Assessment of NO_x Emissions from Soil in California Cropping Systems

FINAL REPORT

California Air Resources Board, Contract No. 09-329

Principal Investigators:
William R. Horwath
Martin Burger

Prepared for:
California Air Resources Board

Prepared by:
Martin Burger and William R. Horwath
Dept. of Land, Air & Water Resources
University of California, Davis
One Shields Avenue
Davis, CA 95616
(530) 754-6029

November 27, 2013

Disclaimer

Acknowledgements

We would like to thank Alia Tsang, Cristina Lazcano, Nick Monte, Matthew Ong, the Nickels Soil Lab, and five farmers in the Sacramento and San Joaquin Valleys and their staff for contributing their time, efforts, equipment, and land to make this study possible.

This Report was submitted in fulfillment of ARB Contract No. 09-325 *Determinng NO_x Emissions from Soil in California Cropping Systems to Improve Ozone modeling* by the University of California, Davis, under the sponsorship of the California Air Resources Board. Work was completed as of November 27, 2013.

Determining NO_x Emissions from Soil in California Cropping Systems to Improve Ozone Modeling

Disclaimer	ii
Acknowledgements	iii
List of Figures	v
List of Tables	vi
Abstract	vii
Executive Summary	vii

	Section	Page
1.	Introduction	1
2.	Materials and Methods	1
2.1.	Description of field sites by cropping system	1
2.2.	NO_x flux measurements	6
2.3.	Effects of environmental variables on NO_x emissions	7
3.	Results	8
3.1.	Almonds	8
3.2.	Alfalfa	12
3.3.	Tomato	14
3.4.	Wheat	20
3.5.	Dairy silage corn	21
3.6	Relationship between NO_x flux and soil temperature	29
4.	Discussion	30
5.	Summary and Conclusions	33
6.	Recommendations	34
7.	References	34
8.	Glossary	36
	APPENDIX	38

List of Figures

1. Mean NO_x flux, soil ammonium concentration, water-filled pore space, and soil temperature in an almond orchard. 10
2. NO_x flux vs. soil nitrite concentrations in the almond orchard. 11
3. NO_x and N_2O flux, soil ammonium concentration, water-filled pore space, and soil temperature in alfalfa. 12
4. NO_x and N_2O flux, soil temperature, water-filled pore space, and soil ammonium concentration in furrow-irrigated tomato fertilized at 0, 162, and 300 kg N ha^{-1}. 15
5. NO_x and N_2O flux, soil ammonium concentration, water-filled pore space, and soil temperature in furrow-irrigated winter cover-cropped tomato. 17
6. NO_x and N_2O flux, soil ammonium concentration, water-filled pore space, and soil temperature in subsurface drip-irrigated tomato. 19
7. NO_x and N_2O flux, soil temperature, water-filled pore space, and soil ammonium concentration in dairy silage corn system (Farm A). 22
8. NO_x flux and soil nitrite concentrations in dairy silage corn system. 24
9. NO_x and N_2O flux, soil temperature, water-filled pore space, and soil ammonium concentration in dairy silage corn system (Farm B). 25
10. NO_x and N_2O flux, soil temperature, water-filled pore space, and soil ammonium concentration in dairy silage corn system (Farm C). 27
11. NO_x flux and soil nitrite concentrations in dairy silage corn system (Farm C). 29

1A. NO_x flux measurement equipment 38

2A. Calibrating equipment for NO_x analyzer 38

List of Tables

1.	Soil characteristics at the almond orchard	2
2.	Soil characteristics of the alfalfa fields	2
3.	Soil characteristics of the tomato systems	3
4.	Soil characteristics of the wheat system	4
5.	Soil characteristics of the dairy silage corn systems	4
6.	Nitrogen inputs and application mode in the dairy silage corn systems	5
7.	Average hourly NO_x fluxes in the different systems and treatments	9
8.	NO_x fluxes in the wheat systems	21
9.	Relationship between soil temperature and NO_x flux (Q_{10})	29
10.	Estimates of daily NO_x emissions from agricultural land	33
1A.	NO_x flux data of almond orchard	39
2A.	NO_x flux data of alfalfa systems	41
3A.	NO_x flux data of tomato systems	42
4A.	NO_x flux data of dairy silage corn system (Farm A)	43
5A.	NO_x flux data of dairy silage corn system (Farm B)	44
6A.	NO_x flux data of dairy silage corn system (Farm C)	45
7A.	NO_x flux data of wheat systems	46

Abstract

Soils are a source of oxides of nitrogen (NO_x = nitric oxide and nitrogen dioxide), precursors for the production of ozone (O_3), an air pollutant in the troposphere. Production of nitric oxide (NO) occurs through soil microbial processes using ammonium from nitrogen fertilizer and manure inputs or soil mineral nitrogen (N). Emissions of NO_x were measured in almond, alfalfa, tomato, wheat, and silage corn cropping systems during summer months to obtain estimates of NO_x emissions that could potentially be used in regional models predicting O_3 in the San Joaquin Valley. The lowest average NO_x fluxes (<0.1 g NO_x-N ha^{-1} h^{-1}) were measured at low soil moisture and in subsurface drip-irrigated tomato. The highest average emissions (0.5–2.8 g NO_x-N ha^{-1} h^{-1}) occurred in high N input systems, such as silage corn. In alfalfa, almond, and furrow-irrigated tomato, average NO_x fluxes were intermediate (0.1–0.5 g NO_x-N ha^{-1} h^{-1}). The NO_x emissions were related to N inputs, time since fertilizer applications, temperature, and soil moisture. Under field conditions NO_x fluxes increased 2.5-3.5-fold for each increase in soil temperature of 10ºC. The NO_x emissions seem predictable in systems receiving N at recommended rates, ranging from 0.02 – 2.5 g NO_x-N ha^{-1} h^{-1} in alfalfa, wheat, tomato, and almond, but in systems receiving large N inputs resulting in high concentrations of ammonium, episodes of very high NO_x emissions (>40 g NO_x-N ha^{-1} h^{-1}) were measured. These high NO_x flux events are difficult to predict.

Executive Summary

Background

Soils are one of the sources of NO_x (nitric oxide and nitrogen dioxide), which is involved in reactions producing ozone (O_3), a pollutant in the troposphere. In the San Joaquin Valley, ozone (O_3) levels are often elevated during summer months at many locations. According to the California Emission Inventory Development and Reporting System (CEIDARS), in the San Joaquin Valley, the State's O_3 standards were exceeded on more than 120 days per year during 2004-2007. Knowledge of the major sources of NO_x is essential to regionally predict O_3 dynamics and evaluate the effectiveness of air quality management programs. To date, estimates of NO_x emitted from agricultural soil are not included in CEIDARS. Soil-borne production of NO_x occurs through soil microbial processes using ammonium from synthetic fertilizer and manure, and soil mineral nitrogen (N). The present study provides estimates of NO_x emissions during summer months from five cropping systems, comprising 17 different locations and management treatments.

Methods

The NO_x emissions were measured in an almond orchard, and in alfalfa, tomato, wheat, and silage corn cropping systems following irrigation and nitrogen fertilization events mostly during June to September in 2011 and 2012. In the almond orchard, microjet sprinklers were used for irrigation and fertigation. Alfalfa and silage corn were flood irrigated. In the silage corn systems, synthetic fertilizer was applied before planting or as a side-dress and with most irrigations, liquid manure was mixed with the irrigation water. Tomato was either furrow-irrigated and most nitrogen fertilizer was applied as side-dress, or subsurface drip-irrigated and fertigated. Wheat, being a rainfed crop receiving N fertilizer in winter, was maturing at the time of the measurements. The NO_x-flux measurements were made by placing a chamber connected to a NO_x-analyzer on the soil surface for 3-5 minutes. The headspace air in the chamber was constantly circulated through the NO_x analyzer, and readings of the concentration of NO_x were taken every 15 seconds. The flux was calculated on a per area basis by taking the rate of change of NO_x concentration, chamber volume and temperature into account. Soil moisture, soil ammonium and temperature were also measured to characterize how environmental conditions and management affected NO_x emissions.

