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



### **Project Cooperators and Personnel:**

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## **Objectives**:

- 1) To compare greenhouse gas (GHG) emissions of nitrous oxide, methane and carbon dioxide  $(N_2O, CH_4$  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  $N<sub>2</sub>O$  fluxes we've developed to capture  $N<sub>2</sub>O$  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 marketing issue in addition to subjecting growers to increasing scrutiny from regulatory agencies. During 2014 and 2015, our research investigated different proposed BMPs for N fertilizer application regimes in order to reduce GHG emitted from almond orchards in central San Joaquin Valley. In addition, we investigated the correlations between environmental parameters such as temperature, water content, etc. and  $N<sub>2</sub>O$  emissions in order to facilitate prediction of those emissions for models proposed to drive decision support systems.

The three treatments applied were: Advance Grower Practice (AGP), in which fertilizer was applied 3-4 times during the season and adjusted with Spring leaf N analysis. Pump & Fertilize (P&F), in which N present in irrigation ground water (GW) was subtracted from the total applied

N fertilizer. Fertilization timing and total amounts were the same as in the AGP treatment. High-frequency, low N concentrations (HFLC), where N fertilizer was injected weekly with irrigation water throughout the entire growing season.

N<sub>2</sub>O emissions were highest in the AGP treatment and lowest in the HFLC treatment. However percentage of N emitted relative to N applied was higher 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. 15 cm deep soil samples were taken to measure environmental parameters but did not provide good correlations between the measured parameters and  $N<sub>2</sub>O$  emissions. In other words, the environmental factors we measured were not successful in improving models' predictions of emissions (HYDRUS and DNDC) using general correlation procedures as compared with water distribution pattern.

Under drip irrigation, surface  $N_2O$  emissions were best modeled using a sinusoidal function and was successfully accomplished in this work. This function enables integrating point measurements for scaling up to the field level, and allows for fewer measurements to predict the total emissions. Under microjet irrigation, no useful emissions pattern was determined resulting in more measurements needed to characterize the total emission from an orchard.

Data from this research project are being used to calibrate and conduct sensitivity analyses for the DNDC model. The first step was to subject the data to weighted multifactor correlations using principle components analyses. Detailed soil sampling around both drip and microjet emitters revealed that topsoil  $N_2O$  concentration was the best weighting factor for  $N_2O$ emissions. This was important because it verifies consistency with the soil gas diffusivity model. In our case it was also well correlated with ammonium (NH<sub>4</sub><sup>+</sup>) and soil CO<sub>2</sub> concentration. These results indicated that nitrification may be the governing process that affects N<sub>2</sub>O emissions at our site. As  $CO<sub>2</sub>$  concentration increased and NH<sub>4</sub><sup>+</sup> decreased the correlation shifted toward nitrate (NO<sub>3</sub>) but N<sub>2</sub>O emissions were much lower at that time. The next step is in identifying nitrification as the primary  $N_2O$  source by the DNDC model, and to detect such changes in soil NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub> to predict N<sub>2</sub>O emissions. This will allow us to better identify BMPs.

#### **Materials and Methods:**

Objective 1. Compare GHG emissions ( $N_2O$ , CH<sub>4</sub> and CO<sub>2</sub>) 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<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>4</sub> were acquired from static chambers placed over permanently affixed array 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 Exetainers® (Labco Ltd, High Wycombe, UK). The Exetainers were evacuated to roughly 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 and can be stored long term. We have tested this several times and the containers exhibit very little leakage.

N<sub>2</sub>O was analyzed on a gas chromatograph (GC) with a Poropak Q Column (1.8 m, 80/100, 90 $^{\circ}$ C) with N<sub>2</sub>O detected using a 63Ni electron capture detector. CO<sub>2</sub> and CH<sub>4</sub> were analyzed on the GC with Poropak Q Column using a flame ionization detector (300 $^{\circ}$ C). Rates of N<sub>2</sub>O and  $CO<sub>2</sub>$  emission or  $CH<sub>4</sub>$  production and consumption were calculated using modifications to the methods described by Smart and coworkers (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:

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

where J is the apparent net flux of N<sub>2</sub>O (or CO<sub>2,</sub> CH<sub>4</sub>) from the soil surface (nmol m<sup>-2</sup> min<sup>-1</sup>),  $d[N_2O]/dt$  is the change in N<sub>2</sub>O (or CO<sub>2</sub>, CH<sub>4</sub>) 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<sup>-1</sup>) mol<sup>-1</sup>) and A is the chamber area (m<sub>2</sub>). 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 (**Figure 1**). At each flux chamber position during experiments to constrain spatial variation in  $N<sub>2</sub>O$  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).

