# **Nitrous Oxide Emissions from an Almond Orchard**

**Project No.: 09-AIR2-Smart**

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### **Objectives:**

Nitrogen mobilization (offsite transport of reactive forms of N, including NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub>, NO<sub>3</sub> plus the gaseous forms of  $NH_3$ ,  $N_2O$ , and  $NO_x$ ) has become an important environmental concern of State and Federal regulatory agencies. As a Greenhouse Gas (GHG), N2O is being regulated under the California Global Warming Solutions Act, Assembly Bill 32 in June of 2006 (AB32), and under the Clean Air Act, with the US EPA's recent endangerment finding for Greenhouse Gases (GHGs) such as  $CO<sub>2</sub>$ , N<sub>2</sub>O and CH<sub>4</sub> [\(http://www.epa.gov/climatechange/\)](http://www.epa.gov/climatechange/). The current project represents a merging of two previous projects whose overarching objective is to constrain (quantify accurately) nitrogen use efficiency of almond (NUE), here defined as enhancing nitrogen retention in orchards and fostering economically favorable production while minimizing offsite transport of reactive forms of nitrogen. The project integrates efforts with 7 other principal investigators through a highly coordinated investigation under the direction of Dr. Patrick Brown. The larger project highlights the enhancement of sustainable practices through better understanding of how irrigation and fertigation practices influence N mobilization. Among a number of objectives being pursued under this larger investigation, we are focusing on the following aspects:

- 1) To compare  $N_2O$  soil emissions from two different forms of nitrogen (N) fertilizer, urea ammonium nitrate (UAN) and calcium ammonium nitrate (CAN).
- 2) To evaluate seasonal variability of  $N<sub>2</sub>O$  soil emissions before and after fertilizer application and integrate observations for seasonal comparison.
- 3) To identify factors such as water-filled pore space, soil temperature, inorganic N concentration and pH to develop a greater understanding of the controls of  $N_2O$  soil emissions from almond orchard floors.
- 4) To develop spatially explicit models of  $N<sub>2</sub>O$  soil emissions for improved quantification under drip and microjet sprinkler fertigation applications in almond orchards.
- 5) To estimate orchard fluxes of N (NH<sub>4</sub><sup> $#$ </sup>, NO<sub>3</sub>, NH<sub>3</sub>, and N<sub>2</sub>O) using an isotopic tracer approach to better understand NUE at the orchard scale.

## **Interpretive Summary:**

Our preliminary results have indicated that soil nitrous oxide emissions ( $N<sub>2</sub>O$ ) are diminished when calcium ammonium nitrate (CAN) is the N-source as compared with urea ammonium nitrate (UAN) as N-source. During summer, peak  $N_2O$  emissions from applications of UAN fertilizer were significantly lower than emissions from CAN application (p<0.0001). This result was unexpected in as much as nitrate ( $NO<sub>3</sub>$ ) is the main substrate for denitrification and CAN contains more  $NO<sub>3</sub>$  per unit fertilizer N than does UAN. In a like manner,  $N_2O$  emissions appear to be diminished under microjet spray fertigation compared to conventional drip irrigation, but this result is not an unequivocal finding until it can be integrated spatially and temporally. This is a consequence of the complex spatial distribution of N and water during fertigation. Microjet sprinklers apply N and water to a more extensive area of the orchard floor which dries more rapidly than the zone of drip applied water. For this reason, quantitative differences remain uncertain over an entire growing season. Nitrous oxide emissions after fertilizer applications followed distinct patterns depending on seasonal factors (soil and ambient temperature and soil moisture conditions). Peak emissions occurred between 11 and 60 hours after fertilizer application depending on season. This appeared to be related to the duration of time where soils exceed 50% of soil pore space filled with water, and points to the real possibility of modifying water (and N) application to diminish  $N_2O$  emissions. Additional factors, such as inorganic N concentration, appear to control the potential for  $N_2O$  production and subsequent loss.

