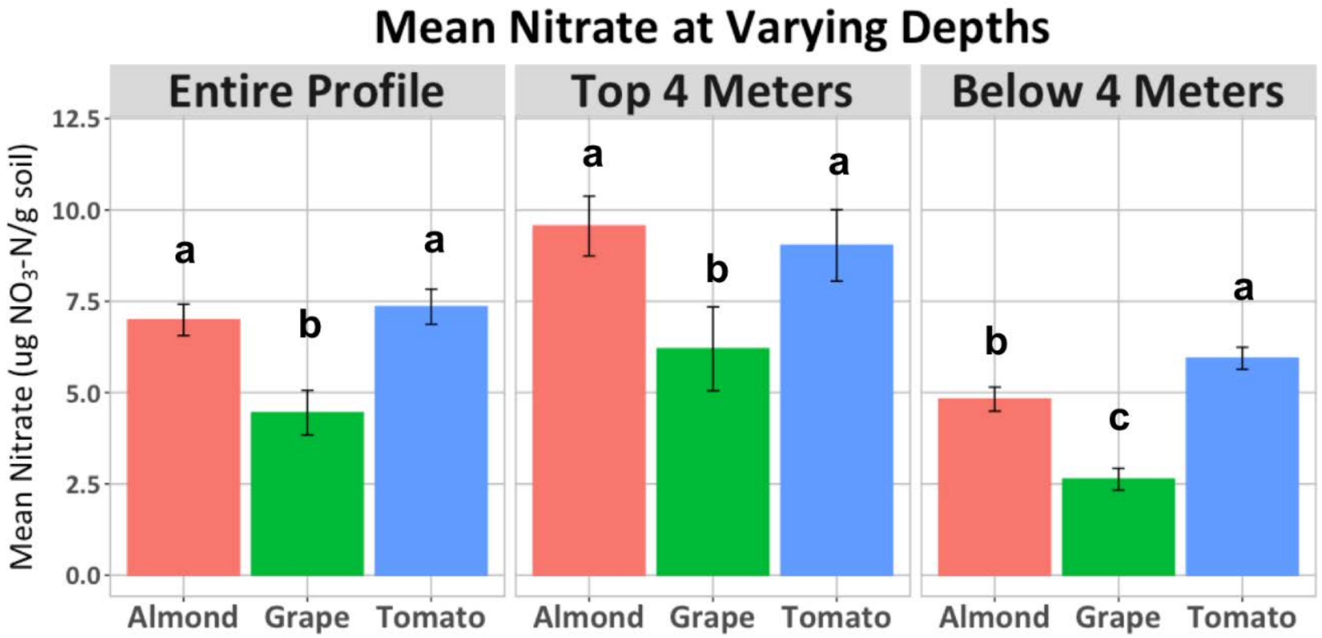


Figure 4. Mean soil nitrate concentrations (ug N/g soil) across almonds, grapes, and tomatoes across the entire nine-meter profile, top four meters, and below four meters. Error bars represent standard errors and differing letters signify 8statistically different means using Tukey means separation.

Total nitrate (kg N/ha) was also highest in the almonds and tomatoes compared with grapes across the entire nine meter profile and below four meters, however there was no difference in cropping system when the top four meters was examined (**Figure 4)**. When isolating the top four meters, the lack of difference could be due to a few farm's N management in grapes being higher than others, and thus the high variability and outliers in these nitrate not allowing for differences in means to be detected **(Figure 5**). It is interesting to note that the pattern below four meters for total nitrate does not match the pattern for nitrate concentration. This is due to the concentration data taking into account moisture. The fact that tomatoes, an annual crop, tends to have higher nitrate concentrations could imply that tomatoes have lower water and nitrogen use efficiencies than almonds and grapes, and thus more nitrate is lost below the rooting zone.