Results

The average hourly NO_x-fluxes were lowest (<0.1 g NO_x-N ha^{-1} h^{-1}) in dry soil, such as maturing wheat and a tractor row in an almond orchard, and under subsurface drip irrigation in tomato. Intermediate fluxes (0.1-0.5 g NO_x-N ha^{-1} h^{-1}) comparable to NO_x emissions reported in earlier studies were observed in almond, alfalfa, and in furrow-irrigated tomato fertilized at recommended N rates. The highest average hourly NO_x fluxes (0.4-2.8 g NO_x-N ha^{-1} h^{-1}) took place in the systems receiving high N inputs, such as dairy silage corn and furrow-irrigated tomatoes fertilized at an excessive N rate. The emissions were related to N inputs leading to high soil ammonium concentrations. On some occasions the magnitude of NOx emissions, which closely followed large N inputs of synthetic N fertilizer and/or liquid dairy manure, matched those of the highest fluxes ever measured. The NO_x fluxes decreased with time since N fertilization. Within a given day, NO_x fluxes increased 2.5-3.5-fold for each increase in soil temperature of 10ºC. The NO_x fluxes were also dependent on soil water content with the highest fluxes occurring at intermediate soil moisture values (30-60% water-filled pore space) and lower fluxes at higher water content.

Conclusions

The emissions at each location varied over time, depending on soil moisture, temperature, and time since N fertilization. The results suggest that NO_x emissions are related to ammonium availability and nitrification rates. Enhanced NO_x fluxes occurred under intermediate soil water contents (water-filled pore space 30-60%), whereas in relatively dry soils or at high water content, NO_x-fluxes were low. Field experiments showed that NO_x emissions increase on average 2.5- and 3.5-fold with each increase of 10°C in soil temperature at 1 and 5 cm depth, respectively. The study showed that NO_x fluxes are fairly predictable in cropping systems fertilized at recommended N rates ranging from 0.02 – 2.5 g NO-N ha^{-1} h^{-1} in alfalfa, wheat, tomato, and almond. However, in the systems receiving high N inputs, such as silage corn, the emissions following N additions resulting in high soil ammonium concentrations can be enhanced by an order of magnitude, reaching hourly fluxes up to 40 g NO-N ha^{-1} h^{-1} for several days. To regionally quantify NO_x emissions from agricultural land would require elaborate models that account for the mosaic of cropping systems and management events, such as N fertilization and irrigation, in individual fields.

Introduction

Measurements of NO_x (nitric oxide or NO and nitrogen dioxide or NO_2) emissions from agricultural soil in the Central Valley, where ozone (O_3) levels are often elevated during summer months at many locations, are needed as inputs in air quality models. Oxides of nitrogen (NO_x) are required for O_3 formation. The build-up of O_3 depends on the ratio of volatile organic compounds (VOCs) to NO_x, and the influence of these precursors on O_3 production varies temporally and spatially across the landscape (Blanchard and Fairley, 2001). When the ratio of VOCs to NO_x is low, the availability of VOCs limits O_3 formation. However, when the ratio of VOCs to NO_x is high, the availability of NO_x controls O_3 formation, and under these conditions, reducing NO_x will decrease O_3 production while reducing VOCs has little effect on O_3 formation. Therefore, quantifying all major NO_x sources is essential to regionally predict the dynamics of O_3 in the troposphere and evaluate the effectiveness of air quality management programs.

About 16% of the world's annual NO_x emissions originate from microbial activity in soils (Olivier *et al.*, 1998). Agricultural soils and associated fertilizer management are known to be sources of NO_x (Williams *et al.*, 1995). However, only few data of NO_x emissions from California agricultural soils have been reported (Matson and Firestone, 1995; Venterea and Rolston, 2000b; Lee *et al.*, 2009). Estimates of NO_x emissions from biogenic (non-anthropogenic) and fertilizer applications are conspicuously absent in the California Emission Inventory Development and Reporting System (CEIDARS), and this lack of information restricts CARB's ability to develop accurate O_3 predictions through modeling.

The objectives of the present study were to determine NO_x emissions in cropping systems typical for this region and to characterize NO_x flux in response to various amounts of N fertilizer inputs under varying soil and air temperature conditions, with a focus on daytime emissions during summer months when O_3 concentrations are problematic in the San Joaquin Valley. This research benefits the staff of CARB and the San Joaquin Valley Air Pollution Control District by providing important data to improve modeling predictions of O_3 production.

2. Materials and Methods

2.1. *Description of field sites by cropping system*

This project assessed the NO_x emissions in five different cropping systems including tomato, wheat, alfalfa, corn and almonds. Measurements of NO_x fluxes in the different systems were carried out at sites selected for N_2O emission monitoring in other projects commissioned by CARB ("Assessment of Baseline N_2O Emissions in California Cropping Systems" and "Assessment of Baseline Nitrous Oxide Emissions in California's Dairy Systems, with Dr. Horwath as the PI). The different experimental sites were chosen so that a wide range of management strategies are represented such as different fertilizer inputs (inorganic N, manures), and irrigation systems (furrow, flood and sprinkler irrigation).

2.1.1. *Almond*

The NO_x emissions in almond production systems were assessed in the Nickels Soil Laboratory in Colusa County, CA. Soil at this site is classified as a Fine-loamy, mixed, superactive, thermic Typic Haploxeralf with slightly acidic pH (Table 1). The trees were fertilized with 50 kg N ha^{-1} as UAN32 four times during each summer 2011 and 2012. The NO_x flux was measured following fertigation events in the tree rows where water and fertilizer solution were applied through microjet sprinklers and in the tractor rows, which were neither irrigated nor fertigated. The tractor row measurements thus served as experimental control. Sampling was carried out at 3 locations both in the tree and tractor rows.

Table 1. Soil (0-25 cm) characteristics at the almond site in Colusa County, CA (http://casoilresource.lawr.ucdavis.edu/drupal/).

Sand (%)	66.8
Silt (%)	19.2
Clay (%)	14
pH (H_2O 1:1)	6.7
Bulk density (g cm^{-3})	1.62
Organic Matter (%)	0.75
Total N (g kg^{-1})	nd

2.1.2. *Alfalfa*

Two adjacent grower fields in the vicinity of Winters, CA, were used to measure NO_x fluxes from alfalfa. The soil at this site is classified as a Myers clay, which is a fine, montmorillonitic, thermic Entic Chromoxerert (Table 2). One of the fields was a one year-old stand, the other a 5 year-old stand. Fields were flood irrigated approximately every 30 days. No N fertilizers were supplied. Alfalfa was harvested 6 times in 2011. Sampling was carried out on 8 dates, including immediately following a flood irrigation event, as well as on days when the fields were relatively dry. Measurements were made at six locations within each field.

Table 2. Soil characteristics (0-30 cm depth) of the alfalfa fields near Winters, CA.

