Evaluating Nitrogen Use Efficiency in Almond Using an Isotopic Tracer Approach

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Objectives:

The overarching objective we are addressing in this project builds upon the experiments established at the Nickels Soil Laboratory to diminish emissions of N_2O and acquire information on soil C sequestration for almond. These objectives are designed to get preliminary information concerning the application of a ^{15}N tracer to experiments being conducted at the Belridge almond orchard near Lost Hills, California, which is part of a larger experiment examining nitrogen use efficiency under different N input amounts and irrigation systems.

1) *To conduct preliminary experiments on the use of ^{15}N enriched (10% to 50%) CAN17, as a tracer to examine N-loss and thus have better constrained estimates of nitrogen use efficiency by almond as well as potential environmental impacts.*

Interpretive Summary:

The increase in concentration of the three major greenhouse gases (GHGs) of carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4) is leading to indisputable changes in global climates. Climatic alterations that will adversely affect California agriculture include increased temperatures, more restricted water resources (snowpack), flooding and shifts in seasonal precipitation patterns (Prather et al. 1994; Hayhoe et al. 2004; Houghton et al. 1995). During the past 250 years CO_2 has

increased by 31±4%, CH_4 by 151±4% and N_2O by 19±5% (Forster et al. 2007). The current concentration of N_2O, the major subject of this investigation, was 319 ppb in 2005 (Forster et al. 2007) as compared to its pre-industrial concentration of 270 ppb. Nitrous oxide has 298 times the global warming potential (GWP) of CO_2 based on radiative forcing characteristics and atmospheric lifetimes of the respective gas molecules (IPCC, 2001). Although the rate of increase of N_2O in the atmosphere (at about 0.27% per year), is slower than that of CO_2 (and CH_4), this slower rate is offset by its higher GWP. The primary global sink for N_2O involves photolytic reactions with excited oxygen [$O(^1D)$] in the stratosphere to produce nitric oxide (NO) which consumes stratospheric ozone(Cicerone, 1987). For these reasons, the importance of N_2O as a GHG, whose anthropogenic emissions need to be understood and constrained has not been underestimated, and its link to nitrogen (N) fertilizer use is currently under increasing scrutiny by regulatory organizations.

At the global scale, annual emissions of N_2O from cropped soils are estimated at 3.3 Tg N_2O-N yr^{-1}, which is about 6% of the global anthropogenic CO_2 emissions from fossil fuel combustion (Forster et al. 2007; Kroeze et al. 1999). This quantity, and the factors that contribute to it, remain very poorly estimated (Boumann et al. 2002; Stehfest and Boumann, 2006). Uncertainty surrounding N_2O emissions ranges from 30 to 300% (IPCC, 2001) and recent comprehensive reviews of the N_2O literature place confidence intervals around N_2O emissions from agricultural systems at from -81 to 621% with coefficients of variation on annual N_2O emissions from over 1000 observations at -40 to +70 % (Olivier et al. 1990; Winiwarter and Rypdal, 2001). Winiwarter and Rypdal (2001) reported coefficients of variation on N_2O emissions from agricultural soils that ranged from 100 to 900%. The skewed positive distribution is typical for a gas with emissions that are greatly accelerated by events such as precipitation, irrigation, N fertilizer application and non-uniform distribution of organic C (Parkin, 1987). Disaggregation of N_2O emissions estimates based on environmental parameters (climate, soil organic C, texture, drainage and pH); and management-related factors (N application rate, fertilizer type, type of crop, eg. N fixation versus non-N fixing, and forage type) (Stehfest and Boumann, 2006; Winiwarter and Rypdal, 2001) verifies that N fertilizer application is the primary variable driving agricultural N_2O emissions. Variation in N_2O emissions is the main source of uncertainty in efforts at national inventories of agricultural GHG emissions, and current estimates of N_2O production by agricultural soil management is the subject of much debate.