## **Materials and Methods:**

## *Seasonal N2O Emissions*

Gas emissions sampling was conducted during the primary tree phenological stages thought to correspond to periods of diverse nitrogen demands, soil and ambient temperatures and soil moisture. We hereafter refer to these stages as Spring, Summer, Fall and Winter for 2009 and 2010. The above mentioned seasonal (and phenological) periods occurred during the following general dates: Winter, Nov. 1-Jan. 31; Spring, Feb. 1-April 30; Summer, May 1-July 31 and Fall, Aug. 1-Oct. 31 (Lopus et al., 2010). The investigations were conducted at Paramount Farming Company's Belridge Almond Ranch near Lost Hills, CA on a sandy (sandy-clay) loam soil and at the Nickels Soil Laboratory (sandy loam) in Arbuckle California. The timing of all cultural practices, in particular water and nitrogen applications, was carried out in close conversation with University of California Cooperative Extension, Kern Co, under the guidance of Blake Sanden.

Fertilizer applications were on June 22<sup>nd</sup>, 2009 (Summer<sup>a</sup>), Oct. 20<sup>th</sup>, 2009 (Fall), Feb. 22<sup>nd</sup>, 2010 (Spring<sup>a</sup>), April 7<sup>th</sup>, 2010 (Spring<sup>b</sup>) and June 30<sup>th</sup>, 2010 (Summer<sup>b</sup>). The experimental design was a completely randomized block design with two treatments and five blocks for a total of ten field plots. The treatments consisted of UAN and CAN as a nitrogen form at the same rate of 200 lb acre<sup>-1</sup> N split into 40 lbs acre<sup>-1</sup> N during Spring<sup>a</sup> and Fall and 60 lbs acre<sup>-1</sup> N during Spring<sup>b</sup> and Summer. We intensively monitored gas emissions and soil mineral nitrogen concentrations following the fertilizer applications for up to eleven days. Summer 2009 and 2010 data followed similar patterns and were combined and analyzed as replications.

In each plot, one 8 inch polyvinyl chloride (PVC) ring placed mid-way between fanjet applicators on the berm and at the edge of the berm; where they remained in the same location. Sampling of the alley was conducted using chambers without collars due to the perturbation effect of installing collars on highly compacted and high traffic space. In April 2009, we conducted multiple daily rounds to see when emissions peaked. During the following year, we captured peak emissions in late afternoon and additional temporal variability during predawn and morning.

Gas was sampled from a 3.3-L polyvinyl chloride chamber (PVC) placed over the ring at 0, 40 and 80 min using 20 cc syringes and injected in evacuated vials. Analysis of  $N<sub>2</sub>O$ showed a linear flux using the aforementioned sampling method and we reduced headspace sampling to 0 and 40 min. A digital multimeter (Fluke Corporation, Everett, WA, USA) attached to a thermocouple inserted into the headspace determined chamber temperature and a digital 8 inch thermometer was used for soil temperature.

Soil samples collected in adjacent plots of the same treatment were extracted to 30 cm depth, roots and debris were removed, and mixed. An aliquot of soil placed into soil tins weighed, dried at 105 $^{0}$ C for 48 h and reweighed was used to determine of gravimetric water content. Standard cores of 325  $cm<sup>3</sup>$  were used to determine soil bulk density and to calculate volumetric water content and water-filled pore space (WFPS). A separate aliquot of soil placed in cups containing 2M KCI was used to determine soil NH<sub>4</sub><sup>+</sup> and  $NO<sub>3</sub>$  colorimetrically. Data was analyzed using PROC GLM (SAS Cary, NC) and power transformed when appropriate.

### *Spatial Modeling of N2O Emissions*

The main objective of this experiment was to assess if the total  $N<sub>2</sub>O$  emitted per hectare of orchard was substantially influenced by the micro-irrigation system used (microjet spray versus conventional drip). To achieve this objective,  $N_2O$  emissions were monitored after fertigation events and over time using a series of transects in a microsprinkler and in a drip irrigated almond orchard (**Figure 1**).