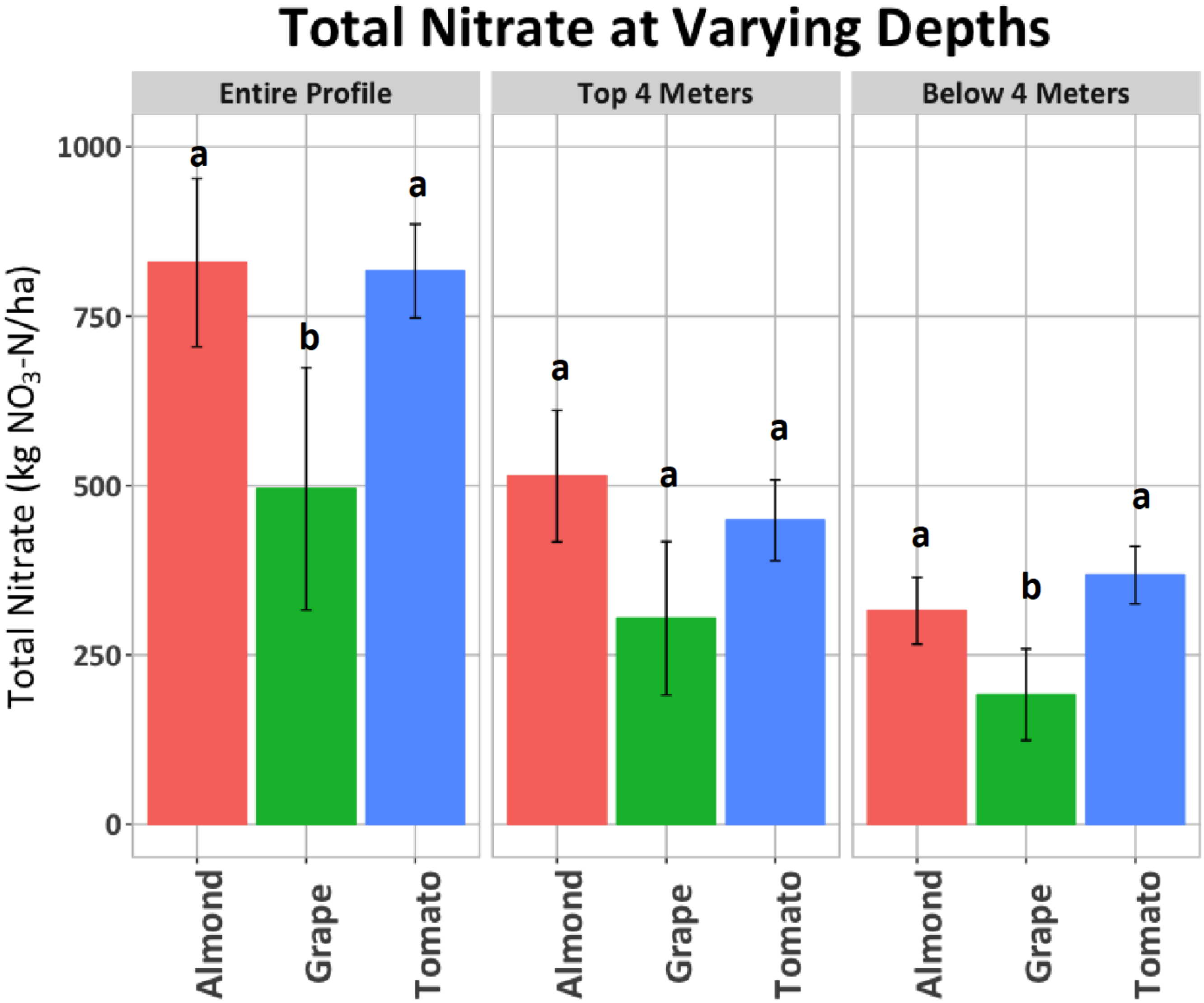


Figure 5. Total nitrate loading (kg/ha) by crop and depth.

It is clear that there is wide variability in mean nitrate concentrations within almonds (**Figure 5**). This could be due to management of fertilizer and water applications, however we only have management history data for two out of the four almond farms (Alm-A-2 and Alm-CD-2) and thus conclusions can only be speculative. Farm Alm-A-2 is irrigated with sprinklers, while Alm-CD-2 is irrigated using subsurface drip irrigation which could be the reason for the difference in mean nitrate levels.

