Mitigation of Reactive N Mobilization (N_2O and NO_3^-) Using Injected, High Frequency Nitrogen Fertigation (HFLN) and Nitrification Inhibitors in Almond

Project No.: **12-AIR2-Smart**

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Objectives:

1) Quantify seasonal N_2O-N produced by continuous ‘high frequency’ N fertigation (HFLC) (15 lbs N per acre per application) of UAN as compared with seasonal N_2O-N emitted during conventional split applications of 60-90 lbs N per acre per application as fertigation events.
2) Determine the influence of high frequency, low nitrogen concentration (HFLC) on yield and water use efficiency so that both yield based greenhouse gas emissions and yield based water use can be gathered.
3) Introduce and validate the concept of adopting continuous nutrient feeding during highest N demand and fine root growth for Californian almond and other nut production systems (e.g. pistachio).

4) To compare N_2O production in the soil profile and estimated total surface emissions from two different forms of nitrogen (N) fertilizer: (1) urea ammonium nitrate (UAN) and (2) potassium nitrate with calcium nitrate (KN+CN), both under HFLC fertigation.
5) To identify controlling factors on soil N_2O production such as water-filled pore space, soil temperature, inorganic N concentration, pH, texture, and soil carbon (organic and inorganic) to develop a greater understanding of the controls on N_2O emissions from arid fertigated soils and almond orchards

Interpretive Summary:

This project evaluates reactive nitrogen mobilization, mainly nitrate (NO_3^-) leaching and emissions of the greenhouse gas nitrous oxide (N_2O) during 'high frequency' split nitrogen applications (HFLC) to almond. Standard practice is to apply 20-40% of N during 4-5 fertigation events that ramp up N concentration during periods of high N demand like nut fill. HFLC applies about 5% of total N during most irrigation sets. Data collection for our two field studies began in February, 2013, in an orchard in Belridge, California, managed by the Paramount Farming Company. An experiment was initiated there by Dr. Patrick Brown's Laboratory (UC Davis) in 2011 in concert with Farm Advisor Blake Sanden. The purpose of the experiment was to test the effects of HFLC or fertigation (20x/year) against conventional fertigation (4x/year). The experiment also includes various N sources to be tested within the HFLC practice. Dr. Brown's laboratory is studying effects on yield and on almond root foraging and N uptake. Our work complements theirs by studying the effects of these practices on N_2O emissions and NO_3^- movement below the root zone.

Our first study assessed the effects of HFLC on the emission of N_2O, directly compared to conventional fertigation. HFLC fertigation has received very little attention, despite its potential to reduce nitrate leaching and nitrous oxide emissions while improving N provision to crops. We have found no field studies of HFLC fertigation in sandy loam soils, which are typical of almond orchards in California. One lab-based study on a sandy loam soil has suggested that HFLC should lower overall N_2O emissions (Ciarlo *et al.*, 2008).

It was our hypothesis that the steady provision of N in smaller quantities under HFLC has two possible benefits. Firstly, the microbial community can be expected to produce a proportionally lower amount of N_2O under conditions where NO_3^- is less abundant; lower concentrations of NO_3^- should mean a higher proportion of N applied undergoes complete denitrification to N_2 (Senbayram *et al.*, 2012). Secondly, the possible "conditioning" of the microbial community under HFLC fertigation means that more denitrifying bacteria may be present in the soil under HFLC fertigation. Again, higher competition for the principle substrate of NO_3^- when it is scarce may cause more N to be completely denitrified to N_2 rather than being released as N_2O.

Our second field study, undertaken simultaneously, tested a high-ammonium N source (urea ammonium nitrate solution (UAN)) against a nitrate-only N source (potassium nitrate (KN)+ calcium nitrate (CN)), both under HFLC fertigation. UAN is said to be a high-ammonium source because most of the urea applied will be quickly hydrolyzed to ammonium by soil bacteria. A few publications have observed lower N_2O emissions from nitrate fertilizers using subterranean drip systems (eg. Burger, 2011), but none have done so in the context of HFLC fertigation.