Agricultural related activities in California are thought to account for up to 70% of N_2O production (Franco et al. 2002). We estimate that 52% of this amount is related to soil management, mainly N fertilizer applications (Carlisle et al. 2009), while the rest is attributed to manure management. Agriculture accounts for over 12% of the total State GHG budget when forest sequestration (CEC, 2004) is excluded. It is for the above reasons it has been concluded that N management in agriculture plays an unequivocal quantitative role in statewide GHG production by regulatory agencies. The State is committed to reduce its GHG emissions to the 1990 level by 2020 as stipulated in approval of the Global Warming Solutions Act of 2006 (AB 32), and to an 80% reduction of the 1990 GHG emission levels by 2050 as mandated by Executive Order S-3-05 signed by the by the Governor on June 1, 2005. Greater than half of agricultural N_2O

production in California derives from application of N fertilizer, and manure management (IPCC, 2001), and this is true for California's terrestrial ecosystems as well (Franco et al. 2002). It is therefore critical that we develop an enhanced understanding of the biophysical factors controlling N_2O emissions to foster development of mitigation strategies. Accurate quantification requires robust measurements of annual budgets of N_2O emissions and accurate ground verification exercises to calibrate biogeochemical simulation models that can estimate annual N_2O budgets for a range of representative crop management systems in California. Not only are N_2O strongly influenced by environmental conditions such as climate, soil type, and cropping system (Mosier et al. 1996; Boumann et al. 2002b) but an explicit spatial component exists in directed fertilization and irrigation events. Uncertainties in estimates of N_2O emissions from California agricultural systems exemplifies a lack of data, but also our inability to understand the mechanisms that contribute to temporal and spatial heterogeneity of emissions. Clearly, a more dynamic approach that includes spatial and temporal variation in N_2O emissions following fertilization and irrigation is needed. Such refinements must be grounded in improved information concerning temporal and spatial variation of water and N management. The vast majority of research concerning N GHG emissions from cropping systems in continental North America has been conducted for dryland farming systems in Midwest of the USA (Kahlil et al. 2002). In the arid climatic regimes of the West, irrigation events saturate soil water-filled-pore-space (WFPS), and intervening periods of high temperatures and aridity are the rule rather than the exception.

The primary goal of this investigation is to examine the concept of NUE where an opportunity exists within a vertically integrated project on nutrient use efficiency being conducted by Dr. Patrick Brown and colleagues at UC Davis in the Departments of Plant Sciences and Land, Air & Water Resources. The purpose of that project is to establish new critical values for potassium (K) and nitrogen (N) fertility and re-evaluate the amounts of N applied relative to both production and environmental impacts. The effort described in this proposal that will be conducted within the project being led by Dr. Patrick Brown represents an attempt to help 'close' the N budget within the context of more practical definitions of NUE e.g .yield per unit N. We are currently conducting a comprehensive project examining various forms of fertigation (surface drip, micro-sprinkle and subterranean drip) to examine ways in which emissions of N_2O loss from N fertilizer application can be mitigated. The current proposed project will provide more comprehensive information on the fate of N lost during fertigation, including that of the denitrification products of N_2, N_2O and the (mostly) nitrification products of NO and NO_2, and that which is absorbed and translocated to wood, leaf and fruit production. Thus, it will provide critical information concerning nutrient use efficiency for nitrogen in California almond production systems. During the current funding period we have been successful in conducting experiments concerning the duration of NO_3^- in the drip irrigation zone following CAN applications and in measuring gas fluxes using isotopic enrichment approaches.

Materials and Methods:

$^{15}N_2$ and $^{15}N_2O$ Gas Flux

Our objective was to simulate an application of "CAN17" fertilizer at a rate of 50 lbs N/acre with 25 and 50 atoms percent labeled ^{15}N. CAN17 is a mixture of Calcium Nitrate and Ammonium Nitrate and contains 17% N. Of this 17%, 11.6% is Nitrate-N and 5.4% is Ammonical-N. Using these proportions we used labeled and unlabeled potassium nitrate and ammonium phosphate instead.

