Evaluating Nitrogen Management Strategies to Minimize Greenhouse Gas Emissions from California Almond Orchards

Project No.: **15-AIR2-Smart**

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Objectives:

1) To compare greenhouse gas (GHG) emissions (N_2O, CH_4 and CO_2) from three proposed nitrogen (N) best management practices (BMPs): pump & fertilize (P&F), split applications targeted to N demand root growth and adjusted with Spring Leaf N analysis (AGP) and high frequency low N applications (HFLC).
2) To evaluate temporal variability of GHG emissions with respect to environmental factors such as volumetric water content and seasonal temperature variation.
3) Acquire ground verification data using the spatial models of event related N_2O fluxes we've developed to capture N_2O emissions episodes for soils that have not been previously evaluated.
4) To use the instantaneous emissions measurements information acquired to assemble annual emissions budgets for GHGs from almond orchards under the practices outlined under Objective 1.
5) To provide ground verification data of other soil series for the HYDRUS and DeNitrification DeComposition (DNDC) modeling efforts.

Interpretive Summary:

Mitigating greenhouse gas (GHG) emissions is rapidly becoming a key regulatory and marketing issue subjecting growers to increasing scrutiny from regulatory agencies. Metrics on proposed best management practices (BMPs) to mitigate GHG emissions are lacking. During 2014 and 2015, our research investigated different proposed BMPs for N fertilizer application approaches in order to reduce GHGs emitted from almond orchards in the central San Joaquin Valley. In addition, we have been investigating the correlations between environmental parameters such as temperature, water content, soil NH_4^+ and NO_3^- and others. with N_2O emissions in order to facilitate prediction of emissions by modeling efforts of HYDRUS and DNDC proposed to drive decision support systems.

The three treatments tested were: Advanced Grower Practice (AGP), in which fertilizer is applied 3-4 times during the season and adjusted for Spring Leaf N analysis; Pump and Fertilize (P&F), in which N present in irrigation ground water (GW) is subtracted from the total fertilizer N applied and High Frequency Low N Concentration applications (HFLC, spoon feed) where split applications occur approximately 20 times during the season. Fertilization timing and total amounts were approximate in the AGP and P&F treatments. For the HFLC treatment where N fertilizer was injected roughly weekly with irrigation water, the total N load was somewhat lower throughout the entire growing season.

Under both drip and microjet fertigation emitters GHG emissions were spatially modeled to more accurately represent the spatial distribution of emissions in the orchards (see Alsina et al. 2013). This approach enables the integration of instantaneous emissions point measurements for scaling up to the field level, and allows for fewer measurements to estimate the total emissions.

During 2014 and 2015, N_2O emissions were highest in the AGP treatment and lowest in the HFLC treatment. The percentage of N emitted relative to N applied nonetheless was highest in the HFLC treatment. Spatial patterns of N_2O emission under microjet emitters were subject to its water distribution pattern, with higher emissions where most of the water was deposited regardless of treatment. Soil edaphic factors like extractable NH_4^+ and NO_3^- did not provide good correlations between the measured parameters and N_2O emissions. In other words, the soil edaphic factors we measured were not entirely successful in improving model predictions of emissions by as compared with simply the water distribution pattern. We currently work with HYDRUS and DNDC modelers in order to actuate this observation. N_2O emissions were only gathered in the almond orchard during the 2015-16 season and they are currently undergoing scrutiny.as per 2014 and 2015.

Detailed soil sampling around both drip and microjet emitters revealed that topsoil N_2O concentration was the best predictor of N_2O emissions, and this was expected as consistent with the diffusion gas flux mechanistic model (Rolston, 1986). N_2O emissions were also well correlated with NH_4^+ and soil CO_2 concentration. These results strongly suggest that nitrification was the governing process that affects N_2O emissions at our research site but verification of this observation will be required. As CO_2 concentration increased and NH_4^+ decreased the correlation shifted toward NO_3^- , but N_2O emissions were much lower at that time. This represents an important observation because in identifying nitrification as the primary N_2O source, it should allow the use of a model (DNDC), being calibrated for Decision Support, to calculate changes in soil NH_4^+ and NO_3^- in order to better predict N_2O emissions and thus better identify BMPs.