Preliminary results can be summarized as follows:

1) HFLC fertigation appears to have reduced N_2O emissions per unit UAN applied by about 17% on a sandy loam soil in the San Joaquin Valley, but the difference is not statistically robust.
2) Within the HFLC system, use of Calcium Nitrate+Potassium Nitrate (CN+KN) has significantly reduced N_2O emissions per unit N applied by about 45% compared to UAN.
3) Comparing our data to that of Schellenberg *et al.* (2012), who worked in the same orchard in 2009-2010, it appears that fanjet application of UAN results in approx. 62% lower N_2O emissions than from aboveground drippers. This agrees very well with other work studying drip and fanjet N_2O emissions from an almond orchard in more Northern and cooler climates near Arbuckle, California (Alsina, 2013).
4) Gas sampling at various depths in the soil profile following fertigations suggests that nitrification at shallow depths under UAN leads to higher N_2O emissions than from CN+KN. Results also show that CN+KN locates N lower in the soil profile, where less can be lost to the atmosphere as N_2O through partial denitrification.
5) The first year of data collection is still under way and analyses of controlling factors on N_2O production have not yet been carried out.

Materials and Methods:

Site description and orchard fertility practices: The experiments were conducted in a 13 year old high productivity orchard in Kern County. The average three-year yield in the orchard has been about 4,000 lb/ac/yr. The site has low native K fertility but received 200 lb/ac K for the past three years as winter banded sulfate of potash (SOP). Average ammonium acetate extractable K in an adjacent field with identical age, management and soil class has been recorded at 104 ppm in the top 18 inches and 81 ppm in the 18 to 36 inch depth. July tissue K levels averaged 1.2 % and range from 0.7 to 1.8%. Grower standard management consists of 275 lbs N applied as UAN in 4 fertigation events (Feb, April, June and post-harvest). K is supplied at 200 lbs K applied as 125 lbs SOP applied as a band in the wetted zone in January and 75 lbs K as potassium thiosulfate (KTS) applied at the same time as UAN fertigation. The orchard was irrigated using micro sprinklers (static jet, Bowsmith Fanjet®) on a weekly average irrigation cycle of 24 or 48 hour irrigation set as needed to match almond ET over a one to three week interval. A total of 52 to 56 inches of water has been applied seasonally. This is a very low rainfall region (<5 inches) with total effective rainfall (actually stored in the profile) of around 2 inches plant available water. The soil in the western set of this orchard is very uniform and classed by the USDA Natural Resources Conservation Service soil survey as a Kimberlina sandy loam, but is closer to a hybrid between the Kimberlina and Millham sandy loam with a slight bit of Panoche sandy clay loam (especially below a two foot depth) with respect to texture and fertility. There are no structural limitations/hardpans/layers, and infiltration and lateral subbing are excellent with irrigation being extremely efficient with little leaching past the 7 foot depth. Nonetheless, salts have tended to accumulate between the 4 to 7 foot depths (**Table 1**).

Table 1. Average soil properties

Depth	SP %	pH	EC dS/m	Ca (SP) meq/L	Mg (SP) meq/L	Na (SP) meq/L	Cl (SP) meq/L	HCO3 (SP) meq/L	CO3 (SP) meq/L	NO3-N ppm	Olsen-P ppm	X-K Ppm
0-18"	35	7.8	0.99	4.62	1.41	3.68	3.33	1.6	<0.1	1.1	4.2	104
18-36"	37	7.9	1.92	5.28	0.89	11.84	9.17	1.5	<0.1	0.9	2.0	81
4-5'			4.12				25.50			4.91		
6-7'			3.37				22.44			7.30		
8-9'			1.91				5.56			2.57		

Treatments: We evaluated only one rate of N application of 300 lb N per acre. For the last three years data was collected on yields and nitrogen use efficiency in association with the SCRI supported N-K rate fertility trial, and have shown a significant and economical marginal yield increase is realized when 350 lb/ac N applied, so that a treatment of 300 lb/acre N represented a reasonable comparison with the 275 lb/acre standard and insured that yields would be maximized. The results we acquire concerning N_2O emissions and NO_3^- leaching will be widely applicable to other systems with similar soils because the experiments were evaluated on an event (split application) basis. The following sub-treatments were evaluated:

A: 300 lb N as UAN in 4 in seasonal drip applications of 20% February (60 lbs), 30% April, 30% June, 20% post-harvest with 200 lb K. 125 lb K as a SOP band in February, 75 lb as potassium thiosulphate (KTS).
B: 300 lbs N as UAN, continuous drip fertigation at 15 lbs per event, 200 lb K. 125 lb K as SOP band February, 75 lb as KTS.
C: 300 lbs N and 200 lbs K as KNO_3 + $Ca(NO_3)_2$, continuous drip fertigation at 15 lbs N per event.