**Figure 1**. Collar distribution (scheme and picture) for sprinkler irrigation and for drip irrigation. Pictures correspond to the collars installed in Nickels soil lab Almond Orchard in Arbuckle, CA

The experiments were carried out in a University of California experimental almond orchard in Arbuckle, (39°01′N 122°03′ W) during the fall of 2009 and are ongoing in 2010. Irrigation amounts were regulated at approximately 40% of the estimated evapotranspiration demand  $(ET_c)$  as estimated from the Penmann-Monteith relationship, evaporation from a Class A pan (Pritchard 1992) and adjusted using an almond crop coefficient (K<sub>c</sub>). Two different microirrigation systems were compared: single hose drip irrigation, consisting of four 3.8L/hour emitters per tree and microjet sprinkler, with one emitter per tree. Total hours of irrigation were calculated to deliver the same amount of water in both treatments during each fertigation event. In a previous report (2009) we focused on seasonal emissions. In the current report we focus more on modeling and understanding emissions during individual fertigation events, which are then incorporated into the seasonal trajectory.

### **Results and Discussion:**

Nitrous oxide emissions after fertilizer applications followed distinct patterns according to season. During Spring<sup>a</sup>, N<sub>2</sub>O emissions peaked after 60 hours at 154 nmols N m<sup>-2</sup> min  $^{-1}$  for UAN and at 100 nmols N m<sup>-2</sup> min  $^{-1}$  for CAN. In Spring<sup>b</sup>, N<sub>2</sub>O emissions

peaked after 25 hours at 260 nmols N m<sup>-2</sup> min<sup>-1</sup> for UAN and 182 nmols N m<sup>-2</sup> min<sup>-1</sup> for CAN. Summer  $N_2O$  emissions peaked after 10 hours at 467 nmols N m<sup>-2</sup> min<sup>-1</sup> for UAN and 167 nmols m<sup>-2</sup> min<sup>-1</sup> for CAN and showed a significant difference ( $p$ <0.0001). In Fall, peak N<sub>2</sub>O emissions appeared following 60 hours and peaked lower at 128 nmols N m-2 min -1 for UAN and 86 nmols N m-2 min -1 for CAN (**Figure 2 and Table 1**). Past work by scientists in different geographical locations has observed seasonal variability of N2O emissions in relation to fertilizer management practices (Venterea et al., 2010; Verma et al., 2006).

**Table 1.** Time elapsed to peak N<sub>2</sub>O emissions, rate of N<sub>2</sub>O emissions at the peak and soil temperature. Shown are data from seasonal fertilizer application of urea ammonium nitrate (UAN) and calcium ammonium nitrate (CAN). Statistical significance at P≤0.05 and nonsignificance (NS) for P>0.05 (Lost Hills, CA 2009-2010).



After fertilizer application with irrigation water, plots were allowed to dry for up to 9 days. The soil drying rate was different for each season with the most rapid drying rate in Summer, followed by equal rates in Spring $<sup>b</sup>$  and Fall and the slowest rate in Spring<sup>a</sup></sup> (**Figure 2**). Soil temperature during the soil drying periods explains the velocity of each rate. Average soil temperature during Summer was 25°C; 17°C and 18°C in Spring<sup>b</sup> and Fall respectively, and the lowest soil temperature with the slowest soil drying rate was in Spring<sup>a</sup> at 14°C (Table 1). During sampling rounds, we experienced rain on Day 4 in Spring<sup>a</sup> and an irrigation event on Day 9 in Summer (**Figure 2**). Research under laboratory conditions examined  $N_2O$  production during a soil drying phase (Beare et al., 2009). The wetting, drying and rewetting phases of California irrigated almond orchards present a valuable opportunity to make similar observations under field conditions.



**Figure 2**. Nitrous oxide (N<sub>2</sub>O) soil emissions during baseline sampling one day prior to the application of fertilizer. At time = 0 (Day 0) N as urea ammonium nitrate (UAN) and calcium ammonium nitrate (CAN) was applied through the microirrigation system. Applications were allocated during the season with 20% in Spring<sup>a</sup>, (40 lbs acre<sup>-1</sup>), 30% in Spring<sup>b</sup>, (60 lbs acre<sup>-1</sup>), 30% in Summer and 20% in Fall (Lost Hills, CA 2009-2010).