During the summer of 2009, and coinciding with N fertilization events at the Belridge Almond Orchard in Lost Hills, California, 8" diameter (326.85 cm^2) and 2" high PVC soil collars were installed. Following installation the next day, 4 L of ultrapure water was added to the collar to wet up the soil over a 2 hour interval. Next, one more liter containing a total of 0.185g N was slowly dripped onto the soil surface at a rate of about 50 ml min^{-1}. The volumetric water content of a sandy clay loam at field capacity is approximately 0.22 with a soil bulk density of 1.4 g/cm^3. Thus we calculated that the application of 1L of solution will saturate the collar area to 10 cm depth. In total, 5 L of water was added into the collar area which we measured to wet up about 50cm deep of soil. The treatments were in replicates of 3 and all contained 0.185g N/collar (50 lbs/acre) at 11.6% NO_3-N and 5.4% NH_4-N. Treatment 1 was 0% ^{15}N (control), treatment 2 was 25% ^{15}N and treatment 3 was 50% ^{15}N. We applied 0.185g of unlabeled N to three collars (the control) and sacrificed one of the control collars each day to determine the initial N concentration as well at the rate of decline.

A fabricated soil gas chamber (4.4L headspace including ring) equipped with a manual mixing fan, thermocouple and atmospheric port was placed on the soil collars and 18 ml gas samples were collected using a 20 ml syringe at 3 hours and 24 hours post treatment at 0, 30, 60 min time intervals. The gas samples were first analyzed on a Shimadzu 2014 GC equipped with an ECD detector to measure nitrous oxide fluxes. The samples were then sent to the UC Davis Stable Isotope Facility for measurement of atomic ^{15}N% and $\delta^{15}N_2$. After the last flux on the third day, soil KCl extract samples for nitrate and ammonia were collected on the rest of the collars.

^{15}N enrichment in the gas samples was calculated according to:

$$\delta^{15}N = (R_{sample}/R_{standard} - 1) * 1000 \text{ per mil (‰)}$$

where R is the ratio of the abundance of ^{15}N on the sample as compared with a natural atmospheric N_2 standard of 0.3663% ^{15}N (the naturally occurring concentration of ^{15}N in the Earth atmosphere) and expressed as a 'per mil' rather than the conventional 'percent', although when enrichment levels were high, we have used percent in some cases.

Results and Discussion:

When an isotopic tracer of ^{15}N is employed, estimating a gas flux from soil involves knowing the concentration and ^{15}N abundance on resident soil NH_4^+ and NO_3^- and the abundance of ^{15}N within those soil pools. In the current experiments we assumed the abundance of ^{15}N in the soil mineral pools was equal to the natural abundance at 0.3663%. The duration of NH_4^+ and NO_3^- in the soil pool was longer than we had expected based on gas flux analyses alone, and NH_4^+ pools declined somewhat faster than NO_3^- pools (**Figure 1**). This result was not entirely unexpected in as much as 1) the soil NH_4^+ pool may degas to some extent since the pH is slightly basic, thus driving losses of NH_3 gas, or, 2) that oxidation of NH_4^+ to NO_3^- by nitrification simultaneously depletes and enriches the soil NH_4^+ and NO_3^- pools, respectively. During the fertilization event where 15N enriched NH_4^+ and NO_3^- were applied, the dynamics of mineral N in the soil were quicker, with both pools becoming depleted to nearly 25% of their initial enrichment levels within 48 h following application (see Table 2).