Trial design – varieties and irrigation split-plots: The experiments were part of a larger effort examining HFLC and K fertilization on almond. **Figure 1** illustrates the trial design, where each plot in Reps 2-5 consisted of 3 rows by 15 trees long for 45 trees total (0.521 acres). In Rep 1 the hose run was 16 trees, for 48 trees total (0.555 acres). This configuration allowed for both varietal by irrigation split plot analysis where one row was Nonpareil with Fanjet irrigation, the second row was Monterey with Fanjets and the third row was Nonpareil retrofitted with double-line drip applying water at an identical rate to the Fanjets (21.4 gph). In between each plot was a buffer row of Monterey. The Monterey buffer rows and one of the treatments received the grower standard practice rate and timing of fertilizer application. Grower management practices allowed for individual green weight harvest yields of all trees. New mainlines and manifolds were installed with the help of Paramount Farming Company with pipe, hose and fertilizer controllers provided by Bowsmith and Toro irrigation companies. The new plumbing allowed for control of continuous fertigation treatments from stock tanks at the filter station while still allowing for infield replication. This sub-experiment focused on Nonpareil.

Replication: Prior research in adjacent irrigation sets of this orchard suggested the use of 5 replicated plots for each treatment represents an ideal balance of statistical power and experimental practicality. We used five replicate 'plots' for each treatment for a total of 40 treatment plots for the experiments. Monitoring of all parameters in all trees allowed us to use both standard analysis of variance (ANOVA) and capture both tree scale and orchard scale geospatial analysis for scaling exercises (Smart et al. 2011). This level of replication improved the opportunity for contrasting tree responses and acquiring 'yield based N_2O' emissions.

Data collection approach: The team we're working with has conducted individual tree yield and nutrient sampling on a subset of three trees in each treatment plot and variety/irrigation split plot. The bulked yield of these trees and averaged nutrient sampling in the entire set provided 5 true replicated observations. For one tree individual in each of the five replicates we gathered a seasonal N_2O flux and soil NH_4^+ and NO_3^- movement through the root zone for potential leachable NO_3^-. The overall design was a randomized complete block design. However collection of data from multiple individual trees within a plot allowed for use of relational analyses. We have found this kind of approach provides the best statistical opportunity to determine treatment differences. To outline the data we gathered in 2012-2013:

- Tree yield (whole plot and sub sample trees, 360 total)
- Leaf nutrient status at two sample dates from 360 trees (April and July: Multiple elements including saline salts)
- Spur survival and re-bloom intensity. Twenty-single fruited spurs in each of two trees in each treatment and replicate will be tagged each year and their survival and fruit set will be determined (20 x 2 x 6 x 5)

Data collection: To determine how fertigation and application techniques influenced the solubility of K in the soil, and, therefore, plant response, the following soil analyses were conducted at the start and conclusion of the trial for the 0-18 and 18-36 inch depth:

- Particle size--sand, silt, clay, and sieve sand fractions
- Soil organic matter, total N and NH_4-N
- Clay minerals by x-ray diffraction for selected locations
- K fixation potential by our lab method (Murashkina 2006)
- Total cation exchange capacity (CEC) and extractable cations -- K, Na, Mg, Ca
- K by sodium tetraphenyl boron method

Annual soil sampling to track salinity and industry standard tests for nutrient levels (2 sets for start and end of 2012) were taken adjacent to the 36 neutron probe soil moisture monitoring sites:

- Saturated paste pH, EC, Na, Mg, Ca, Cl, HCO_3, NO_3, and B
- Sodium bicarbonate (Olsen) extract P
- Standard ammonium acetate extract K

Deeper soil samples were taken from the 4-5, 6-7 and 8-9 foot depths to track salinity and nitrate leaching and analyzed for EC, Cl and NO_3-N.

N_2O (CH_4) flux calculation: We used the same transect design as in Smart and co-workers (Smart et al. 2011) to collect centimeter scale N_2O fluxes. Seasonal emissions were acquired from integration over space and time of the fluxes measured in two sizes of chamber (a 25 cm diameter chamber that better constrains emissions where the rates are extremely high, and a smaller 12.5 cm diameter chamber to measure soil surface N_2O fluxes when rates were low). . Gas samples of 13 cc were removed from the chambers at 0, 30 and 90 minutes (or 0, 15 and 45 minutes depending on rates and objective) and injected into evacuated 12 cc exetainers. N_2O was analyzed on a gas chromatograph (GC) using a Poropak Q Column (1.8 m, 80/100, 90ºC) with a ^{63}Ni electron capture detector. Methane (CH_4) was analyzed on the same GC after methanization to CO_2 using a Poropak Q Column and a flame ionization detector (300ºC). Thus, when the data are completed we will provide an estimate of CH_4 emissions or absorption as an in kind contribution to the project. Rates of N_2O emission were calculated using modifications to the approach described by Smart and co-workers (Schellenberg et al. 2011; Smart et al. 2011). Each exetainer measured was sampled in duplicate. N_2O (or CH_4) emissions are calculated according to:

$$J_{N2O} = d[N_2O]/dt * Vn/RA * P_a/P_s * T_a/T_s$$

where J is the apparent net flux of N_2O (or CH_4) from the soil surface (umol m^{-2} s^{-1}), $d[N_2O]/dt$ is the change in N_2O (or CH_4) concentration in the chamber over time, V is the chamber volume (L), P_a, P_s, T_a and T_s are ambient (a) and standard (s) atmospheric pressures (Pascals) and temperatures (Kelvin), R is the universal gas constant, and A is the chamber area (m^2). At each flux chamber position during experiments to constrain spatial variation in N_2O emissions, three 5 cm diameter by 20 cm depth soil cores are extracted, and returned to the laboratory for physical evaluation. In order to tease out relationships between gas fluxes and soil properties we are gathering soil moisture data (neutron probe), temperature (thermistor), lysimeter collected soil-NH_4^+ and -NO_3^-, texture, bulk density, percent organic-C, -N and inorganic-C, root density, mineralization rates, and denitrification potential. These samples were collected at multiple depths including the conversion, for example of water content measurements using bulk density for an estimate of water filled pore space (WFPS).

Concentrations of N_2O are measured at the same depths and throughout the soil profile with individual, permanently installed gas sampling tubes, and analyzed on a gas chromatograph. Neutron probe measurements give WFPS from 15 cm down, while a Theta probe is used to measure WFPS in the 10 cm at surface range. Temperature probes are used as well.

Suction lysimeters allowed for measurement of NO_3^- and NH_4^+ concentration in soil solution at 15, 30, 60 and 180 cm depth and 20, 40 and 60 cm from the dripper laterally. Knowledge of NH_4^+ and NO_3^- concentrations, their rates of transformation and rates of consumption, along with corresponding N_2O gas concentrations, allow study of the scale of nitrification and denitrification over time. The comparison of (test of) NH_4^+-derived N_2O under UAN and KNO_3 + $CaNO_3$ under CAN was predicted to be robust (testable) if N_2O production estimates are reliable. The samples are now being analyzed colorimetrically using phenate (for NH_4^+) and vanadium (III) chloride (for NO_3^-).