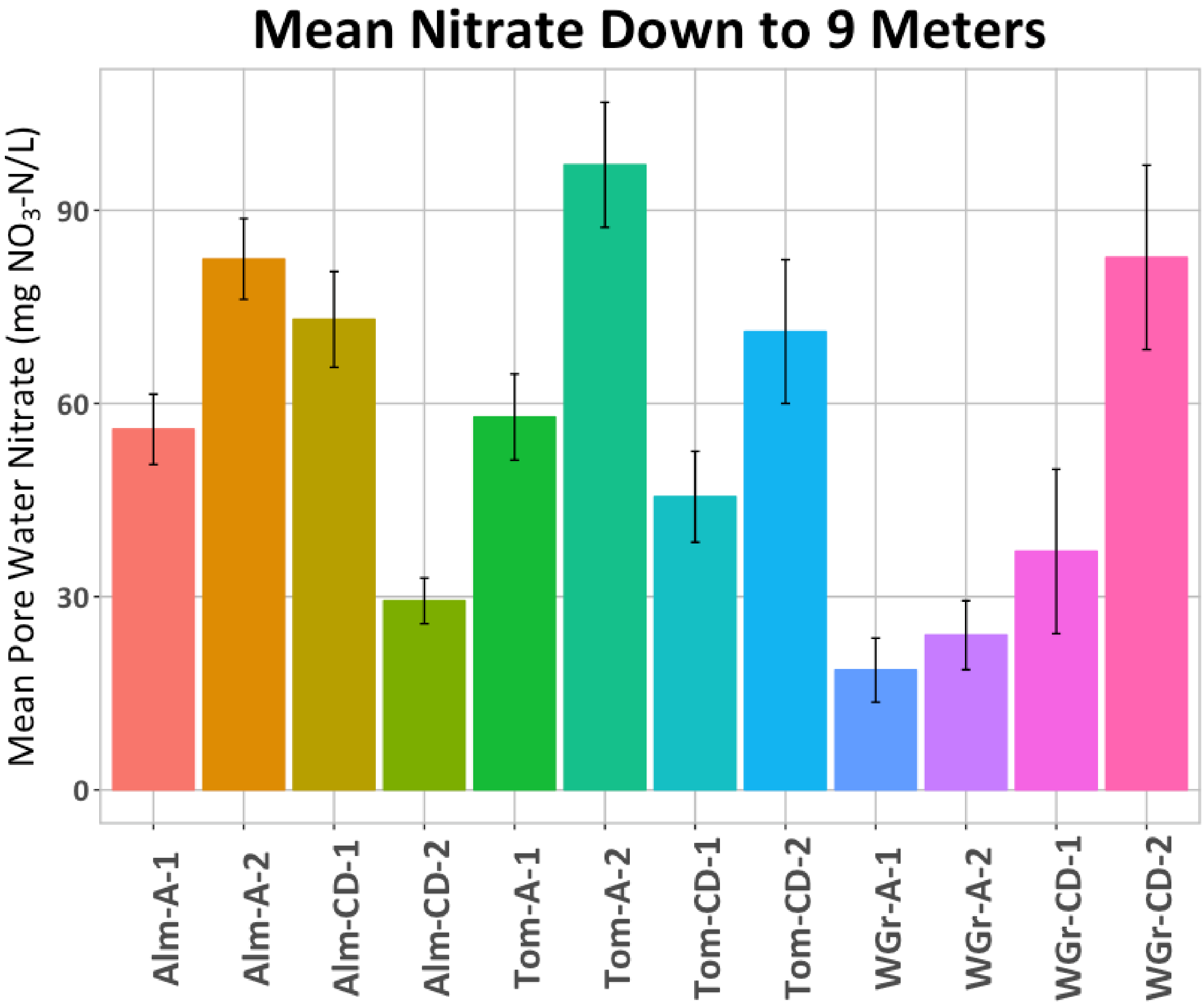


Figure 6. Mean pore water nitrate by farm. Error bars represent standard errors**.**

<u>Soil Factor Effects</u>

Statistically significant differences in NO_3^- (ug N/g soil) were found between soil hydrologic classes A (5.26 ug N/g soil) and C/D (7.18 ug N/g soil) in the top 4 meters, with group C/D soils having higher NO_3^- levels compared to group A soils. However, this relationship disappeared below the top 4 meters with no statistical difference between soil hydrologic classes. This suggests that while hydrologic grouping may affect the upper portion of the soil column, that vadose zone stratigraphy better correlates to nitrate concentration with depth. Hydrologic group C/D soils may be able to retain nitrate and moisture in the upper soil profile and delay the leaching of nitrate to lower layers.

Moisture, total dissolved solids (TDS), sand, silt, and clay were able to explain 33% of the variation in pore water NO_3^- concentrations (adjusted R^2= 0.33). Sand, silt, and clay were standardized by the associated thickness of the layer. All three fractions were positively correlated with NO_3^- but only clay and silt were significantly correlated, with clay having a larger influence on NO_3^- concentration (coefficient estimate for clay = 2.10). Nitrate was also significantly negatively correlated to moisture. This could suggest that clay layers are the limiting layers for water and nitrate movement, with implications for timing of nitrate to groundwater.

Table 2. Mixed effects model for nitrate in pore water using %Sand, %Silt, %Clay, moisture, and TDS as predictor variables.

	Coefficient Estimate	p-value
(Intercept)	4.183994	0
% Clay	2.097796	0***
% Sand	0.004632	0.5806
% Silt	0.070602	0***
Moisture	-4.503058	0***
TDS	-0.000122	0.6139
R^2=0.33		
Significance Values: 0 (***), 0.001 (**)		

On one farm, we examined the relationship between dissolved organic carbon (DOC) and nitrate. We regressed nitrate in the pore water against sand, silt, clay, moisture, TDS, and DOC (Table 3) . When DOC was added to the model, all other variable became insignificant with the updated model. The model accounted for 21% of the variation (adjusted R^2=0.21). However, the relationship between DOC and NO_3^- is unexpectedly positive, meaning more DOC correlated to more NO_3^-. These results were further explored in an intensive sampling in an almond orchard.

Table 3. Linear regression model of nitrate on sand, silt, clay, moisture, TDS, and DOC.