Sand (%)	23
Silt (%)	43
Clay (%)	34
pH (H_2O 1:1)	7.7
Bulk density 5-15 cm (g cm^{-3})	1.43
Total C (g kg^{-1})	12.58
Total N (g kg^{-1})	1.15

2.1.3. *Tomato*

Measurements in tomato systems were conducted at the UC Davis Russell Ranch Sustainable Agriculture research site. Soils at this site are classified as Yolo silt loam, a fine-silty, mixed, non-acid, thermic Typic Xerorthent and Rincon silty clay loam, a fine monmorillonitic, thermic Typic Haploxeralf (Table 3). The NO_x fluxes were measured in the tomato beds at several dates between May and August in furrow- and subsurface drip-irrigated systems. In the furrow-irrigated systems, the NO_x fluxes were assessed at three levels of N fertilization, i.e. 0, 162, and 300 kg N ha^{-1} in a conventional, winter-fallow tomato-wheat rotation, and additionally, a winter cover cropped (oats-vetch-bell beans mixture) system fertilized with 162 kg N ha^{-1}. Fifty kg N ha^{-1} were applied on April 12, 2011, as NPK-15-15-15 starter fertilizer (8.7% NH_4^+, 6.3% NO_3^-) in granular form banded at a depth of about 16 cm. The remainder of the N applications were applied as side dress N in the form of urea ammonium nitrate (UAN32), banded on May 13, three weeks after planting, at a depth of 17 cm. Furthermore, NO_x fluxes were measured in subsurface drip-irrigated (SDI) tomato systems in two treatments. One was a winter-fallow and the other a cover-cropped system as above. Both systems were fertilized with a total of 179 kg N ha^{-1}. The starter application was the same as in the furrow-irrigated systems, but the remainder of the N fertilizer was applied as UAN32 as fertigations of 22-33 kg N ha^{-1} between May 19 and July 15, 2011. All treatments were replicated 3 times.

Table 3. Soil characteristics (0-30 cm depth) of the tomato cropping system at the UC Davis Russell Ranch Sustainable Agriculture facility.

Sand (%)	21.83
Silt (%)	47.00
Clay (%)	31.17
pH (H_2O 1:1)	6.80
Bulk density beds 5-15 cm (Mg m^{-3})	1.37
furrows	1.52
Organic C (g kg^{-1})	10.30
Organic N (g kg^{-1})	1.00

2.1.4 *Wheat*

Assessment of NO_x flux from wheat systems was carried out in a grower field near Dixon, CA. The soil in this field is classified as a silty clay loam thermic Typic Chromoxerert, its main physical characteristics are summarized in Table 4. The NO_x flux was measured in beds and furrows in three treatments at the end of May: 0, 210 kg N ha^{-1} applied either as ammonium sulfate and urea or as anhydrous ammonia and urea (112 kg N ha^{-1} as starter in early November, and 98 kg N ha^{-1} as aerial application in February). In addition to winter rainfall, the field received irrigation from April 16-22. The NO_x flux was also measured in a wheat field at the Russell Ranch Sustainable Agriculture research site (see Table 1 for main physicochemical characteristics). Flux measurements from the Dixon field were collected in 2011 while the measurements at the Russell Ranch were made in 2012. At the Russell Ranch, 112 kg N ha^{-1} was applied in the form of urea as starter, and 80 kg N ha^{-1} was added as foliar N application in early March. In both fields NO_x flux was assessed in beds and furrows, and values were weighted according to area (70% bed, 30% furrow) to calculate average field emissions. Two replications were used per treatment (n=2).

Table 4. Main soil characteristics (0-30 cm depth) at the wheat field located near Dixon, CA.

Sand (%)	21.3
Silt (%)	43.7
Clay (%)	35
pH (H_2O 1:1)	7.4
Bulk density 5-15 cm (Mg m^{-3})	1.29
Total C (g kg^{-1})	14.9
Total N (g kg^{-1})	1.3

2.1.5. *Dairy silage corn*

Assessment of NO_x flux in corn systems was carried out in three forage production systems surrounding dairy farms, located in the counties of Stanislaus (Farms A and B) and Sacramento (Farm C). It is characteristic of the dairy farms in the Central Valley of California to use the farmland surrounding the facilities to produce silage corn and other forage crops which are in part fertilized with the manure generated at the dairy farms. Forage cropland land typically receives high annual inputs of nitrogen (N) compared to other cropping systems. According to our previous research, the N inputs into these silage corn/winter forage cropping systems range from 500 to 1200 kg N ha^{-1} yr^{-1}, versus 350 to 600 kg N ha^{-1} yr^{-1} removed in the harvested crop (Geisseler *et al.*, 2012). Manure generated at the farms is either collected as solids from the stables and applied to the fields or flushed with water and stored in anaerobic ponds. The liquid effluent is processed before storage in the lagoons to separate particles larger than a few millimeters from the liquid components. Manure is generally applied as liquid ("lagoon water") and mixed with the irrigation water, although fields may also receive the different forms of solid manure. Liquid manure with high concentrations of NH_4^+ is diluted with irrigation water. In addition, inorganic N fertilizers are added. Irrigation is carried out through flooding of the fields. Monitoring of the NO_x fluxes was carried out before and after the irrigation events at four locations within each field (n=4).

Table 5. Soil characteristics (0-30 cm depth) of the silage corn systems.

	Farm A		Farm B		Farm C
	Field 1	*Field 2*	*Field 1*	*Field 2*	
Sand (%)	78	70	84	84	31
Silt (%)	16	23	12	10	28
Clay (%)	7	7	4	6	41
pH (H_2O 1:1)	6.7	7.2	6.8	7.3	7.47
Bulk density 5-15 cm (Mg m^{-3})	1.67	1.43	1.37	1.44	1.51
Total C (g kg^{-1})	10.4	12.5	11.8	6.8	12.4
Total N (g kg^{-1})	1	1.2	1.1	0.6	1.3

Table 6. Dairy silage corn nitrogen inputs and application method.

Year	Dates		N inputs					
	Planting	Harvest	Synthetic Fertilizer-N		Manure- N			Total available N per fertigation event (kg N ha^{-1})
			Rate (kg N ha^{-1})	Application method	Soluble (kg N ha^{-1})	Solids (kg N ha^{-1})	Application method	
Farm A								
2011	15 April	22 August	298	Irrigation water	198	69	Irrigation water	20-40
2012	6 May	24 August	182	Irrigation water	172	114	Irrigation water	20-40
Farm B								
2011	15 May	31 August.	104	Injected	245	713	Solid & irrigation water	20-50
2012	13 May	3 September	118	Injected	268	72	Irrigation water	20-50
Farm C								
2011	20 June	14 October	224	Injected	159	35	Irrigation water	159
2012	18 June	21 October	224	Injected	460	100	Irrigation water	89-115

At Farm A, two fields characterized as a coarse-loamy, mixed, active, thermic Typic Haploxeralf with neutral to slightly acidic pH, a total soil C content in the topsoil of 10.4 and 12.5 g kg^{-1} soil, and a high sand content (70-78%)(Table 5). Fertilizer inputs consisted mainly of lagoon water and inorganic N fertilizer (UAN32) applied via the irrigation water (20-40 kg available N ha^{-1} per irrigation event). The total N inputs were categorized as synthetic mineral N, solids (organic N, which has to undergo mineralization before becoming available to plants and microbes), or soluble organic N, which is readily available for plant or microbial uptake (Table 6).

The soil in Farm B was classified as a mixed, thermic Typic Xeropsamment. It was characterized by a high sand content (84%), a neutral to acidic pH, and a total C content in the topsoil of 11.8 g kg^{-1}soil. Solid corral manure, partially composted, and the solid fraction, so called 'separator manure', remaining after mechanical separation of the liquid manure were incorporated into the soil in spring 2011 after disking and two weeks before corn planting. Synthetic N fertilizer as UAN was applied in early June at the rate of 104 and 117 kg N ha^{-1} in 2011 and 2012, respectively. In addition, lagoon water was mixed into the irrigation water (approx. mixing rate 3:1 fresh water: lagoon water) resulting in N applications of 20-50 kg available N ha^{-1} per irrigation event.