In Summer,  $NH_4^+$  and  $NO_3^-$  reached the maximum concentrations on Day 1 after fertilizer application in the UAN treatment and Day 2 in the CAN treatment (**Figure 3**). The availability of inorganic N substrate for nitrification and denitrification is a known requirement for the production of  $N_2O$  gas (Davidson et al., 1996). Treatment differences in  $N_2O$  emissions may be the result of less inorganic N substrate availability in CAN as compared to UAN. Maximum concentrations of  $NH_4^+$  and NO<sub>3</sub> in CAN on Day 2 coincided with a 5% reduction in water-filled pore space from the previous day. Simultaneous processes of nitrification in aerobic soil pores and denitrification in anaerobic soil microsites are responsible for  $N<sub>2</sub>O$  production (Abbasi and Adams, 2000; Khalil et al., 2004). The combination of maximum inorganic N concentration and waterfilled pore space on Day 1 may explain the greater  $N_2O$  emissions from the UAN treatment.

Our results indicated that  $N_2O$  emissions from almond orchards occur after fertilizer applications and subsequent irrigations (See Summer Day 9 in **Figure 1**). Our results confirm the requirement to focus intensive measurements after fertilizer applications to accurately quantify emissions. Multiple microbial processes contribute to the production of N2O. Past work demonstrated the equivalent contribution of nitrification and denitrification to the total  $N_2O$  emissions over a fertilization period (Panek et al., 2000). Our work contributes to a growing understanding of seasonal variability and the effects of fertilizer treatments.

Our results have also suggested that water filled pore space (WFPS) is a more important variable in determining the rates of  $N_2O$  emissions following fertigation (**Figure 5**). There was a significant relationship between WFPS that strongly suggested pore space at greater than approximately 40% water had higher  $N<sub>2</sub>O$  emission rates, while mineral N (NH4<sup>+</sup>) did not show a clear relationship with the emission rates.



Figure 3. Relationship between water-filled pore space and  $N_2O$  emissions and soil  $NH_4^+$ concentration (Nickels Soil Laboratory, 2009-2010). The relationship between other variables like soil  $NO<sub>3</sub>$  concentration and temperature are being processed.



**Figure 4.** Inorganic N concentrations of ammonium  $(NH_4^+)$  and nitrate  $(NO_3)$  during baseline sampling time = -1 days and after fertilizer application on day = 0 of urea ammonium nitrate (UAN) or calcium ammonium nitrate (CAN). Applications were allocated during the season with 20% in Spring<sup>a</sup>, (40 lbs acre<sup>-1</sup>), 30% in Spring<sup>b</sup>, (60 lbs acre<sup>-1</sup>), 30% in Summer and 20% in Fall for a total of 200 lbs N/acre (Lost Hills, CA 2009-2010).

For the comprehensive data set, it is likely that multiple environmental variables will best explain temporal (and spatial) variability in  $N_2O$  emissions. For example, it can be seen in **Figure 4** that inorganic N contents in experiments being conducted at the Lost Hills site have dynamics of inorganic N content in soils that are similar to those observed for N2O emissions (**Figure 2**).

### *Spatial Distribution of N2O Emissions around Water Emitters*

In order to better quantify soil generated  $N_2O$  around emitters, we designated a circular area of 1 m of diameter for drippers and of 5 m diameter per sprinklers. In three different trees  $(n = 3)$  for each of the irrigation systems we established two transects forming axes crossing at the drip or sprinkler irrigation emitter impact zone which was designated as the origin (0,0). One transect (N-S, Y-ordinate) was established parallel to and directly in the tree row, and the other (E-W, X-ordinate) perpendicular to the tree row and into the alley (**Figure 1**). In each of these transects we determined 5 locations where soil  $N_2O$  flux was sampled. These 10 points per site were used to determine the N<sub>2</sub>O emission distribution around the sprinkler or dripper. Drip irrigation showed a peak of emission in the center (emitter location) followed by a rapid decline as the distance from the emitter increased, reaching values close to zero at distances of about 1 m from the center (**Figure 5**). In contrast to drip, sprinkler distribution showed the peak of emission at a distance around 1m from the center and then it decreased exponentially until values close to zero were reached at distances of  $2.5 - 3$  m form the emitter (**Figure 6**).