	Estimate	**Pr(>|t|)**
(Intercept)	0.710122	0.0243*
Clay	0.242808	0.4269
Sand	-0.075595	0.1788
Silt	0.12106	0.1525
DOC	0.041557	3.11e-05***
moisture	-0.997848	0.5702
R^2= 0.21		
Significance Values: 0 (***), 0.001 (**), 0.05 (*)		

For the intensive sampling a similar statistical analysis was conducted, however, this time the addition of iron measurements was included in the analysis. Iron can act in similar ways as DOC by donating electrons to reduce NO_3^- to N_2. At depth, iron may be more important than DOC in facilitating this process. With preliminary data we found that DOC is still significantly correlated with NO_3^- and the same trend is found (positive correlation of DOC and NO_3^-). Iron fractions, including currently available iron and that which could potentially be available to the microbial community, were not significantly correlated at the 0.05 level, however currently available iron is significant at the 0.1 level. The relationship between NO_3^- and currently available iron is negatively correlated which could signify the reduction of NO_3^- to N_2 by iron (II).

Table 4: multiple linear regression of nitrate concentration and DOC, iron, silt and clay

Nitrate = DOC + Currently Available Iron + Potentially Microbially Available Iron + Silt + Clay		
	Coefficient Estimate	**Probability**
Intercept	2.138×10^{-16}	1.000
DOC	2.72×10^{-1}	0.001440 **
Currently Available Iron	-3.497×10^{-1}	0.108760
Potentially Microbially Available Iron	4.358×10^{-2}	0.827962
Silt	-1.99×10^{-1}	0.250041
Clay	3.872×10^{-1}	0.000183 ***
R^2 = 0.1531		
Significance Values: 0 (***), 0.001 (**)		

We assessed the NO_3^- distribution with depth throughout the 16 cores. We found that NO_3^- was concentrated in the top meter and decreased with depth except for a few hotspots. This is due to the flooding event prior to sampling most likely leaching the NO_3^- below the nine meters or due to denitrification. We need to analyze the cores taken prior to the flooding event to calculate the mass balance. These data are still being analyzed.

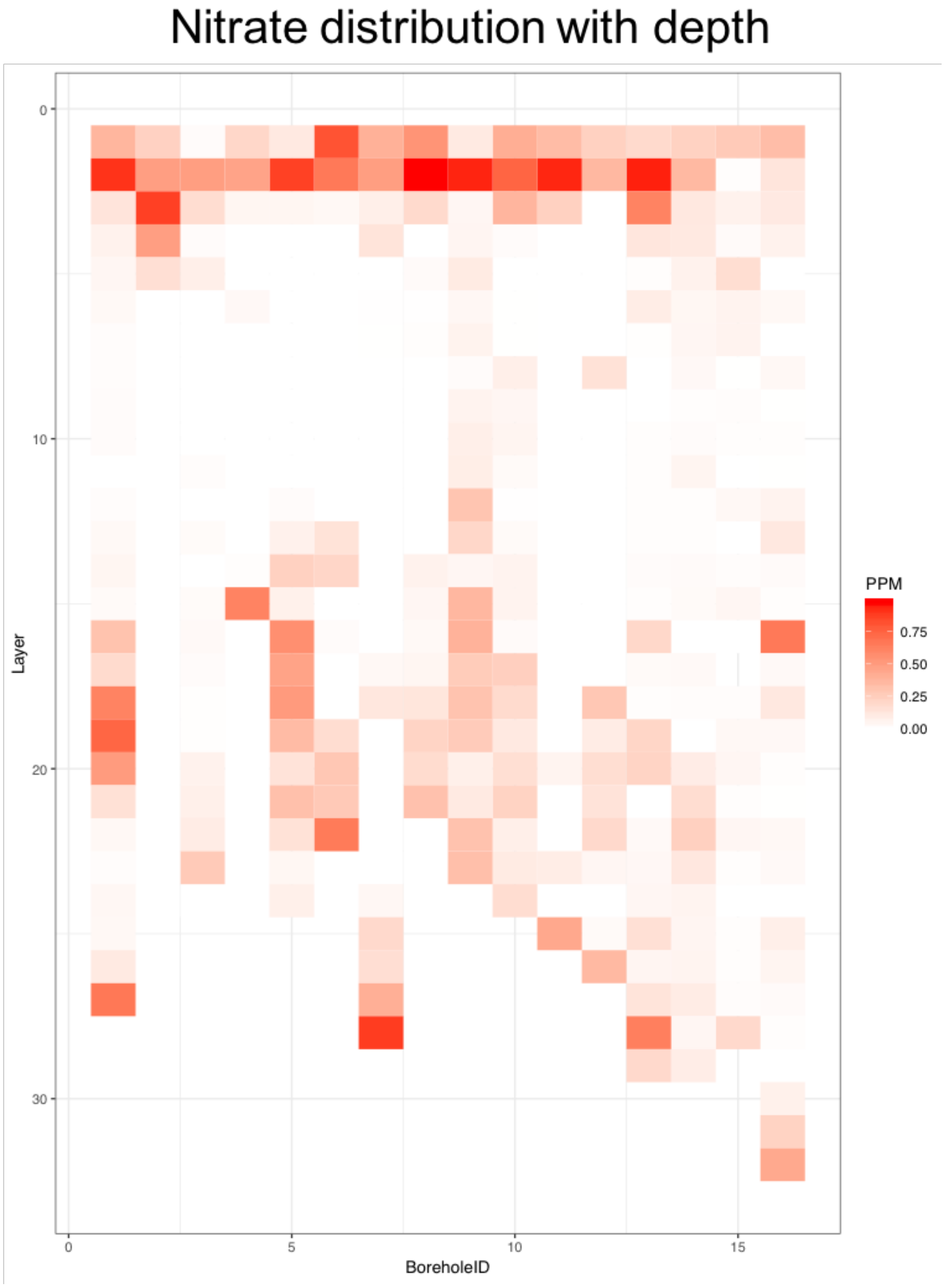
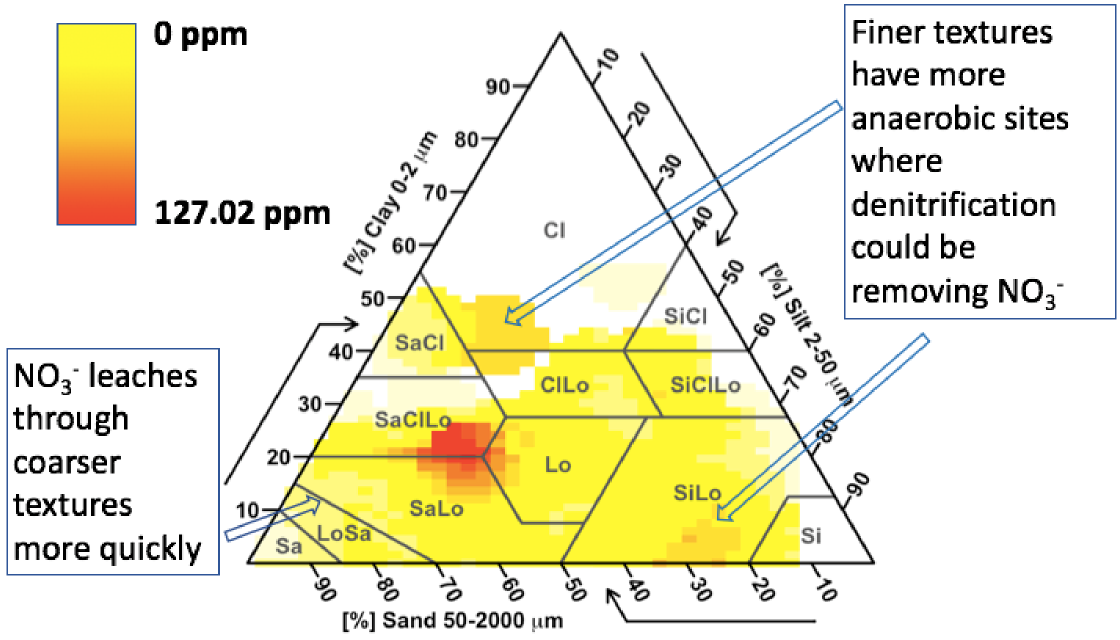