Materials and Methods:

Objective 1. Compare GHG emissions (N_2O, CH_4 and CO_2) from three nitrogen (N) management practices: pump & fertilize, split applications targeted to N demand and root growth, and high frequency low N applications

Seasonal emissions of N_2O, CO_2, and CH_4 were acquired from static chambers placed over permanently affixed arrays of collars at the soil surface. Three gas samples of 20 ml were

removed from the chamber at 0, 10 and 20 minutes and injected into evacuated 12 ml sample tubes (Exetainers®, Labco Ltd, High Wycombe, UK). The sample tubes were evacuated to approximately 45 mTorr (= 6 x 10^{-5} atmospheres, or 6 Pa). A silicon 'cap' was placed over the septum after evacuation so that sample containers do not leak significantly and can be stored long term. We have tested this several times and the containers exhibit very little leakage.

N_2O was analyzed on a gas chromatograph (GC) with a Poropak Q Column (1.8 m, 80/100, 90ºC) with N_2O detected using a ^{63}Ni electron capture detector. CO_2 and CH_4 were analyzed on the GC with Poropak Q Column using a flame ionization detector (300ºC) following methanation. Rates of N_2O and CO_2 emission or CH_4 production and consumption were calculated using modifications to the methods described by Smart and coworkers (Smart et al. 1999). Each sample over time was taken in duplicate.

Once the samples were analyzed the instantaneous N_2O and CH_4, emissions were calculated according to:

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

where J is the apparent net flux of N_2O (or CO_2, CH_4) from the soil surface (mol m^{-2} min^{-1}), $d[N_2O]/dt$ is the change in N_2O (or CO_2, CH_4) concentration in the chamber over time, Vn is the chamber volume (L), P_a, P_s, T_a and T_s are ambient (a) and standard (s) atmospheric pressures (Pascals, Pa) and temperatures (Kelvin, K), R is the universal gas constant (8.314 L kPa K^{-1} mol^{-1}) and A is the chamber area (m^2). Sampling frequency during the year occurred on a weekly basis during periods of low and constant flux, and then at hourly and daily intervals around event related emissions, mainly N fertigation, irrigation and precipitation since soil water and nitrogen are the major factors driving emissions (*e.g.* **Table 1**). At each flux chamber position during experiments to constrain spatial variation in N_2O emissions, 5 cm diameter by 15 cm depth soil cores were extracted, and returned to the laboratory for soil physical and chemical evaluation. Water content and temperature were measured using a 5TE sensor (Decagon Devices, Pullman, WA). The gathering of a season's worth of emissions data was carried out as explained under Objective 3 (below).

Objective 2. Evaluate temporal (and spatial) heterogeneity of N_2O fluxes (Objective 1) with respect to environmental factors (fertilizer N and soil N, temperature, soil moisture, texture, etc.)

During 2014-15 soil samples were collected for chemical analysis. The soil samples were placed in a 2 molar solution of potassium chloride and placed on a shaker for 24 hours. Then the solutions were extracted using Whatman #2 filter papers. The extracted solutions were measured for NH_4^+ and NO_3^- content (Mineral-N). Nitrate was determined by reduction to nitrite via a copperized cadmium column. The nitrite was then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethlyenediaminie dihydrochloride. The absorbance of the product is measured at 520 nm. Ammonia was determined by heating with salicylate and hypochlorite in an alkaline phosphate buffer. The presence of EDTA prevents precipitation of calcium and magnesium. Sodium nitroprusside was added to enhance sensitivity. The absorbance of the reaction product was measured at 660 nm and is directly proportional to the original ammonium concentration. The method has a detection limit of

approximately 0.10 ppm (on a soil basis). Data gathered in 2016 comes from arrays of suction lysimeters installed at 30, 60, 90 and 180 cms depths.

Objective 3. Acquire ground verification data for 2-D spatial models of event related N_2O fluxes to model N_2O emissions episodes (Objective 2) for the three treatments.