Soil at Farm C was classified as a fine, mixed, superactive, thermic Abruptic Durixeralf. It was characterized by a neutral pH (7.47), a total soil C in the topsoil of 12.4 g kg^{-1}, and a lower sand and higher clay content than on Farms A and B. The main N inputs to the corn crop consisted on 227 kg ha^{-1} of anhydrous ammonia injected in the soil one week before planting, and the application of lagoon water through irrigation (mixing rate 1:1 water: lagoon water), on August 29, 2011 (159 kg available N ha^{-1}) and September 12 and 27, 2012 (115 and 89 kg available N ha^{-1}, respectively).

2.2. *NO_x flux measurements*

The NO_x flux measurements took place during the summer months (2011 and 2012) when O_3 reaches critical threshold values, and measurements focused on soil fertilization events (if applicable, e.g. alfalfa is typically not fertilized) and varied soil moisture conditions. Following N fertilization events in the almond orchard, NO_x fluxes were measured every 2-3 days until the fluxes subsided to the magnitude measured prior to these events, normally after 7-10 days. In addition, the fluxes were measured a few times in between the fertilization events to confirm background values. In alfalfa, we measured the NO_x fluxes every other day during two irrigation events, as well as twice in between irrigations to obtain background values. In tomato, we measured the NO_x fluxes every 2-3 days following two irrigation events. In the silage corn systems, the NO_x fluxes were measured every other day during 5 irrigation events, which coincided with fertilizer applications since on two farms, lagoon water and/or synthetic N fertilizer is mixed with the irrigation water. On Farm C, the NO_x flux was measured almost every day during three periods, twice following synthetic N fertilizer applications and once following lagoon water application. In wheat, we measured NO_x flux twice.

Nitric oxide flux was measured in the field by using a dynamic chamber method. Either rectangular or circular chambers were used depending on the cropping system. Rectangular stainless steel chamber bases were 50 x 30 cm and 8 cm deep with a 2 cm-wide horizontal flange at the top end. Chamber bases were inserted in the soil so that the flanges rested in the soil surface and were left in place unless field operations required their temporary removal. Thin-wall stainless steel (20 gauge) chamber tops (50 x 30 x 10 cm), with flanges facing down and lined with a rubber gasket, were placed onto the bases and secured with metal clamps. In the alfalfa systems, smaller rectangular chambers and bases were used (13.5 x 15 x 10 cm). Round, 20 cm diameter 10 cm tall polyvinyl chloride (PVC) chambers were used in wheat and almond systems. Chambers were placed on PVC rings buried 6-8 cm deep into the soil and sealed with a rubber gasket.

Both rectangular and round chambers were equipped with inlet and outlet ports connected to a chemoluminiscence NO_x analyzer (LMA-3, Scintrex/Unisearch Associates, Concord, ON, Canada) via Teflon™ (PTFE) tubing covered by a layer of opaque material to prevent exposure of the air stream to sunlight. Chamber air was continuously circulated by a pump in the NO_x analyzer, flowing through a chromium tri-oxide (CrO_3) column converting NO to NO_2 and then the luminol chemiluminescence detector. NO_x concentrations were recorded every 15 seconds during 5 minutes right after sealing the chamber. The instrument was calibrated in the laboratory before every field measurement event by mixing NO-free air scrubbed of NO_x by permanganate-coated porous silica and a NO_x gas standard (Scott Marrin, Inc., Riverside, CA) in varied proportions and at known flow rates (Manostat). Upon return to the laboratory after field measurements, the calibration was checked. On most days, values stayed within 10% of the calibration values. On some days, when re-check values diverged from the calibrated ones obtained in the morning, the results were adjusted to a new calibration curve, representing a mean value of before- and after-field measurements. On a few days, field measurement values were discarded due to instrument problems.

The NO_x flux was calculated from the rate of change in chamber concentration, chamber volume, and soil surface area. Chamber gas concentrations determined by the NO_x-analyzer (volumetric parts per billion) were converted to mass per volume units assuming ideal gas relations using chamber air temperature values, which were measured by a thermocouple thermometer during each sampling event. The hourly flux was derived from the flux measured during 2-5 minutes at each chamber location. Typically fluxes at different locations within the same field were measured during the course of 1 hour or more, so we report mean hourly fluxes. The NO_x fluxes were converted to g NO_x-N ha^{-1} h^{-1} to illustrate the relationship between NO_x flux and N inputs, which are usually reported as kg ha^{-1}, and because individual chambers (sampling replicates) in a given system were dispersed over large areas encompassing one to several hectares.

2.3. *Effects of environmental variables on NO_x flux*

2.3.1. *Soil chemical and physical analyses*

In order to gain a better understanding of the conditions affecting NO_x emissions, key soil and environmental variables were recorded in addition to the main management practices and N inputs at each site. Inorganic N (NO_3^- and NH_4^+) content was determined in the 0-15 cm soil layer. Soil samples were collected close to the gas chamber bases by using a 1.83-cm steel corer. Soil samples were immediately extracted with 1 M potassium chloride (KCl) at a 1:5 ratio (soil: extracting solution) and analyzed within one day for nitrite (NO_2^-). Extracts were also analyzed colorimetrically for ammonium (NH_4^+) and nitrate (NO_3^-) by a Shimadzu spectrophotometer (Model UV-Mini 1240). For determining NH_4^+, the phenate (indophenol blue) method was employed (Forster, 1995). Nitrate in the extracts was reduced to nitrite (NO_2^-) with vanadium chloride, and the NO_2^- was analyzed by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine-dihydrochloride (Doane and

Horwáth, 2003). The pH was determined in the supernatant of soil slurries with H_2O by a pH meter (Model 220, Denver Instrument Co., Arvada, CO).

Gravimetric soil moisture was calculated from field-moist and oven-dry (105ºC, 24h) mass of soil collected in the field. Soil texture was determined by a modified pipet method (USDA, 1992). The bulk density was measured twice per growing and rainy season by collecting 10 cm dia. x 6 cm long cores in the 5-15 cm layer of soil, followed by drying the cores to 105ºC. Water filled pore space (WFPS) was calculated from the gravimetric moisture (w) and measured bulk density values in the 5-15 cm layer as follows:

%WFPS= (w * bulk density)/ [1- (bulk density/2.65)]* 100%,

where w = gravimetric water content.

2.3.2. *Air and soil temperature*

Air and soil temperature at 1 and 5 cm depths were routinely recorded simultaneously with NO_x flux determinations at each individual sampling location. In addition, the relationship between soil temperature and NO_x flux was explored at several field sites by taking measurements of NO_x flux and temperature over the entire course of some days. One of the sites was a sandy loam soil planted to corn and fertilized with 180 kg N ha^{-1} in the form of UAN32 near the UC Davis campus. The other sites were the field locations on Farms B and C. Q10 values were calculated as

$$Q10 = (NO_x\text{-flux}_2/NO_x\text{-flux}_1)^{10/(T2-T1)}$$

where T1 is the temperature in (°C) at 1 or 5 cm depth during NO_x-flux measurement 1 and T2 the corresponding temperature measurement at NO_x-flux measurement 2.
More precisely, soil temperature at 1 and 5 cm depth, and ambient air temperature were recorded simultaneously with NO_x flux determinations at each individual sampling location.

Results

A summary of average hourly NO_x fluxes among all the measurements taken in the different systems is shown in Table 7. The fluxes and results of the ancillary data are explained in detail below and in the accompanying figures.