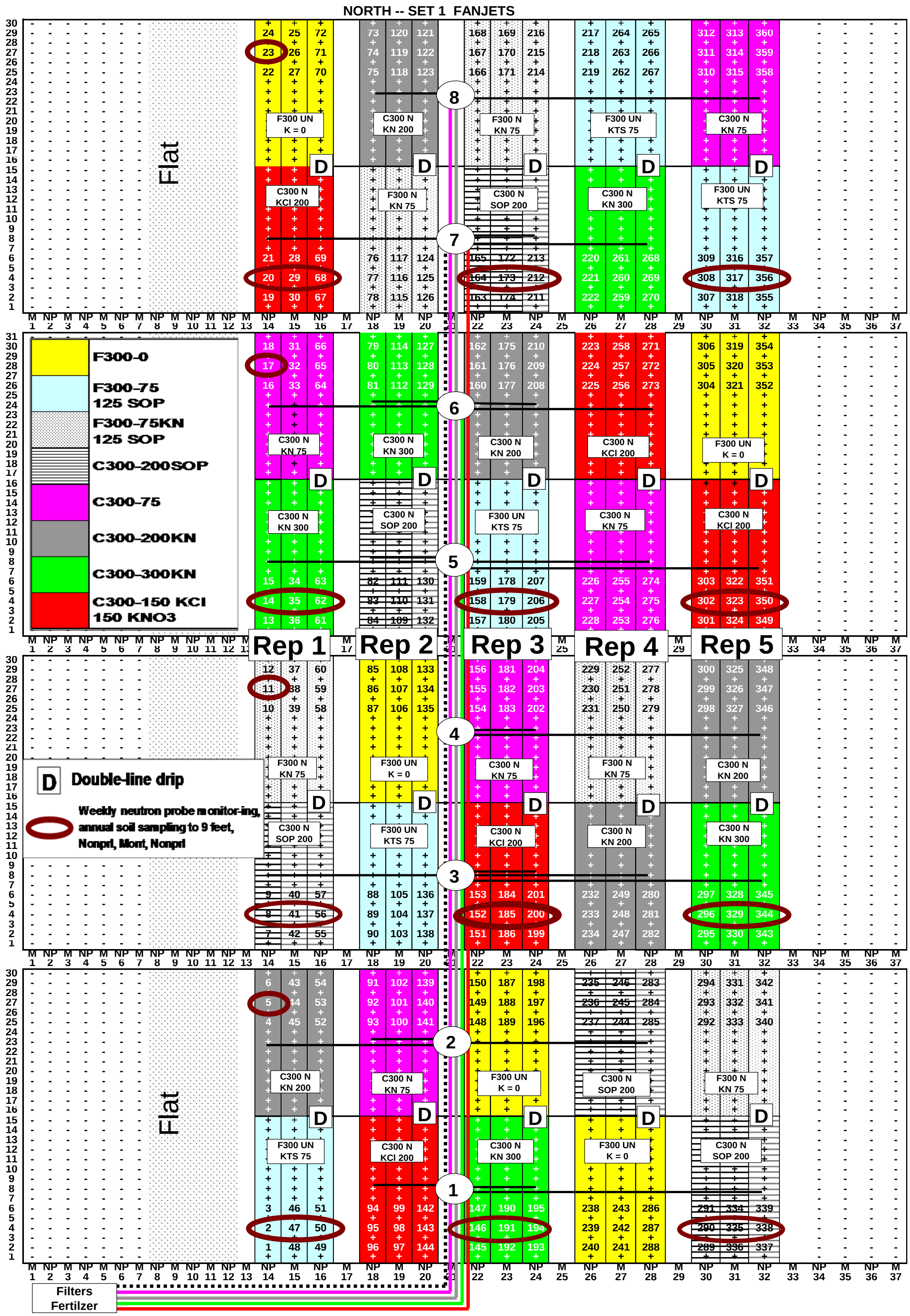

Figure 1. Treatment and plumbing configuration for KNO_3 trial

Results and Discussion:

Preliminary Emissions Estimates

Nitrous oxide emissions, based on a 3 times 6-day N_2O monitoring effort in 2013 indicated that N source is a key factor in the lessening of emissions by HFLC **(Table 2)**. Cumulative emissions for 6 day periods (when each fertigation system delivered approximately the same amount of total-N at 15 lbs per acre) indicated that if NO_3^- was the primary N source then HFLC exhibited about half the emitted N_2O as did predominantly urea ammonium source under both standard and HFLC practice.

Table 2: Fertilizer source and cumulative N_2O emissions for standard fertigation versus HFLC.

Fertigation Strategy	Fertilizer	Emission Factor	Annual N_2O Emissions	Statistical Significance ($p<.05$)
Standard	UAN	1.08%	3.24 kg N_2O-N ha^{-1} yr^{-1}	a
HFLC	UAN	0.90%	2.70 kg N_2O-N ha^{-1} yr^{-1}	a
HFLC	KNO_3 + $Ca(NO_3)_2$	0.49%	1.47 kg N_2O-N ha^{-1} yr^{-1}	b

N_2O Production/Consumption in Soil:

The greatest N_2O production following fertigation on this soil occurs at depths between 15 and 20 cm while relatively little production was seen below 45 cm depth (**Figure 2**):