Figure 7: nitrate concentration with depth by borehole and layer down to 9 meters

We found that NO_3^- was higher in sandy clay loams, loams, and sandy loams compared to coarser textured sediments, as well as very finely textured layers. Finer textures can develop more anaerobic sites where denitrification could be removing NO_3^- compared to coarser soils. Nitrate is found in low concentrations in the coarsest textured layers because it leaches out of them quickly. However, NO_3^- in the medium textured sediments, such as the loams, have the highest NO_3^- concentrations as it is not leached out quickly and perhaps does not develop as many anaerobic sites as compared to the clay layers.

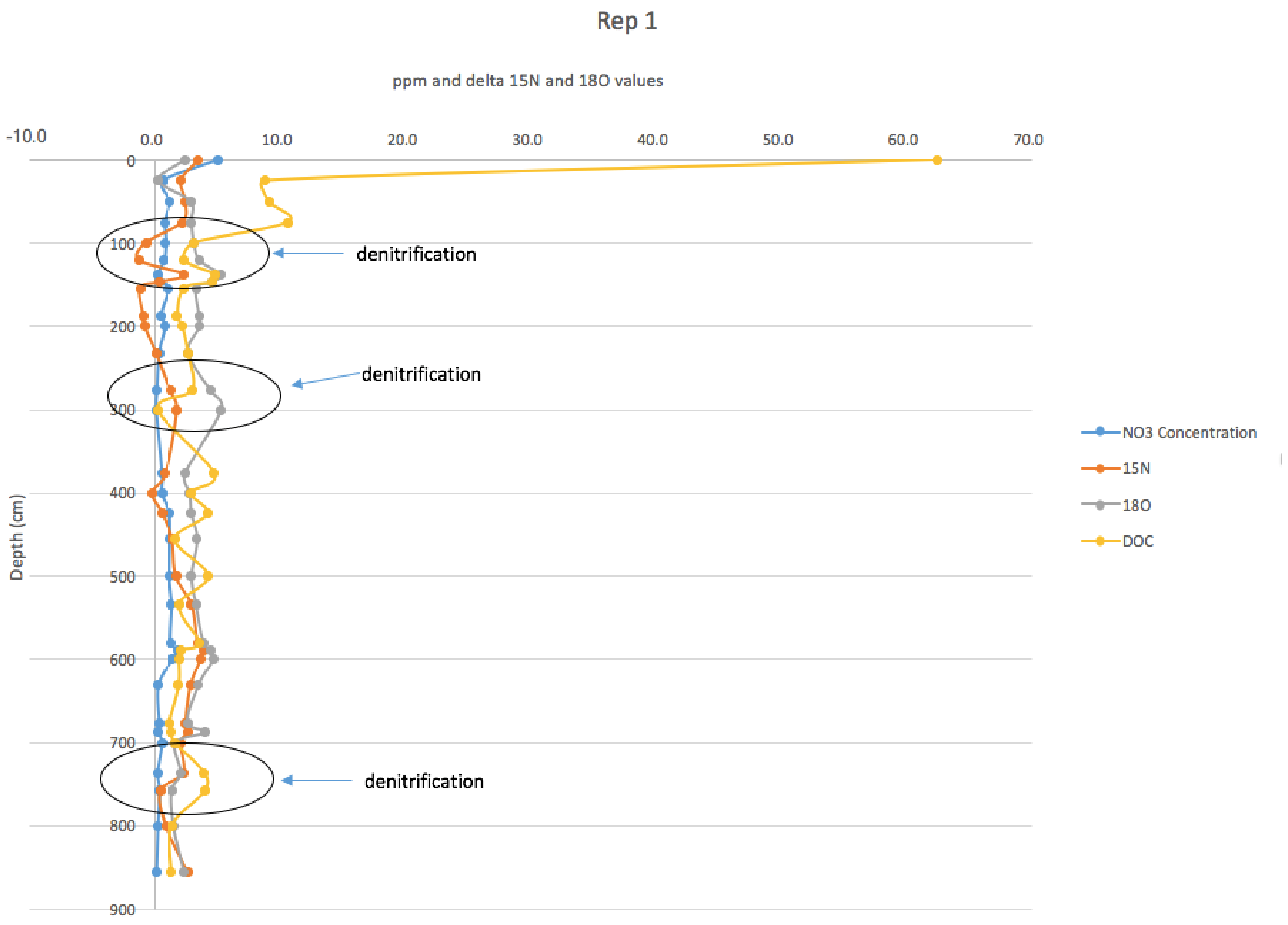


Finer textures have more anaerobic sites where denitrification could be removing NO_3^-