Nitrous oxide emissions measurements around the microjet sprinkler (FJ) treatments were scaled up to the tree level using a weighted average. The wetted area around a tree could be represented by a rectangle of 400 cm (diameter of the wetting radius) by 640 cm (distance between trees). Every measurement then represented a 50 cm wide (distance between collars) by 640 cm long (distance between trees) rectangle of soil (**Figure 1**). The 0 cm (tree row) measurement represented a 25 cm by 640 cm strip. This approach assumes each measurement position was representative of a strip of soil parallel to the tree row and running the length of the within row spacing between individual trees. The basis for this assumption was that the wetting pattern around the FJ was visibly two dimensional (Schellenberg et al., 2012). Calculated emissions were then summed and multiplied by two to give total N_2O emission per area around two trees:

$$[2] \qquad Q_{Tree} = 2 \times \left(25 \times 640 \times q_1 + \sum_{i=2}^{5} 50 \times 640 \times q_i \right)$$

where Q_{Tree} is total emission per tree [ng N_2O-N h^{-1}], q_1 is the emission rate measured at the 0 cm collar [ng N_2O-N cm^{-2} h^{-1}], and q_i is the emission rate measured at the i^{th} collar (i= 2, 3, 4, 5) [ng N_2O-N cm^{-2} h^{-1}].

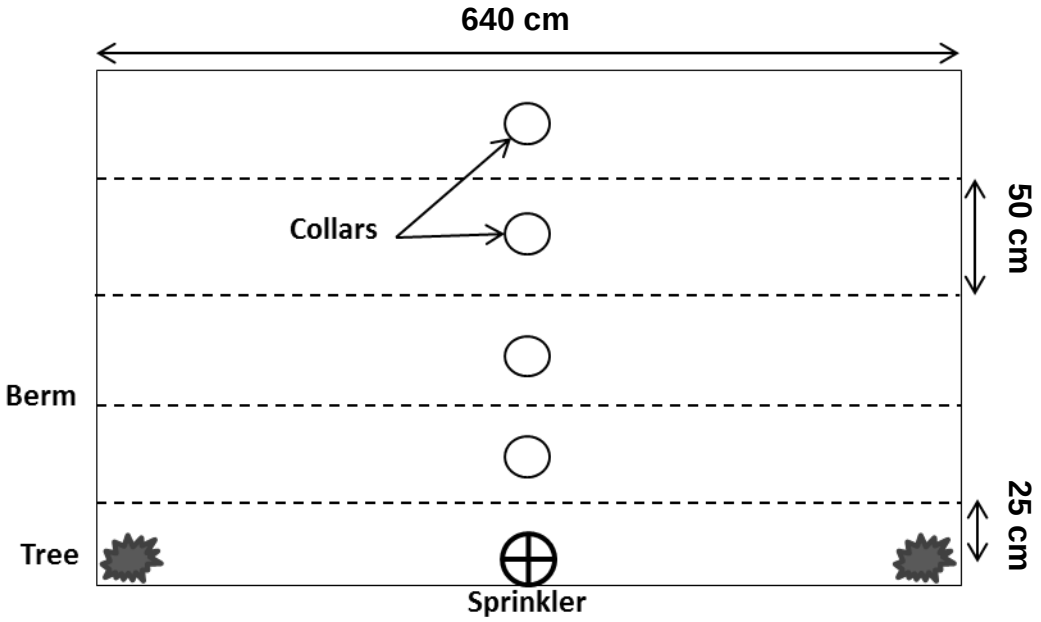

Figure 1: The geometric configuration around microjet sprinkler emitters used for scaling emissions to the tree level followed by scaling to the orchard level (trees per hectare).

N_2O emissions around the dripper showed a pattern of maximum flux close to the dripper which decreased with distance (**Figure 2**). The collected emission data was found to fit a sinusoidal function of the general form:

$$q(r) = A \sin B(r + C) + D \quad [3]$$

where q is the N_2O flux [ng N_2O-N cm^{-2} h^{-1}] and r is the distance from the dripper [cm].