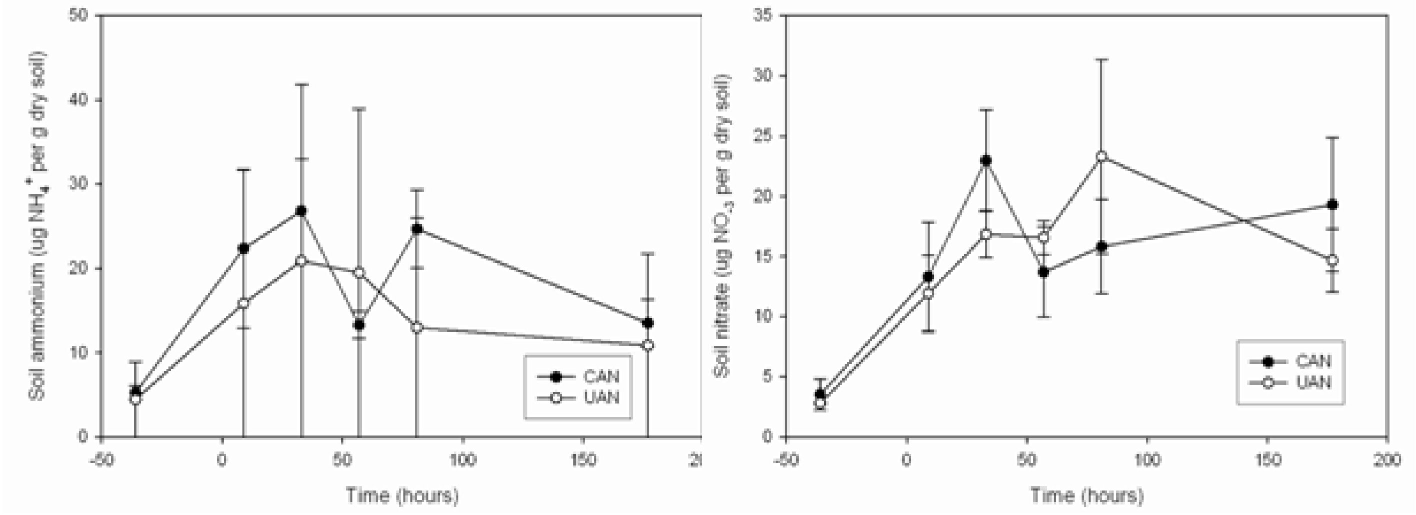

Figure 1: Soil NH_4^+ and NO_3^- concentration trajectories for 24 h prior to and approximately 180 h following a fertigation of 50 lbs. per acre UAN32 (open circles) and CAN17 (closed circles).

During the fertigation events, or the experiments we conducted where CAN17 was enriched with 25 and 50 percent ^{15}N in balanced ratios of $^{15}NO_3^-$ and $^{15}NH_4^+$, we were able to detect sufficient enrichment in N_2O gas emissions from the soil to estimate the flux of N_2O coming from the recently applied fertilizer (**Figure 2**).

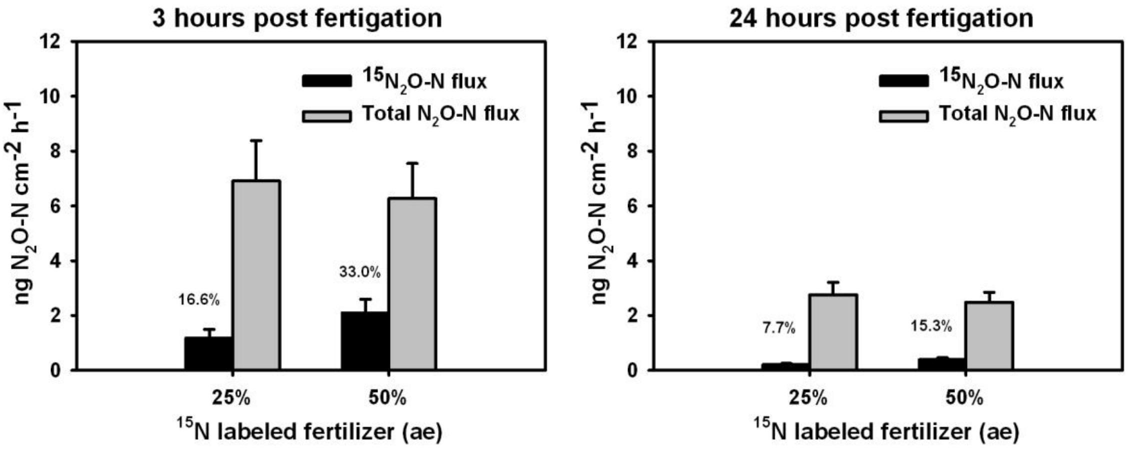

Figure 2: The $^{15}N_2O$-N flux relative to the total N_2O-N flux from the drip zone of a soil fertilized with 25% and 50% ^{15}N enriched CAN17.

We were able to detect some ^{15}N enrichment in the N_2 pool of gas entering the soil chamber (see **Table 1**) but it is uncertain whether this quantity of ^{15}N was sufficient to estimate an N_2 loss rate for the fertilizer event we monitored. Future experiments will have to rely on microcosms where either heliox (78% helium, the MS carrier gas, and 21% oxygen) or argonox environments (78% argon and 21% oxygen). These experiments are underway and are valuable in as much as they will allow us to manipulate soil water contents and other variables that affect the N_2 to N_2O production ratio, and such data can be used to modify the DNDC model for application to almond.