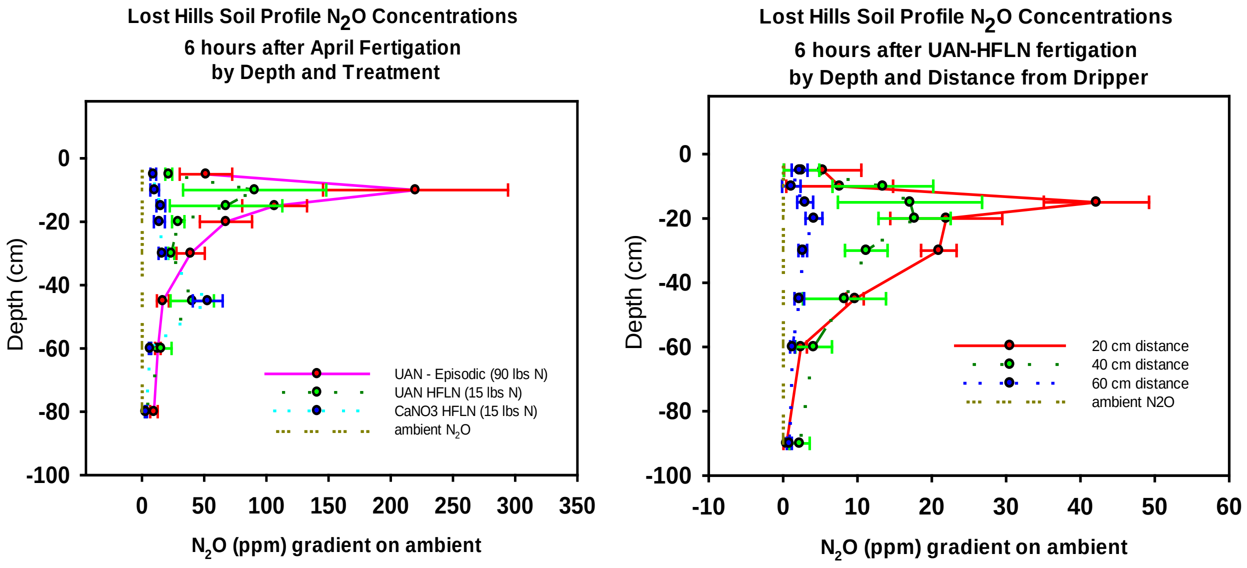

Figure 2. Soil pore space N_2O concentration with soil depth.

Combining results above with observations of WFPS can reveal rates of net N_2O production and consumption, using the 1-D model of Yoh, below (Yoh,1997). Combined with soil parameters, such data may facilitate the development of N_2O predictions using hydrological models.

$$\alpha_i = \frac{q_i - q_{i+1}}{\frac{Z_i+Z_{i+1}}{2} - \frac{Z_i+Z_{i-1}}{2}} + \frac{dc_i}{dt} V_{Ai}$$

Diurnal variation following fertigation under UAN and KN+CN

Spatiotemporal variation of N_2O emissions during fertigation events has been a primary focus of this group for some time and leads to more robust estimates of N_2O when scaled up over space and time. Times of gas flux measurements must be chosen carefully and finally adjusted using a temperature coefficient to reflect daily average emissions. Shown in the upper panel of **Figure 3** is the diurnal variation in N_2O emissions following fertigation with UAN during a 2-day, 48 h period. In the lower panel are similar observations of N_2O emissions for KN+CN.

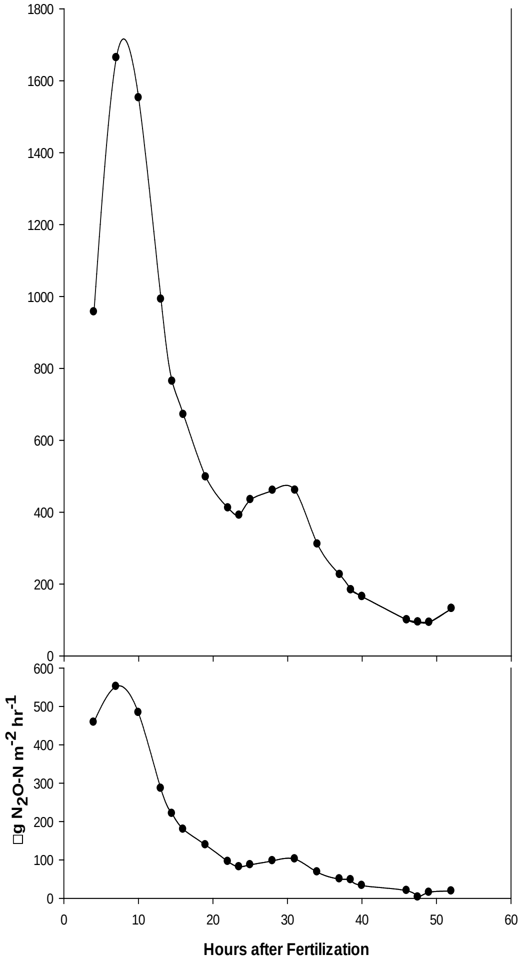

Figure 3. Shown in the upper panel is time dependent N_2O emissions for a standard practice fertigation application of 15 lbs $acre^{-1}$ N as UAN, and in the lower panel is the same rate of N application but using KN+CN.

Spatial Distribution of Drip Zone Emissions

Drip emitters produce characteristic Gaussian spatial distributions of N_2O emissions (Alsina et al. 2013), with the inflection point centered on the drip emitter (**Figure 4**). This requires us to measure N_2O production and emission at least three distances from the dripper. These distributions are then modeled in 3 dimensions to provide estimates of emissions that can be scaled up to the orchard level. We used this on multiple occasions to model the hysteretic effect of soil drying and rewetting on emissions (**Figure 4**).