In this function, D is the vertical shift of the sine function from the x-axis, and can be assumed to equal zero because the N_2O flux in the non-wetted zone was zero. A is the amplitude of the function and equals the maximal emission rate, q_{max}, of N_2O from the area immediately around the dripper (r=0). Measured N_2O data fits a quarter ($\pi/2$) of a sine function with the maximum at r=0 and zero at the edge of the wetting front ($r=r_{max}$). Therefore, the shift of the function, C, equals the wetted radius around the dripper. For the same reason, the period of the function is:

$$Period = 4r_{max} \quad [4]$$

and the frequency of the function, B, is given by:

$$B = \frac{\pi}{2r_{max}} \quad [5]$$

This results in the following equation, to predict N_2O flux as a function of distance from the dripper:

$$q(r) = q_{max} \sin\left[\frac{\pi}{2}\left(\frac{r}{r_{max}} + 1\right)\right] \quad [6]$$

Emissions data from three days of measurements after fertigation and one day after irrigation was used to calibrate the function using q_{max} and r_{max} as fitting parameters (Brown, 2001). q_{max} was 262.6, 143.33, 81.9, and 2.89 ng N_2O-N cm^{-2} h^{-1} for days after fertigation (DAF) 1, 2 and 3 and day after irrigation 1 (DAI1), respectively and with respective R^2 values of 0.98, 0.97, 1, and 0.94, which accurately captures the decreasing emission rates over time. r_{max} was 70.5, 72.5, 73, and 75.5 cm for the same time periods. These values were very similar to the measured wetted radius around the drippers that ranged from 69 to 80 cm.

N_2O emission from the entire surface area around the dripper (q_{drip}) can be calculated by integrating eq. 6:

$$q_{drip} = 2\int_0^{\pi/2}\int_0^{r(\alpha)} q(r)\,dr\,d\alpha \quad [7]$$

where α [Radian] is the angle between the radius and the perpendicular to the drip line, r(□) is the integrated radius and depends on α since in most cases wetting patterns of adjacent drippers overlap:

$$r(\alpha) = \begin{cases} r_{max} & \alpha \le \alpha_c \\ \dfrac{d}{2\sin\alpha} & \alpha < \alpha_c \end{cases} \quad [8]$$

where d is the distance between adjacent drippers [cm] and α_c [Radian] is the angle from the dripper to the point where the two wetting fronts intersect. Assuming that all drippers along a line have the same wetted radius then α_c can be calculated by:

[9] $$\sin \alpha_c = \frac{d}{2r_{max}}$$

Multiplying q_{drip} by the number of drippers per tree (20) will result in cumulative N_2O-N emission per hour per tree (Q_{Tree}).

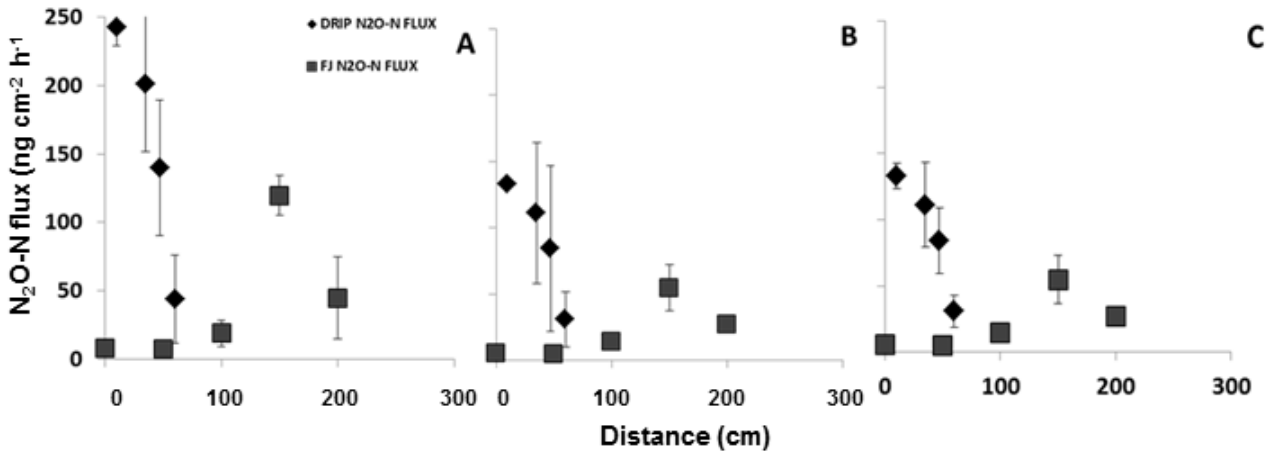

Figure 2: Spatial patterns of N_2O emissions around drip and microjet emitters for days 1 (A), 2 (B) and 3 (C) after a fertigation event for two emitter types, drip and fanjet.