NO_3^- leaches through coarser textures more quickly

Figure 8: heat map of nitrate concentration and soil texture

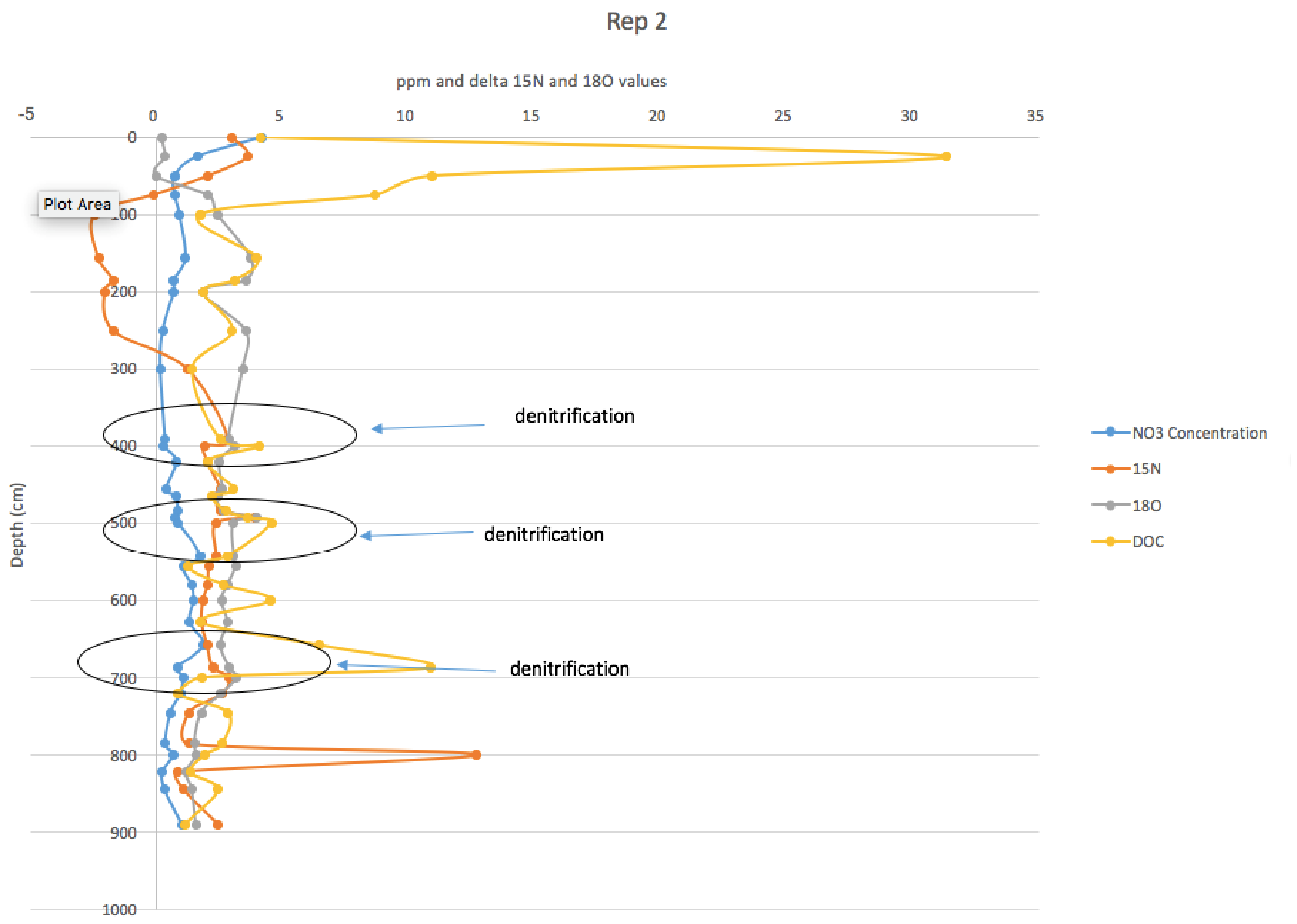
We also assessed the potential for denitrification with depth by measuring nitrogen and oxygen isotopes (**Figure 6)**. Where nitrate concentrations decrease and 15N and 18O increase could indicate that denitrification has occurred. We assessed three reps in one farm and the results are shown below and where denitrification has potentially occurred are highlighted. Evidence for the potential for denitrification was found deep in the profile, even at 700 cm. We further corroborated these findings by conducting denitrification potential assays in the lab on the soils from selected layers throughout the nine-meter depth.