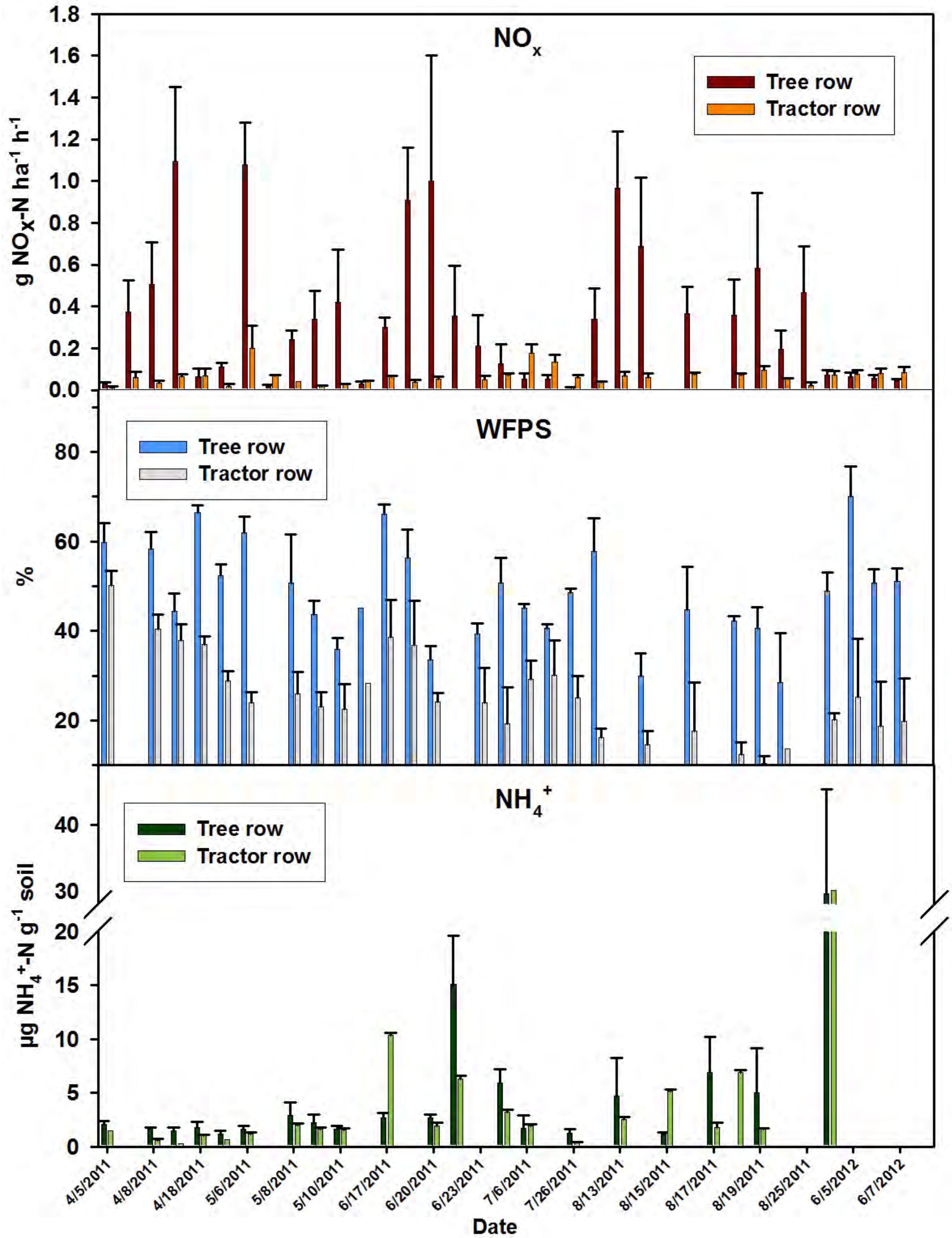
3.1. *Almonds*

The NO_x-flux was higher in the irrigated, fertigated tree than the tractor rows, which remained dry all summer. Following the monthly N fertilizer applications, the NO_x flux reached about 1 g NO-N ha^{-1} h^{-1} and then gradually declined over the course of about 10 d to <0.1 g NO_x-N ha^{-1} h^{-1} (Figure 1). Baseline NO_x emissions in tractor rows were almost always <0.1 g NO_x-N ha^{-1} h^{-1}. In the tree rows, there was a weak correlation of NO_x-flux with nitrite (NO_2^-) (Figure 2). The soil NH_4^+ concentrations did not fluctuate much with the N fertilizer application and were similar in magnitude in the tree and tractor rows. The tractor rows had lower soil moisture content and higher soil temperatures than the tree rows.

Table 7. Summary of mean hourly NO_x fluxes and standard errors (SE) among means per location in different cropping systems.

	# of Measurements	Chamber locations	Average flux	SE	Average flux	SE
			g NO_x-N ha^{-1} h^{-1}		g N_2O-N ha^{-1} h^{-1}	
Wheat (210*, 192** kg N ha^{-1})	9	3	0.04	0.01	0.09	0.02
Alfalfa, 5 year old stand	42	6	0.19	0.02	3.10	1.2
1 year old stand	48	6	0.54	0.31	1.67	0.46
Almond, tractor row	93	3	0.06	0.01	nd	
Tree row (200 kg N ha^{-1})	96	3	0.35	0.05	nd	
Tomato, SDI winter-fallow (179 kg N ha^{-1})	57	3	0.07	0.01	0.11	0.02
SDI, winter cc (179 kg N ha^{-1})	57	3	0.18	0.02	0.15	0.03
FI, zero N applied	60	3	0.10	0.03	0.11	0.03
FI, standard N rate (162 kg ha^{-1})	72	3	0.22	0.05	0.43	0.08
FI, standard N rate, cc	66	3	0.32	0.15	0.88	0.22
FI, 300 kg N ha^{-1} applied	75	3	2.79	0.64	1.22	0.19
Silage corn, Farm A, Field 1 (565*, 468** kg N ha^{-1})	72	4	0.75	0.04	4.13	0.92
Farm A, Field 2 (565*, 468** kg N ha^{-1})	56	4	0.39	0.06	3.20	1.45
Farm B, Field 1 (1062*, 458** kg N ha^{-1})	88	4	2.03	0.28	4.8	0.96
Farm B, Field 2 (1062*, 458** kg N ha^{-1})	44	4	1.98	0.49	1.72	0.28
Farm C (421*, 784** kg N ha^{-1})	324	4	1.61	0.51	6.75	0.90

SDI = Subsurface drip-irrigation; FI = Furrow irrigation; cc = cover crop; * 2011, **2012



NOx
Tree row
Tractor row
g NOx-N ha-1 h-1
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
WFPS
Tree row
Tractor row
%
80
60
40
20
NH4+
Tree row
Tractor row
µg NH4+-N g-1 soil
40
30
20
15
10
5
0
4/5/2011
4/8/2011
4/18/2011
5/6/2011
5/8/2011
5/10/2011
6/17/2011
6/20/2011
6/23/2011
7/6/2011
7/26/2011
8/13/2011
8/15/2011
8/17/2011
8/19/2011
8/25/2011
6/5/2012
6/7/2012
Date