Objective 4. Use the instantaneous emissions measurements information acquired to assemble annual emissions budgets for GHGs from almond orchards under the practices outlined in Objective 1.

Having derived functions that best define spatial patterns of N_2O emission events from the wet-up area around the irrigation water emitters and for the driveways between trees (*e.*g. following precipitation events), the instantaneous rates of N_2O, CO_2 and CH_4 emissions were temporally integrated over the course of the growing season. The 'event' timeline can be considered as the length of time passing before emissions return to baseline values. Emissions from the non-wetted areas of the orchard, for example the driveways, were measured several times during the season and were unequivocally inseparable from zero emissions.

Objective 5. Provide ground verification data of other soil series data for the HYDRUS and DeNitrification DeComposition (DNDC) modeling efforts.

To allow mechanistic models such as DNDC or HYDRUS to predict N_2O emissions, the governing environmental parameters which influence those emissions must be determined. To that end, soil N_2O and CO_2 concentrations, water content, bulk density, NO_3^-, NH_4^+, and temperature were measured at depths of 7, 15, 30, 45, and 60 cm under the gas flux

measurement collars. Correlations between those parameters and N_2O emissions were determined using principal component analysis (PCA).

Results and Discussion:

Objective 1. Compare GHG emissions (N_2O, CO_2 and CH_4) from three nitrogen (N) management practices: pump & fertilize, split applications targeted to N demand and root growth, and high frequency low N applications.

Assuming the measured emissions represented the average daily emissions since the measurements mostly took place during daytime hours, then cumulative Q_{Tree} for three DAF in the FJ treatment was 338 mg N_2O-N and 769.5 mg N_2O-N in the drip treatment. These emissions constituted 0.27% and 0.12% of total N applied in the fertigation event for the drip and FJ treatments, respectively. The percent of N lost in the FJ treatment was very similar to that found by Schellenberg et al. (2012) in a soil with very similar textural characteristics. Percent of N applied lost as N_2O-N for the drip treatment was higher than observed by Vallejo et al. (2014) but this might be a result of the fertilizer being applied in lower concentrations using a Dosatron in their experiment. Eight weeks after fertilizer application, the total N_2O-N emission in the FJ treatment were twofold higher than those observed from the drip treatment, 11.5 versus 4.6 mg N_2O-N per tree respectively. These values are much smaller than the values measured in the first three days following the fertigation event, and along with many other studies (Hanson et al., 2006; Okuda et al., 2007; Burton et al., 2008; Pang et al., 2009; Garland et al., 2011; Smart et al., 2011; Schellenberg et al., 2012; Alsina et al., 2013; Kennedy et al., 2013; Rowlings et al., 2013; Suddick and Six, 2013; Vallejo et al., 2014) suggest that the majority of the N_2O-N losses occur immediately after the fertigation event.

Objective 2. Evaluate temporal (and spatial) heterogeneity of N_2O fluxes (Objective 1) with respect to environmental factors (fertilizer N and soil N, temperature, soil moisture, texture, etc.)

The 5 cm diameter and 15 cm deep soil samples taken near the collars were analyzed for ammonium and nitrate concentrations, water content, porosity, and tortuosity. None of the measured parameters had any correlation with emitted N_2O flux (**Table 1**). These data suggested that the integrated measurement of 15 cm of soil may obscure the reason for the emissions, and that higher resolution of measurement is needed to determine which environmental parameter controls N_2O emissions.