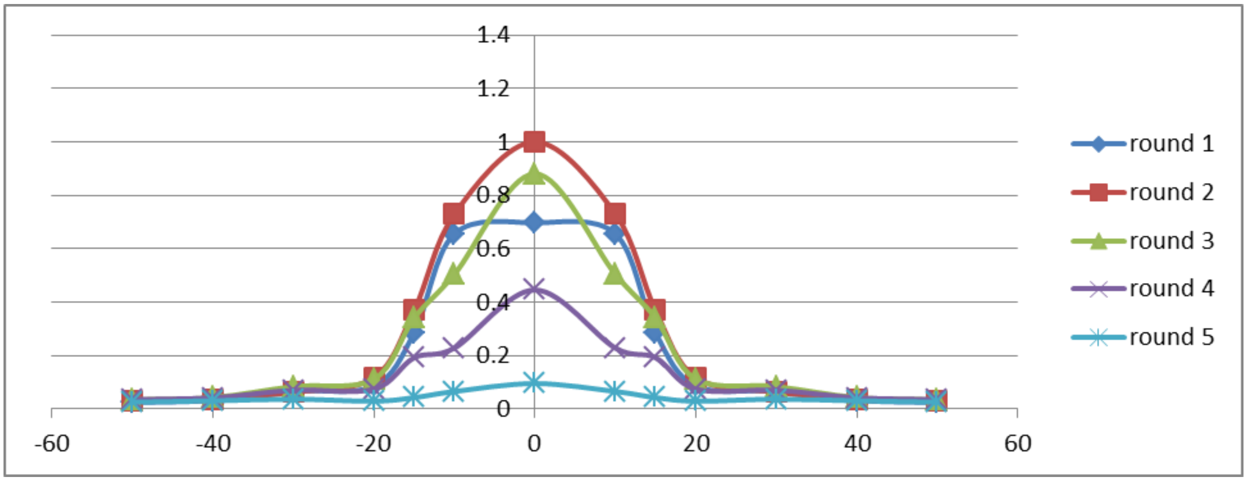

Figure 4. N_2O emissions for 2 transects across the drip emitter area (the x-axis 0 is the center of the drip impact zone). Shown are 5 rounds of measurements (rounds 1-5) taken approximately 3 hours apart.

N_2O Production and Soil NO_3^- Concentration and Water Status after UAN Fertigation

1) Rates of N_2O production following fertigation on this soil reach their peak on the afternoon of the first day following fertigation, and decline at a steady rate over the next three days;
2) Rates of N_2O production appear to be proportional to soil water–filled pore space (WFPS) in this soil;
3) Rates of N_2O production also appear to be proportional to soil water NO_3^- concentration on this soil.

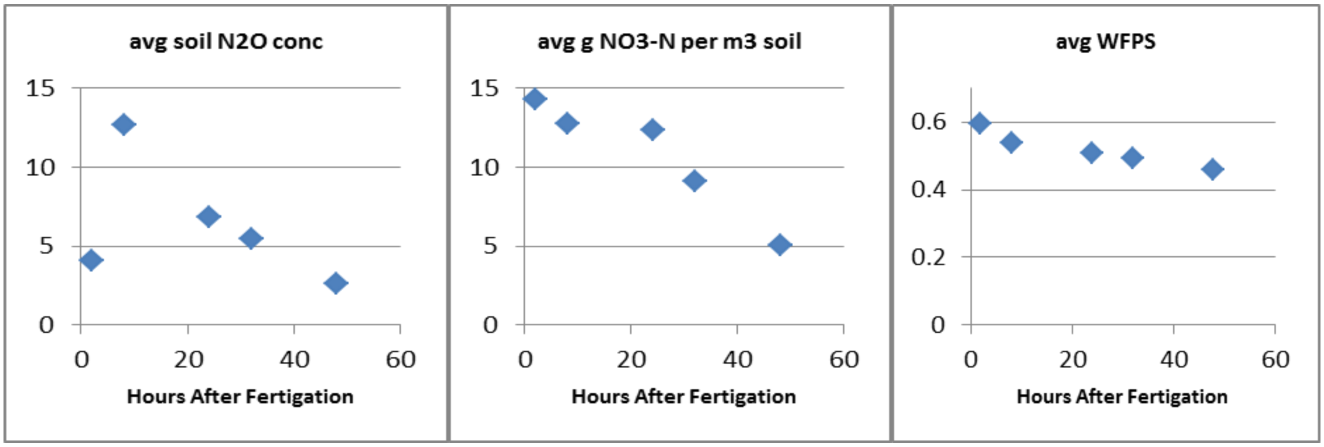

Figure 5: Shown in the left panel is the average (n = 3) soil pore space (15-30 cm) N_2O concentration (ppm), in the middle panel the NO_3^- concentration, and in the right panel the average soil water filled pore space (%).