The  $N<sub>2</sub>O$  emissions patterns and peaks closely mirrored the patterns of wetting the two different microirrigation systems have. Thus, to some extent  $N<sub>2</sub>O$  may be spatially related to soil water content. However, other parameters are also influencing these emissions. From the defined distribution in each of the irrigation system, we calculated the total amount of  $N_2O$  emitted per unit of soil surface and time and extrapolated it to a bigger scale. We obtained the total amount in mass of N from  $N<sub>2</sub>O$  emitted per hectare and hour during the hours when  $N_2O$  emission peaks in the days following to a fertigation event (data not shown). We monitored  $N<sub>2</sub>O$  as described during one month after a fertigation event (UREA, 30 pounds per acre). The maximum instantaneous rates of N<sub>2</sub>O emission corresponded to levels of 59 nmol N m<sup>-2</sup> min<sup>-1</sup> and 48 nmols N m<sup>-</sup>  $2$  min<sup>-1</sup> for drip irrigation and sprinkler irrigation respectively. However, these represent instantaneous rates and therefore cannot yet be scaled to the level of an entire season of emissions. In addition, the area wetted by the microjet sprinkler and conventional drip systems only represents a fraction of the total area of the orchard. For this reason, the total quantities of  $N_2O-N$  loss are uncertain but we are very near to having the requisite databases for making such an estimate for UAN and CAN.



Distance from the center of the emitter impact zone (m)

Figure 5. Examples of N<sub>2</sub>O distribution derived from drip irrigation. The models were derived from three dimensional fits of the Gaussian distribution and illustrate the complexity of constraining emissions from localized irrigation events.



Distance from the center of the emitter impact zone (m)

**Figure 6.** Examples of N<sub>2</sub>O distributions from microjet sprinkler delivered fertigation. The models were derived from three dimensional fits of a 2D function defined by two parts: a second degree polinomy and an exponential decay and illustrate the complexity of constraining emissions from localized irrigation events.

Nonetheless, the emissions rates indicated that total loss of N as  $N_2O$  was still higher for the conventional drip than for sprinkler irrigation. As far as temporal evolution is concerned, sprinkler irrigation showed a peak of emission one day after the fertigation event and then a decrease until it reached base line values 4 weeks thereafter. Under drip the dynamic was slower with peak emissions on day 3 (**Figure 5 and 6**). After delivering the same amount of water in a single irrigation event, soils in drip irrigation appeared to be highly saturated or even flooded in the center of the distribution, while water was distributed in a larger area for sprinkler with less indication of flooding occurrence. As a consequence, soil maximum water content seemed to be lower in sprinkler irrigation than in drip irrigation and soil drying was also faster in the former. During a fertigation event, the soil mineral N concentration is directly coupled to horizontal and vertical distribution of water applied. This and the possibility that water filled pore space exceed 50% (**Figure 3**) for longer duration in conventional drip may help to explain why we are seeing higher emissions.

## **Conclusions:**

The changes the soil physics after a fertigation event differ between drip irrigation and sprinkler irrigation. Our first results show how these differences result in higher N losses per hectare if the same amount of water and N is delivered by drip irrigation in contrast with microjet sprinkler irrigation. Future work includes continued data collection to better describe the conditions after fertilizer application in order to integrate  $N<sub>2</sub>O$  emissions over time. Furthermore, we will continue to describe factors such as water-filled pore space, soil temperature, inorganic N concentration and pH to develop a greater understanding of the controls of  $N<sub>2</sub>O$  emissions. Additional experiments using <sup>15</sup>N tracer will add to our understanding of the multiple processes that control  $N_2O$  emissions and inorganic N concentration such as N mineralization and immobilization.

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