Table 1: Correlations between soil parameters and N_2O emissions under microjet irrigation.

	q N-N_2O	WC	NO_3	NH_4	Porosity	Tortuosity
q N-N_2O	1					
WC	-0.10121	1				
NO_3	-0.01862	-0.21809	1			
NH_4	-0.06102	0.24221	0.510764	1		
Porosity	-0.09782	0.15171	-0.0654	0.189819	1	
Tortuosity	-0.08114	0.802415	-0.14833	0.074354	-0.53481	1

Objective 3. Acquire ground verification data for 2-D spatial models of event related N_2O fluxes to model N_2O emissions episodes (Objective 2) for the three treatments

The approach and equations used to acquire most accurate geospatial N_2O measurements around drippers and fanjet sprinklers are outlined under Objective 2. In brief N_2O emissions showed decreasing emissions with distance from the dripper (**Figure 2**) and were relatively easily modeled using a sinusoidal relationship (see **Figure 2**) for which correlation coefficients were high. Although there was no easily discernable relationship for fanjet emitters, we were able to use a geometric modeling approach (**Figure 1**).

By integrating fluxes over space and time (Objective 2, Materials and Methods) we were able to quantify what we believe are very accurate estimations of the seasonal N_2O emissions. The fits between modeled emissions in example fit very well with the ground verification measurements taken from the orchard (**Figure 3**). There was a surprising absence of substantial emissions spatially around the emitters following the Irrigation events (**Figure 3**) but we have observed this from another arid site on a similar sandy loam soil (Schellenberg et al. 2012).

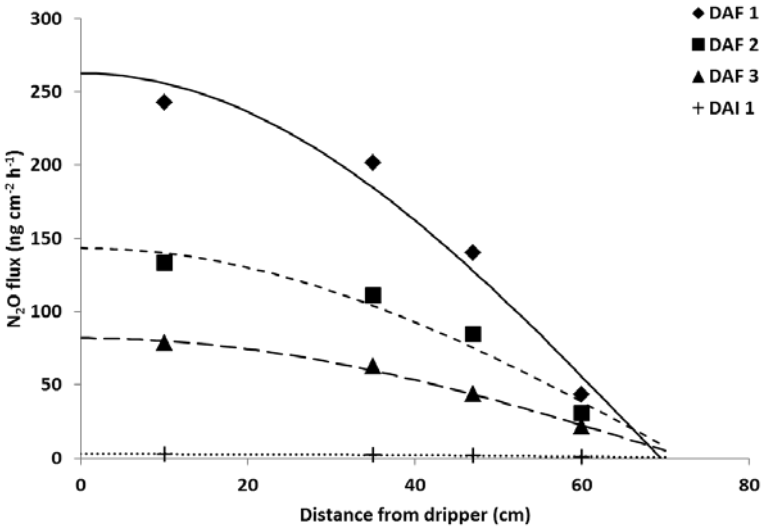

Figure 3: Measured and predicted from the modeling exercises of N_2O emissions as a function of distance from a dripper for days after fertigation (DAF) 1, 2 and 3, and day after irrigation 1 (DAI1).