Objective 2. Evaluate temporal (and spatial) heterogeneity of N2O fluxes (Obj 1) with respect to environmental factors (fertilizer N and soil N, temperature, soil moisture, texture, etc.)

Soil samples were collected for chemical analysis. The soil samples were immediately placed in a 2 molar solution of potassium chloride in the field, returned to the laboratory and placed on a shaker for 24 hours. The solutions were filtered using Whatman #2 filter papers. The filtered solutions were measured for NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub> content (mineral-N). Nitrate (NO<sub>3</sub>) was determined by reduction to nitrite via a copperized cadmium column. The nitrite concentration was then measured by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethlyenediaminie dihydrochloride. The absorbance of the product was measured at 520 nm. Ammonia (NH<sub>4</sub><sup>+</sup>) 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).

Objective 3. Acquire ground verification data for 2-D spatial models of event related  $N<sub>2</sub>O$  fluxes to model  $N_2O$  emissions episodes (Objective 2) for the three treatments.

For experiments to characterize spatial variability in  $N_2O$  emissions around the drip irrigation emitter, transects consisting of flux chamber positions were established across the row and into the alley. The transect line started at the center of the drip irrigation or microjet spray emitter. Nitrous oxide emissions from each of four repetitions of flux chambers were modeled

according to a sinusoidal function for the drip and a 2D distribution for the microjet. The modeled results were then integrated according to the wetting patterns of the emitters.

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 and temporal patterns of  $N_2O$  emission events from the wet-up area around the water emitter and for the driveways between trees (precipitation), these instantaneous rates of  $N_2O$ ,  $CO_2$  and  $CH_4$  emissions can be 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-wet areas of the orchard were measured several times during the season and were close to zero.

Objective 5. Provide ground verification data of other soil series 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<sub>2</sub>O and CO<sub>2</sub> concentrations, water content, bulk density, NO<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, and temperature were measured at depths of 7, 15, 30, 45, and 60 cm under the measurement collars. Correlations between those parameters and  $N<sub>2</sub>O$  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.

Spatial patterns of  $N<sub>2</sub>O$  emissions around a microjet emitter for the three treatments during three days after a fertigation event are presented in **Figure 1.** In all treatments peak emissions occur at a distance of 170 cm from the microjet probably because of its water distribution pattern. Since more water was delivered at this distance and with it, more N fertilizer, substrate for microbial activity was higher there;, hence, we believe this accounted for the higher emissions. Emissions were highest for the AGP treatment since the amount of fertilizer applied in it was highest. P&F emissions were similar to AGP at all distances except for 170 cm in which they were half of that observed in AGP treatment. Unlike in the AGP treatment, in which emissions increased in the second day, in the P&F treatment emissions decreased to almost zero during the second day. In both of those treatments emissions were negligible during the third day following N application. Peak emissions under the HFLC treatment were much lower than for the other treatments during day 1.



Figure 1: Spatial patterns of N<sub>2</sub>O emissions under three treatments (AGP, P&F and HFLC) during three days after an N fertigation event

Objective 2. Evaluate temporal (and spatial) heterogeneity of  $N<sub>2</sub>O$  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 tortosity. None of the measured parameters had any correlation with emitted N2O fluxes (**Table 1**). This data suggests 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.

	q $N-N2O$	WC.	NO <sub>3</sub>	NH <sub>4</sub>	Porosity	Tortosity
q N-N <sub>2</sub> O						
<b>WC</b>	$-0.10121$					
NO <sub>3</sub>	$-0.01862$	$-0.21809$				
NH <sub>4</sub>	$-0.06102$	0.24221	0.510764			
Porosity	$-0.09782$	0.15171	$-0.0654$	0.189819		
Tortosity	$-0.08114$	0.802415	$-0.14833$	0.074354	$-0.53481$	

**Table 1**: Correlations between soil parameters and N<sub>2</sub>O emissions under microjet irrigation.

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.