Table 1: The $\delta\ ^{15}N_2$-N measured after the fertigation treatment. Ambient air contains a $\delta\ ^{15}N_2$-N of -0.81 units. We are able to detect small amounts of $^{15}N_2$.

	$\delta\ ^{15}N_2$	
	3 hrs after treatment	
% ae N applied	**30 min**	**60min**
25	0.42 ± 0.25	0.55 ± 0.18
50	0.15 ± 0.10	0.11 ± 0.08
	24 hrs after treatment	
% ae N applied	**30 min**	**60min**
25	0.37 ± 0.04	0.34 ± 0.06
50	-0.51 ± 0.20	-0.64 ± 0.16

On the other hand, we were able to detect ^{15}N isotopic enrichment in N_2 gas for the pool emitted into the flux chamber consisting of $^{15}N^{15}N$ (mass 30) (see **Figure 3** and **Table 2**). We are currently exploring the possibility this enrichment can be used at the field level for assessing *in situ* losses of CAN or UAN during fertigation events and experiments for which this program was originally mounted, that of examining nitrogen use efficiency at the scale of an entire tree-soil system.

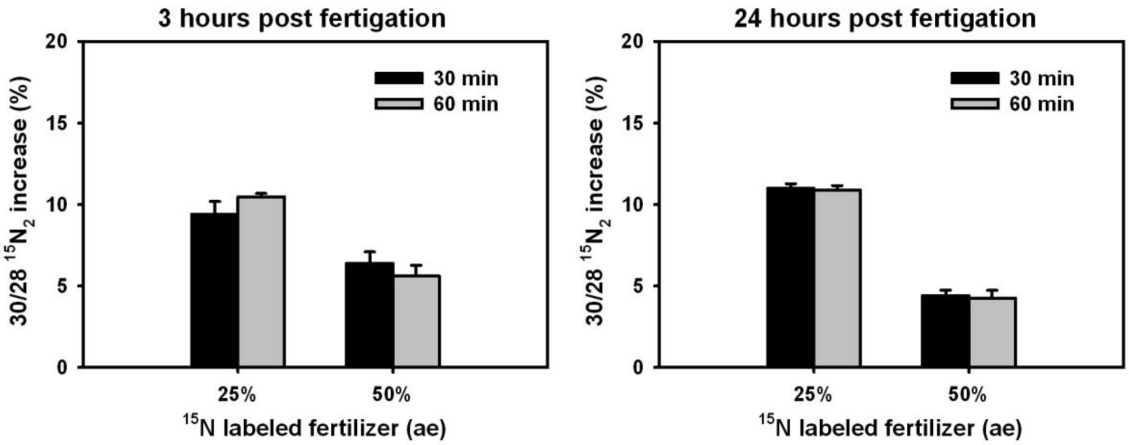

Figure 3: ^{15}N isotopic enrichment (%) of N_2 gas in the flux chamber of the rarer 30/28 N_2 ($^{15}N^{15}N$) enriched pool.

Table 2: Soil ammonium and nitrate concentrations, soil gravimetric water content (GWC) and soil temperature during the short duration of an experiment where ^{15}N enriched NO_3^- and NH_4^+ were added as a CAN17 formulation.

hours after fertigation	ug NO_3^- cm-3 dry soil	ug NH_4^+ cm^{-3} dry soil	Soil GWC	Soil Temp C
-1	10.606	97.416	0.062	-
3	1238.808	795.802	0.133	27.70
24	406.869	184.569	0.077	26.06
48	298.223	232.122	0.078	27.75

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Recent Publications:

Steenwerth, K.L., D.L. Pierce, E.A. Carlisle, R.G.M. Spencer and D.R. Smart (2009) *Tillage disturbance and precipitation affect soil respiration under Mediterranean conditions*. Soil Science Society of America Journal (in press)

Smart, D.R., E.C. Suddick, K.M. Scow, P.H. Brown, T. DeJong (2009) *An Assessment of the Carbon Sequestration Opportunities and Greenhouse Gas Emissions Attenuation by Almond Orchards in California*. (in review)