denitrification

denitrification

denitrification


Rep 2
ppm and delta 15N and 18O values
-5
0
5
10
15
20
25
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Depth (cm)
0
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NO3 Concentration
15N
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DOC

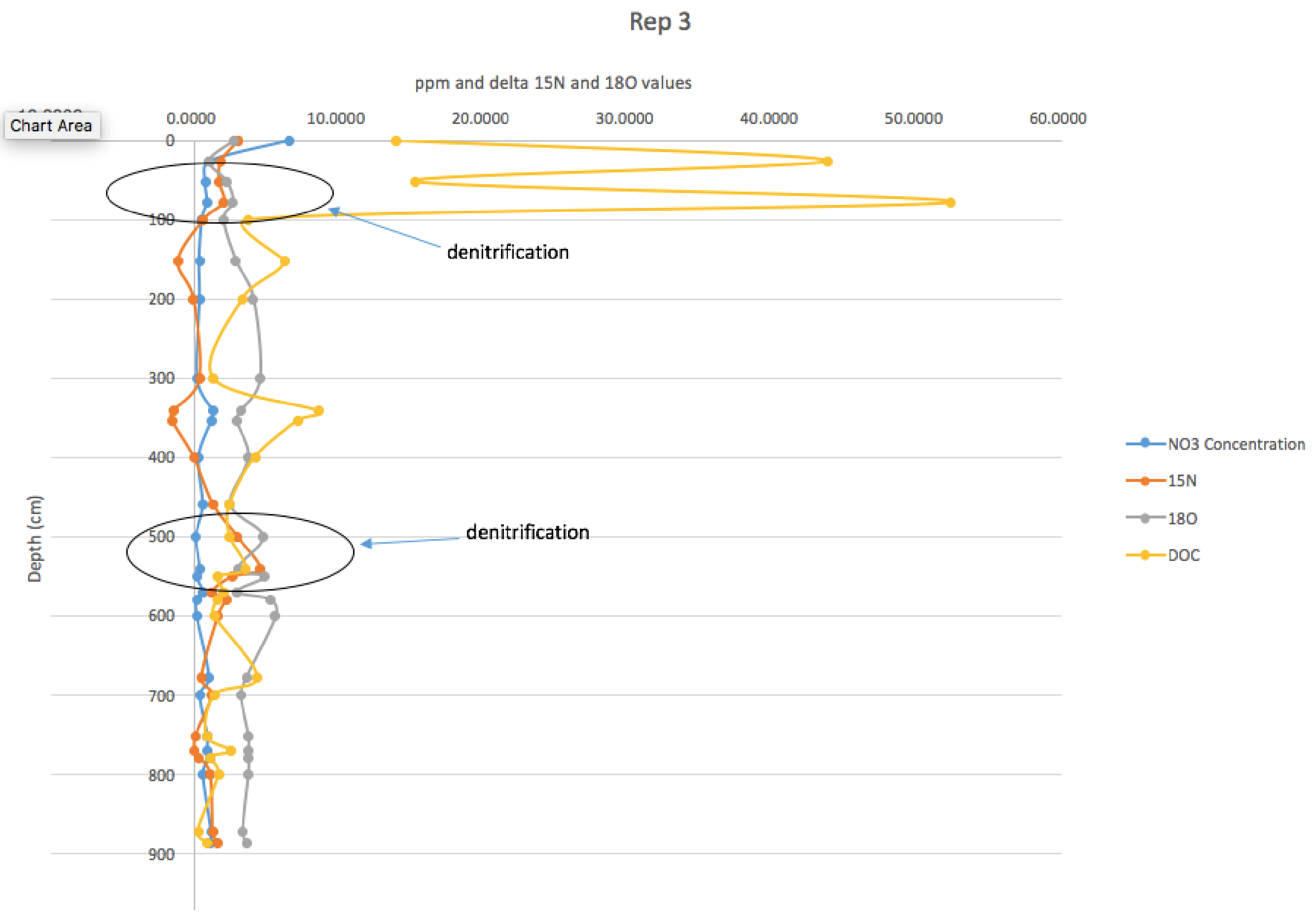

Figure 9. Nitrate concentration, nitrogen and oxygen isotopes, and dissolved organic carbon with depth for one site over 3 reps.

Layers from each meter increment and of contrasting textures down to 9 meters (30 ft) were assessed for their denitrification potential. Soils were tested with and without the addition of NO_3^- and glucose, the substrate to be denitrified and the electron donor needed to reduce the NO_3^- to N_2 respectively. Soils without the addition of NO_3^- and glucose had lower denitrification rates compared to those where substrate was added, however, this could be due to the very low initial NO_3^- concentrations. This lower denitrification potential was found in surface soils and deeper layers alike. When NO_3^- and glucose were added, denitrification rates increased five-fold. This suggests that there exists a microbial community in deeper layers that are able to reduce NO_3^- to N_2O/N_2 when the needed conditions are met including NO_3^- (the substrate to be denitrified), an electron donor to reduce the substrate (in this case glucose, but other electron donors such as reduced iron could also facilitate denitrification), and anoxic conditions. Analysis of denitrification potential with depth and by texture will be conducted and regressed against variables such as iron content and DOC concentration. These experiments will be used to parameterize a water flow and solute transport model, TOUGHREACT, to identify how implementing groundwater banking will affect these environmental conditions.

Because TOUGHREACT cannot model plant dynamics we will use a different water flow and solute transport model, HYDRUS, to model the root zone. These data are being compiled and the output from HYDRUS will be used as the input for TOUGHREACT, which will model the

vadose zone down to groundwater under almond orchards. The baseline scenario has been established and the following scenarios will be tested:
6 stratigraphy scenarios
  Varied in geological heterogeneity (based on data collected)
  Varied in number of soil textures sandy vs clayey layers

For each stratigraphy scenario have 3 different flooding amounts
  3 feet over one week
  6 feet over one week
  12 feet over one week

For 12 ft flooding amount vary frequency of application
  1.7 ft per day for 7 days
  3 feet per week for 4 weeks

The questions we will be focusing on include:

1. Is denitrification happening in the deep vadose zone? If so how much nitrate can be denitrified under normal irrigation practices compared to groundwater banking?
2. Does the timing and frequency of groundwater banking impact whether denitrification in the vadose zone is occurring and the magnitude of that denitrification?
3. What is limiting denitrification in the vadose zone? (This question will be answered using lab incubations and then hopefully we can tweak the model to include multiple conditions for parameters to be met for denitrification to occur)
4. Do different cropping systems lead to different nitrate and carbon distribution patterns with depth in the vadose zone and could this influence rates/amount of denitrification occurring?
5. How does stratigraphy effect amount of denitrification? (one clay layer vs three etc)

Research Effort Recent Publications:

H. Waterhouse, H.E. Dahlke, W.R. Horwath. *Managed Groundwater Recharge: Hydrologic Regime Change and Nitrogen Dynamics.* California Plant & Soil Conference, Fresno, 2018.
H. Waterhouse, S. Bachand, H.E. Dahlke, P. Bachand, W.R. Horwath. (2018, March). *Assessing nitrate leaching from groundwater recharge in almond cropping systems.* UC Cooperative Extension, Fresno, CA.
H. Waterhouse, H.E. Dahlke, W.R. Horwath. *Managed Groundwater Recharge: Hydrologic Regime Change and Nitrogen Dynamics.* Almond Board Meeting, Sacramento 2017.
H. Waterhouse. *A Climate Change Adaptation Tool: Groundwater Banking.* (November 2017). One Health Symposium, Davis, CA 2017.
H. Waterhouse, S. Bachand, H.E. Dahlke, P. Bachand, W.R. Horwath. (2016, December). *Assessing nitrate leaching from groundwater recharge in almond cropping systems.* Almond Board Meeting, Sacramento, CA 2016.

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