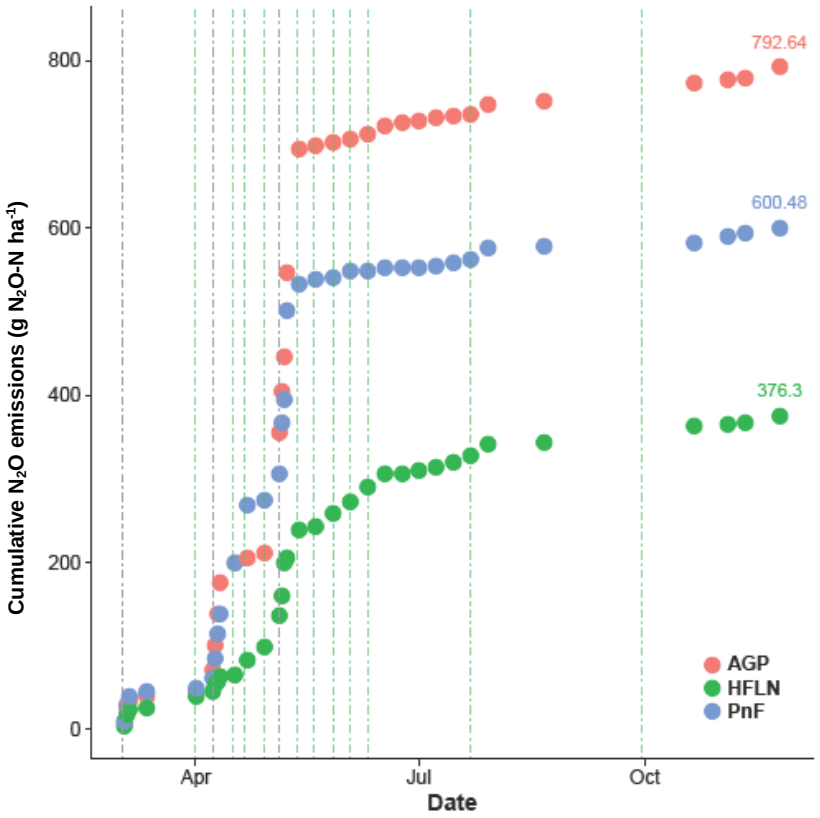

Figure 4: Annual cumulative N_2O emissions for three treatments of AGP (red), PnF (blue) HFLN, and (C) PnF in the almond orchard. Dashed green vertical lines represent HFLN fertigation events while dashed blue vertical lines represent AGP and PnF fertigation events.

Objective 4. Use the instantaneous emissions measurements information acquired to assemble annual emissions budgets for GHGs from almond orchards under the practices outlined in Objective 1.

Emission measurements are still being taken weekly at the orchard (2016). Therefore, an annual emission budget for 2016 is not yet fully available. However, based on the high variability of the measurements we are anticipating small differences in the annual emissions budget between the three different treatments. Certainly seasonal variation will play a role in quantifying GHG emissions from these treatments and we may have been fortunate to gather data on emissions during 3 of the 4 years of drought.

During the 2015 season seasonal emissions differed between the treatments with 792.6, 600.5 and 376.3 g N_2O-N ha^{-1} emitted for the AGP, PnF and HFLN respectively (**Figure 4**). The same data have been gathered during the 2016 season but are awaiting quantification and summarization.

Objective 5. Provide ground verification data of other soil series for the HYDRUS and DeNitrification DeComposition (DNDC) modeling efforts.

The intensively monitored sites provided data regarding governing parameters for predicting N_2O emissions. Principal component analysis (PCA, **Figure 5A-D**) revealed that soil N_2O concentration in pore space of the shallowest soil layer sampled (7.5 cm) was the most predictive parameter for N_2O emissions for both drip (**Figure 5B**) and microjet emitters (**Figure 5D**). Under drip irrigation soil N_2O concentration was well correlated with NH_4^+ at DAF1 and with NO_3^- during DAF3 (**Figure 5C**).

These results indicated that nitrification was the primary process governing N_2O emissions. Ammonium concentration decreased with time causing the N_2O flux to decrease as well. As the substrate concentration for nitrification (NH_4^+) decreased and CO_2 levels increased in soil, the governing process seemed to transition to denitrification, probably in anaerobic microsites; hence, the lower correlation with extractable soil NH_4^+ and the positive correlation with extractable soil NO_3^-.

Under microjet irrigation (**Figure 5D**) during DAF1, there were statistically significantly high positive correlations between soil N_2O emission and soil extractable NH_4^+ ($R^2 = 0.82$), WFPS ($R^2 = 0.93$), and soil CO_2 concentration ($R^2 = 0.81$). During the subsequent days' correlation coefficients for all parameters decreased until at DAF 3 they were $R^2 = 0.76$, 0.45, 0.59, and -0.24 for NH_4^+, WFPS, CO_2 and NO_3^- respectively. It appeared that nitrification was the governing process affecting N_2O emissions during the first 3 days of measurement, mainly because of the relatively high correlation with soil NH_4^+; however, the non-uniformity of water and nutrient distribution along with the relatively small sample locations in this treatment made it challenging to discern predictive relationships for N_2O emissions from the reported data.