Relationship Between Soil Pore Space N_2O and N_2O Emissions

Once soil pore space had been measured and calculated (**Figure 5**), the log transformed values of soil N_2O concentration at 15-30 cm were linearly related to the log transformed values of surface N_2O emissions from this soil. Points of high emission compared to soil concentration can be explained in part by soil cracking and preferential gas flow (**Figure 6**).

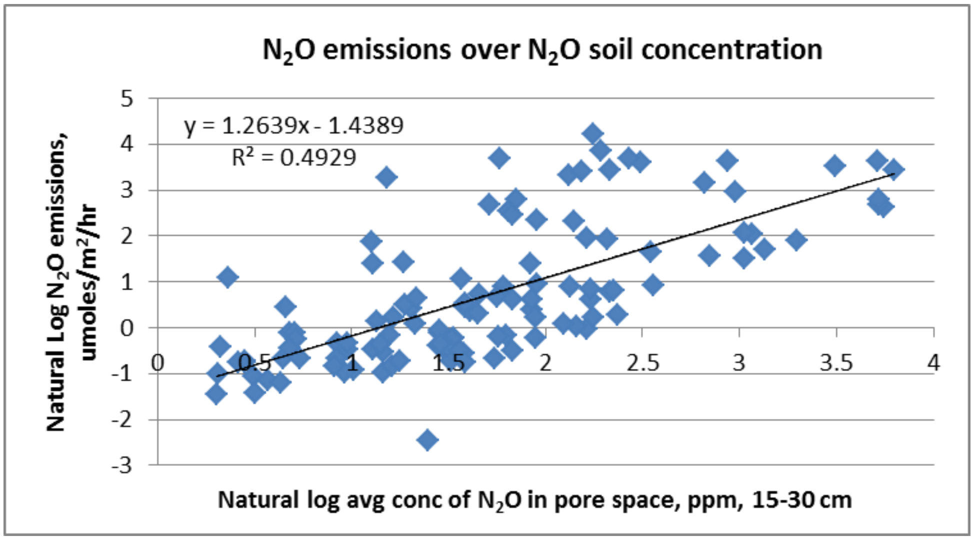

Figure 6. Log transformed values of soil pore space N_2O concentration (ppm) versus N_2O flux at the soil surface.

Research Effort Recent Publications:

Michael W. Wolff, Daniel L. Schellenberg, Maria Mar Alsina, Andres Olivos, Blake L. Sanden, Patrick H. Brown and David R. Smart. (2013) Reducing mobile N-Loss from fertigation: Field and modeling approaches. Improving Nitrogen Use Efficiency in Crop and Livestock Production Systems, hosted by the Soil Science Society of America, Kansas City, Missouri, August 13-15, 2013.

David R. Smart, Kate M. Scow and Christine M. Stockert (2013) Anthropogenic entrainment of microbial organisms involved in N_2O emissions in a California perennial crop. *Soil Biology and Biochemistry* (submitted)

References Cited:

Alsina, M.M., Fanton-Borges, A.C., Smart, D.R., 2013. Spatiotemporal variation of event related N_2O and CH_4 emissions during fertigation in a California almond orchard. *Ecosphere* 4, 1-21.

Burger, V., 2011. Effects of Nitrogen Fertilizer Types on Nitrous Oxide Emissions. pp. 179-202 *In* Guo, L. (Ed.), Understanding Greenhouse Gas Emissions from Agricultural Management. American Chemical Society, Washington DC

Schellenberg, D.L., Alsina, M.M., Muhammad, S., Stockert, C.M., Wolff, M.W., Sanden, B.L., Brown, P.H., Smart, D.R., 2012b. Yield-scaled global warming potential from N_2O emissions and CH_4 oxidation for almond (Prunus dulcis) irrigated with nitrogen fertilizers on arid land. *Agriculture Ecosystems & Environment* 155, 7-15

Ciarlo, E.; Conti, M.; Bartoloni, N.; et al., 2008. Soil N_2O emissions and $N_2O/(N_2O+N_2)$ ratio as affected by different fertilization practices and soil moisture. Biology and Fertility of Soils 44, 991-995

Senbayram, M., Chen, R., Budai, A., Bakken, L., Dittert, K., 2012. N_2O emission and the $N_2O/(N_2O + N_2)$ product ratio of denitrification as controlled by available carbon substrates and nitrate concentrations. *Agriculture Ecosystems & Environment* 147, 4-12.

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Yoh, M., Toda, H., Kanda, K.-I., Tsuruta, H., 1997. Diffusion analysis of N_2O cycling in a fertilized soil. *Nutrient Cycling in Agroecosystems* 49, 29-33