Spatial  $N<sub>2</sub>O$  measurements around drippers showed decreasing emissions with distance from the dripper (**Figure 2**). This pattern fitted a sinusoidal function:

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

where q is the N<sub>2</sub>O flux [ng N<sub>2</sub>O-N cm<sup>-2</sup> h<sup>-1</sup>] and r is the distance from the dripper [cm], q<sub>max</sub> is the maximal emission rate at r=0 [ng N<sub>2</sub>O-N cm<sup>-2</sup> h<sup>-1</sup>], r<sub>max</sub> is the distance to the edge of the wetting front [cm]. Predicted fluxes fit well the measured fluxes around the dripper (**Figure 3**) one to three days after a fertigation event and after an irrigation event.

Predicted fluxes were then integrated using:

$$
q_{drip}=2\int_0^{\pi/2}\int_0^{r(\alpha)}q(r)drd\alpha
$$

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

$$
r(\alpha) = \begin{cases} r_{\max} & \alpha \le \alpha_c \\ \frac{d}{2 \sin \alpha} & \alpha < \alpha_c \end{cases}
$$

where d is the distance between adjacent drippers [cm] and  $\alpha_c$  [Radian] is the angle from the dripper to the point where the two wetting fronts intersect. Multiplying  $q_{drip}$  by the number of drippers in the orchard yields total emission for the orchard.





Spatial  $N<sub>2</sub>O$  fluxes around the microjet yielded a 2-dimensional pattern that could be represented by a rectangle of 400 cm (diameter of the wetting radius) by 640 cm (distance between trees). Every measurement would then represent a 50 cm (distance between collars) by 640 cm (distance between trees) strip of soil. The 0 cm 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. Calculated emissions were then summed and multiplied by two to give total N2O emission per tree (or per microjet):

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

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



**Figure 3:** Measured and predicted  $N_2O$  emission as a function of distance from a dripper. DAF – day after fertigation, DAI – day after irrigation.

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. Therefore an annual emission budget is yet unavailable. However, based on the high variability of the measurements it appears that there will be no significant differences in the annual emission budget between the three different treatments.

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  $N<sub>2</sub>O$  emissions. Principal component analysis revealed that soil  $N<sub>2</sub>O$  concentration at the upper soil layer (7 cm) was the most predictive parameter for  $N<sub>2</sub>O$  emissions for both drip and microjet emitters (**Figures 4A, 4B**). Under drip irrigation soil N<sub>2</sub>O concentration was well correlated with NH<sub>4</sub><sup>+</sup> during the first day following N fertilization (DAF1) and with NO<sub>3</sub> in DAF3 (**Figure 4C**). These results indicated nitrification was the governing process affecting N2O emissions. Ammonium concentration decreased with time causing the  $N<sub>2</sub>O$  flux to decrease as well. As the substrate concentration for nitrification (NH<sub>4</sub><sup>+</sup>) decreased and CO<sub>2</sub> levels increased in the soil, the governing process seemed to shift to denitrification, perhaps in anaerobic microsites, hence the lower correlation with extractable soil  $NH_4^+$  and the positive correlation with extractable soil NO<sub>3</sub>. Under microjet irrigation (**Figure 4D**), during DAF1 there was a statistically significant high positive correlation between soil N<sub>2</sub>O and soil extractable NH<sub>4</sub><sup>+</sup> (R<sup>2</sup> = 0.82), WFPS ( $R^2$  = 0.93), and CO<sub>2</sub> ( $R^2$  = 0.81). During the following 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<sub>4</sub>, WFPS, CO<sub>2</sub> and NO<sub>3</sub> respectively. It seems that nitrification was the governing process affecting  $N<sub>2</sub>O$  emissions during the 3 days of measurement, mainly because of the relatively high correlation with  $NH_4^+$ . However, the non-uniformity of water and nutrient distribution in this treatment makes it harder to try to predict  $N<sub>2</sub>O$  emissions from the gathered data.



Component 1

**Figure 4:** PCA for drip (A, C) and fanjet (B, D) all measurements (A, B) and only measurements taken at a depth of 7 cm (C, D).