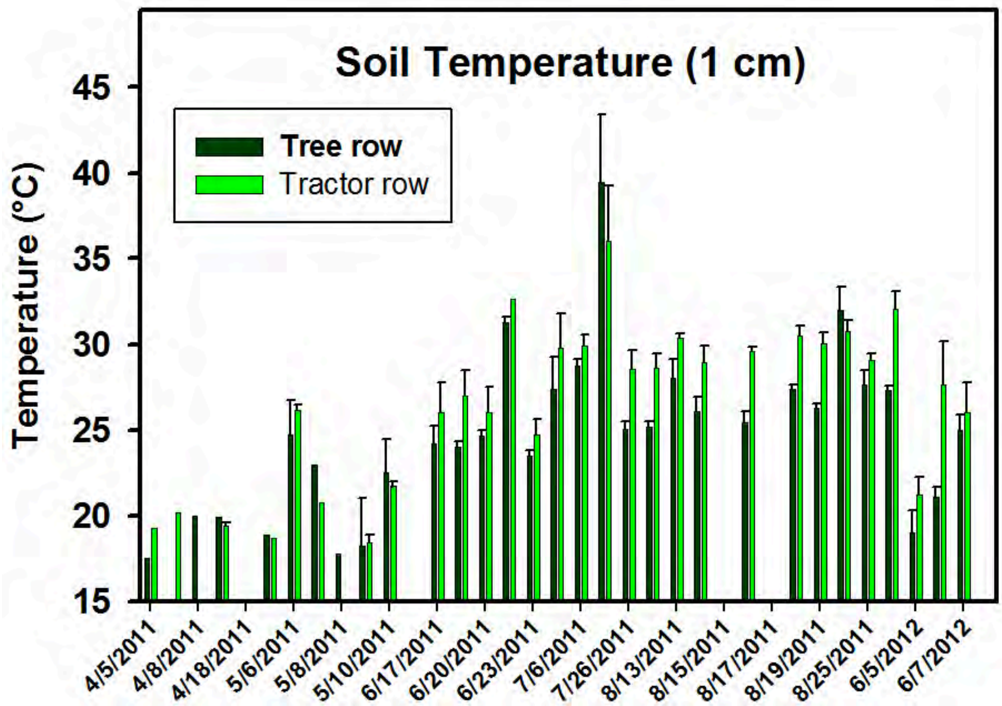


Figure 1. NOx flux, water-filled pores space (WFPS), ammonium (NH_4^+) concentrations, and soil temperature at 1 cm depth in the almond orchard. Standard errors shown as line bars. n=3.

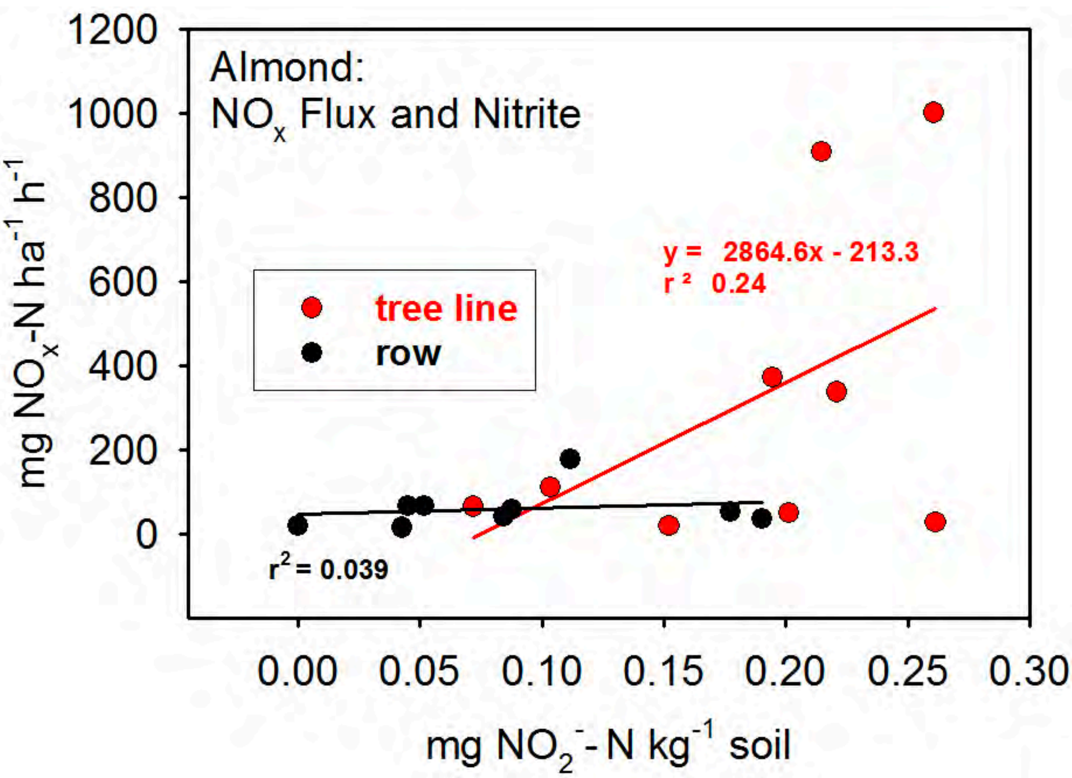
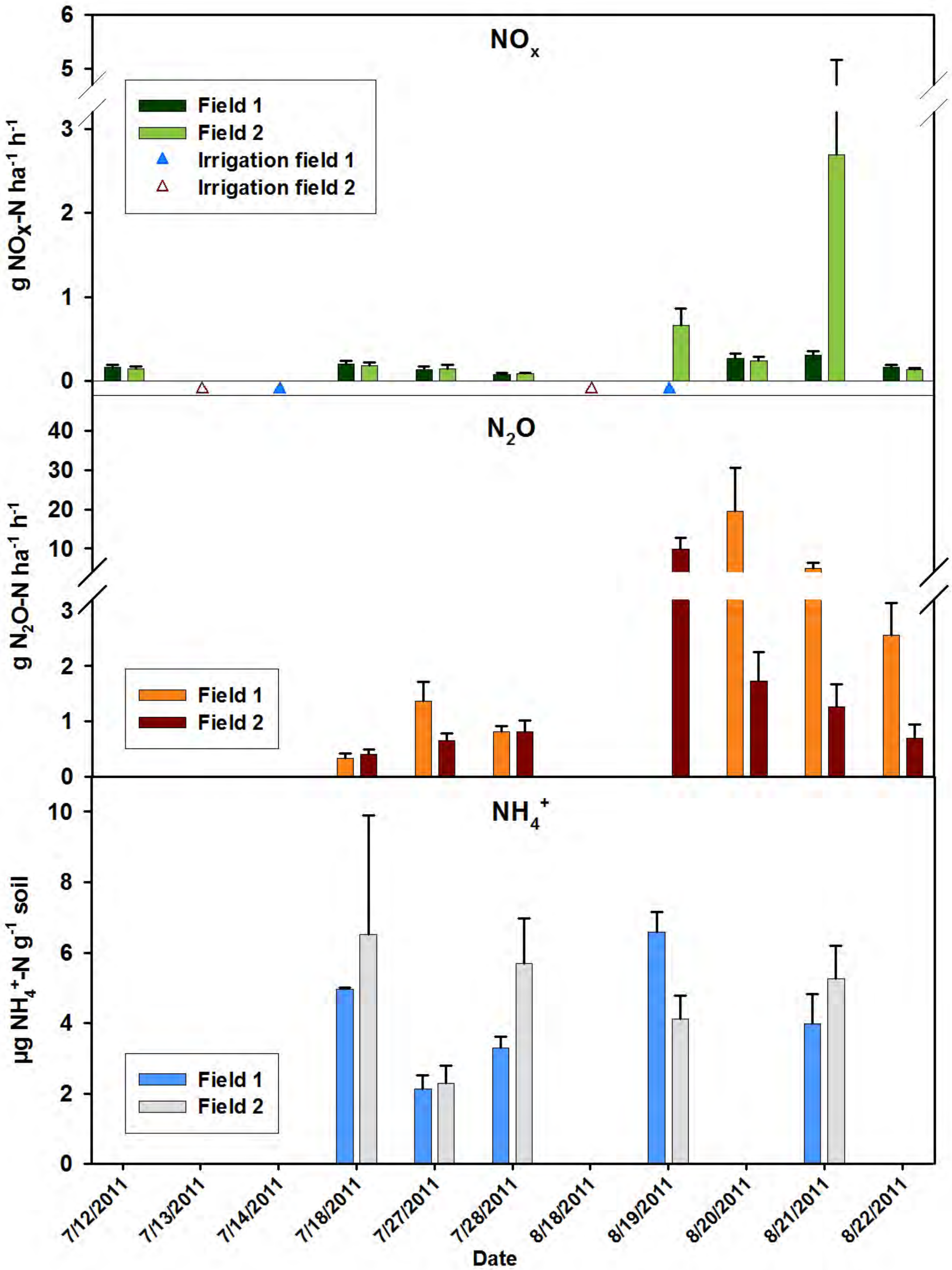


Figure 2. NOx flux vs. nitrite (NO_2^-) concentrations in the soil in the almond orchard.