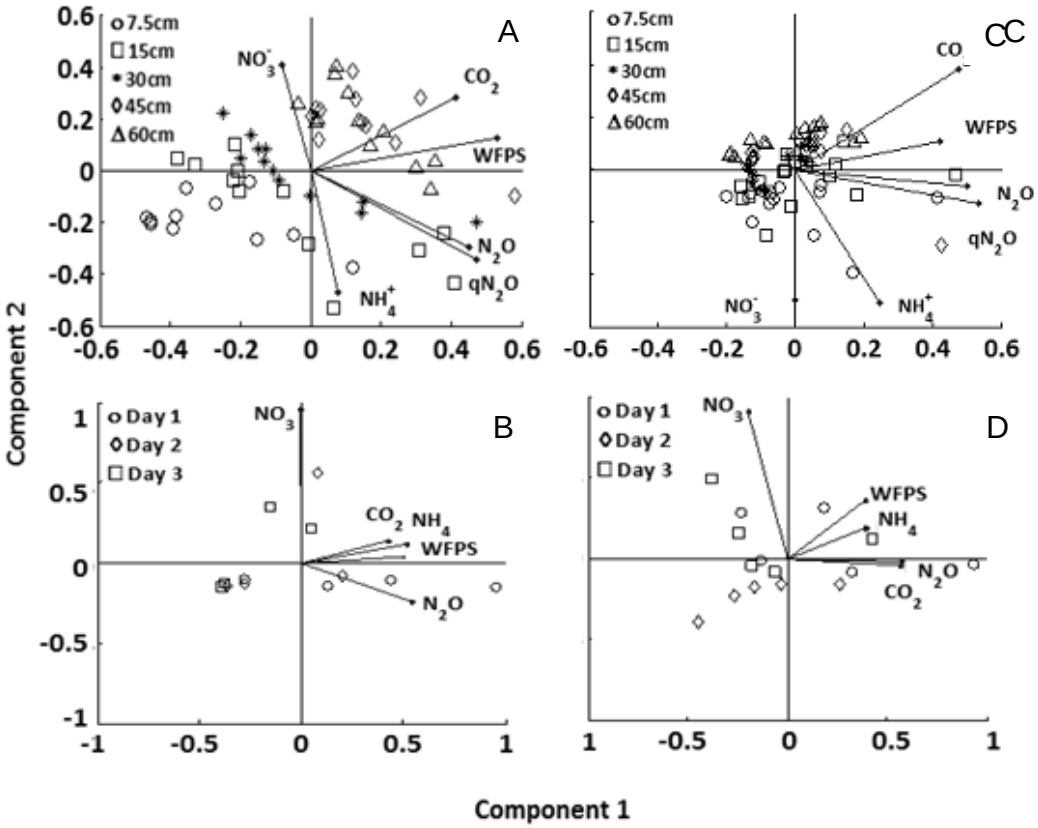

Figure 5: Principle components analysis for drip (A, B) and fanjet (C, D) for all soil depth measurements (A, C) and only measurements taken at a depth of 7.5 cm (B, D).

Research Effort Recent Publications:

Schellenberg, D, M del Mar Alsina, S Muhammad, CM Stockert, BL Sanden, PH Brown and **DR Smart** (2012) Yield-scaled global warming potential from N_2O emissions and CH_4 oxidation for almond (*Prunus dulcis*) irrigated with nitrogen fertilizers on arid lands. *Agricultural Ecosystems and Environment* 155:7–15.

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Khalsa, Sat Darshan S, C.A. Almanza, P.H. Brown and **D.R. Smart (2016)** Leaf litter C and N cycling from a deciduous permanent crop. *Soil Science and Plant Nutrition,* http://dx.doi.org/10.1080/00380768.2016.1188413

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Dabach, S, D Jerszurki, CM Stockert[a], **DR Smart** (2016) Response of N_2O emissions and concentration profiles to irrigation method and implications for upscaling measured emissions in an almond orchard*. Agricultural and Forest Meteorology*, (in revision).

Sat Darshan S. Khalsa, Timothy K. Hartz and Patrick H. Brown (2016) Principles of Nitrogen Cycling and Management. California Department of Food and Agriculture, Fertilizer Research and Education Program Training Manual.

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