3.2. *Alfalfa*

In flood-irrigated alfalfa, the NO_x fluxes were generally <0.3 g NO_x-N ha^{-1} h^{-1} except for one event following an irrigation application when the NO_x flux reached almost 3 g NO_x-N ha^{-1} h^{-1} (Figure 3). This enhanced NO_x flux occurred in the 1 year-old field two days after an irrigation event. At this event, the NO_x was greater than the N_2O flux, but in general, N_2O was greater than NO_x flux by an order of magnitude.



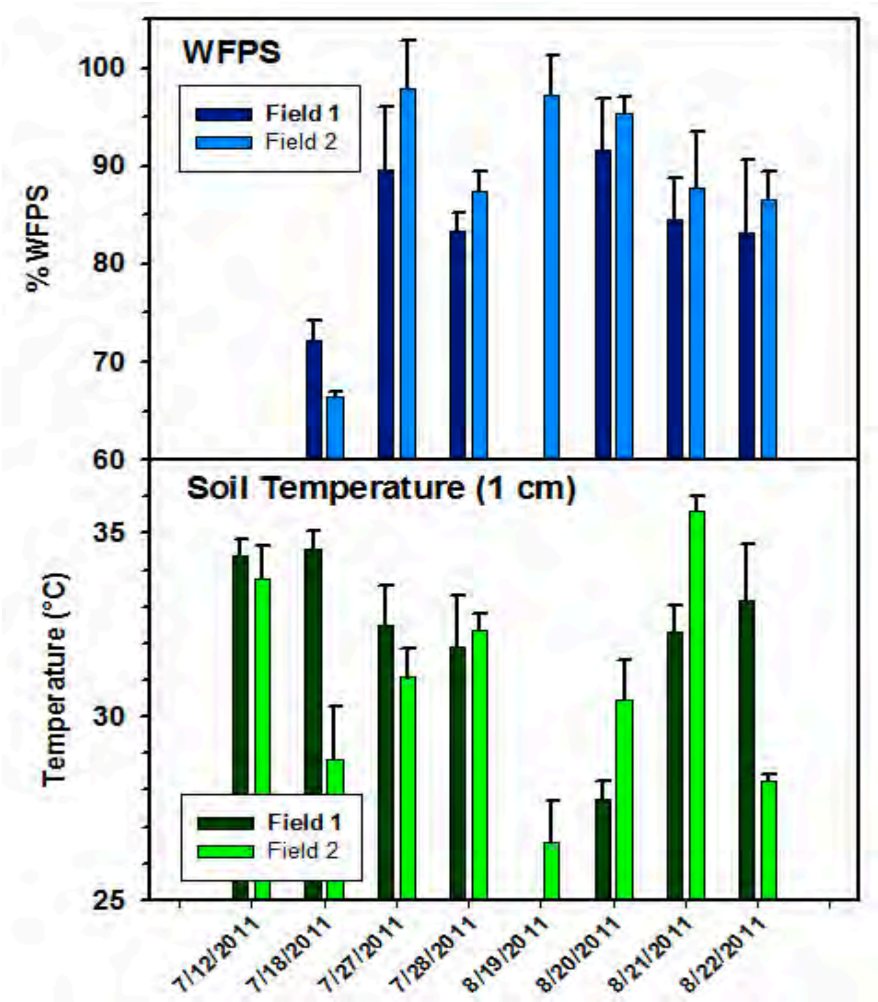


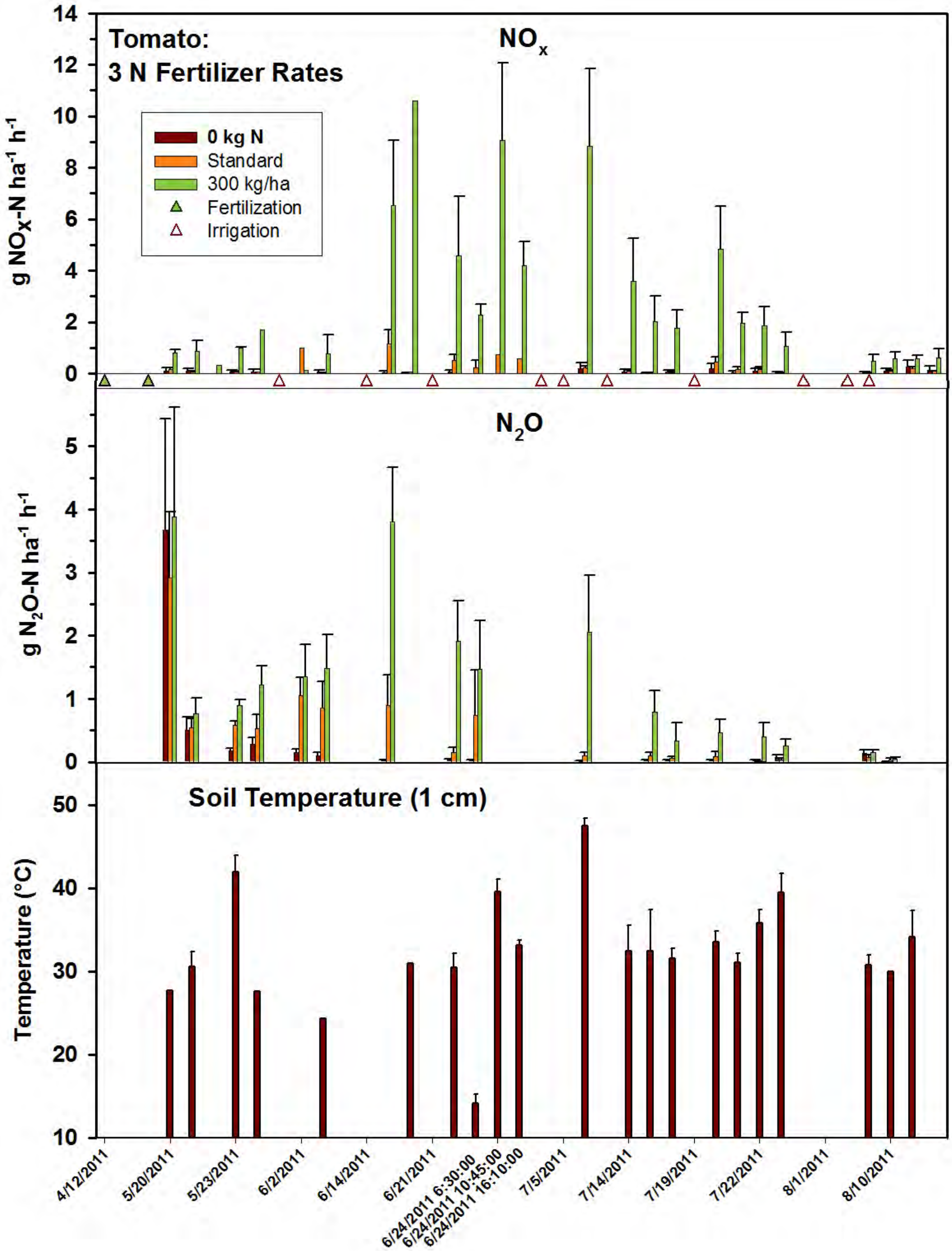
Figure 3. NO_x and nitrous oxide (N_2O) flux, soil ammonium (NH_4^+) concentrations, water-filled pores space (WFPS), and soil temperature at 1 cm depth in the alfalfa fields. Standard errors are shown as line bars. n=6. Triangles along the x-axis indicate irrigation events for Field 1 (blue) and Field 2 (white).

In both fields soil NH_4^+ concentrations were 2-6 μg NH_4^+-N g^{-1}. The soils almost reached saturation (100% WFPS) after irrigations and declined to 60-70% WFPS in between irrigations. Soil temperatures were lowest immediately following an irrigation and increased with drainage.

3.3. *Tomato*

The NO_x flux ranged from 1-10 g NO_x -N ha^{-1} h^{-1} in the tomato system fertilized with 300 kg N ha^{-1} (high N treatment), <1 g NO_x -N ha^{-1} h^{-1} in the system fertilized at the rate of 162 kg N ha^{-1} (standard N treatment), and <0.1 g NO_x-N ha^{-1} h^{-1} in the plots that did not receive any N fertilizer (zero N treatment) in that season (Figure 4). Most measurements were taken at temperatures (soil temperature at 1 cm depth) around 30ºC. On June 24, 2011, at 6:30 am, the soil temperature was 14.1ºC, increasing to 39.6ºC by 10:45 am, and declining to 33.0ºC by 4 pm. Concurrently, NO_x flux in the high N treatment increased from 2.3 to 9.1, and decreased to 4.2 g NO_x-N ha^{-1} h^{-1}. In the standard treatment, NO_x flux increased from 0.2 to 0.8, and declined to 0.6 g NO_x-N ha^{-1} h^{-1} during that day. On the days both NO_x and N_2O flux were measured, the amount of N emitted as NO_x was on average about three times greater than the amount of N_2O-N in the high N treatment and about equal to that in the standard N treatment. The soil water content in the furrow-irrigated tomatoes was mostly between 55 and 70%. Soil NH_4^+ concentrations were 5-20 μg NH_4^+-N g^{-1} soil in the high N treatment, 1-3 μg NH_4^+-N g^{-1} soil in the standard N treatment, and <1.5 μg NH_4^+-N g^{-1} soil in the zero N treatment.

In the winter cover-cropped tomato system, the NO_x fluxes reached as much as 2.5 g NO_x-N ha^{-1} h^{-1} on some days, but during the remaining period were mostly <0.5 g NO_x-N ha^{-1} (Figure 5). The corresponding N_2O-N fluxes were similar in magnitude as the NO_x fluxes. With SDI, the NO_x fluxes ranged from 0.01-0.3 g NO_x-N ha^{-1} h^{-1} (Figure 6). On most days when the fluxes were measured, the NO_x-N emissions were greater in the system a cover crop containing legumes had been grown the previous winter, whereas soil NH_4^+ concentrations were similar between the two SDI systems. The N_2O fluxes ranged from 0.05-0.5 g N_2O-N ha^{-1} h^{-1}. The WFPS ranged from about 35-50%.


Tomato:
3 N Fertilizer Rates
NOx
0 kg N
Standard
300 kg/ha
Fertilization
Irrigation
g NOX-N ha-1 h-1
N2O
g N2O-N ha-1 h-1
Soil Temperature (1 cm)
Temperature (°C)
4/12/2011
5/20/2011
5/23/2011
6/2/2011
6/14/2011
6/21/2011
6/24/2011 6:30:00
6/24/2011 10:45:00
6/24/2011 16:10:00
7/5/2011
7/14/2011
7/19/2011
7/22/2011
8/1/2011
8/10/2011

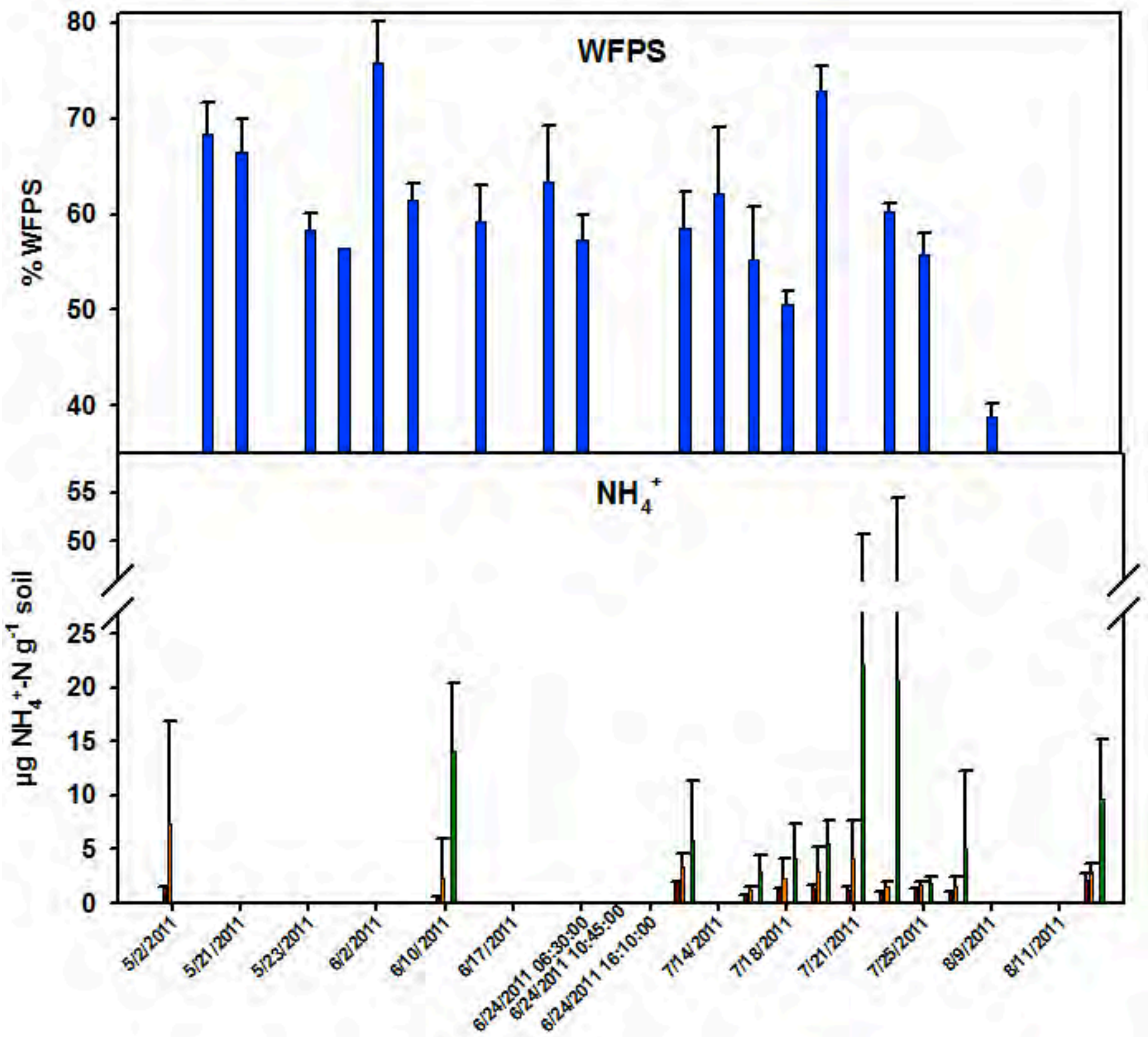
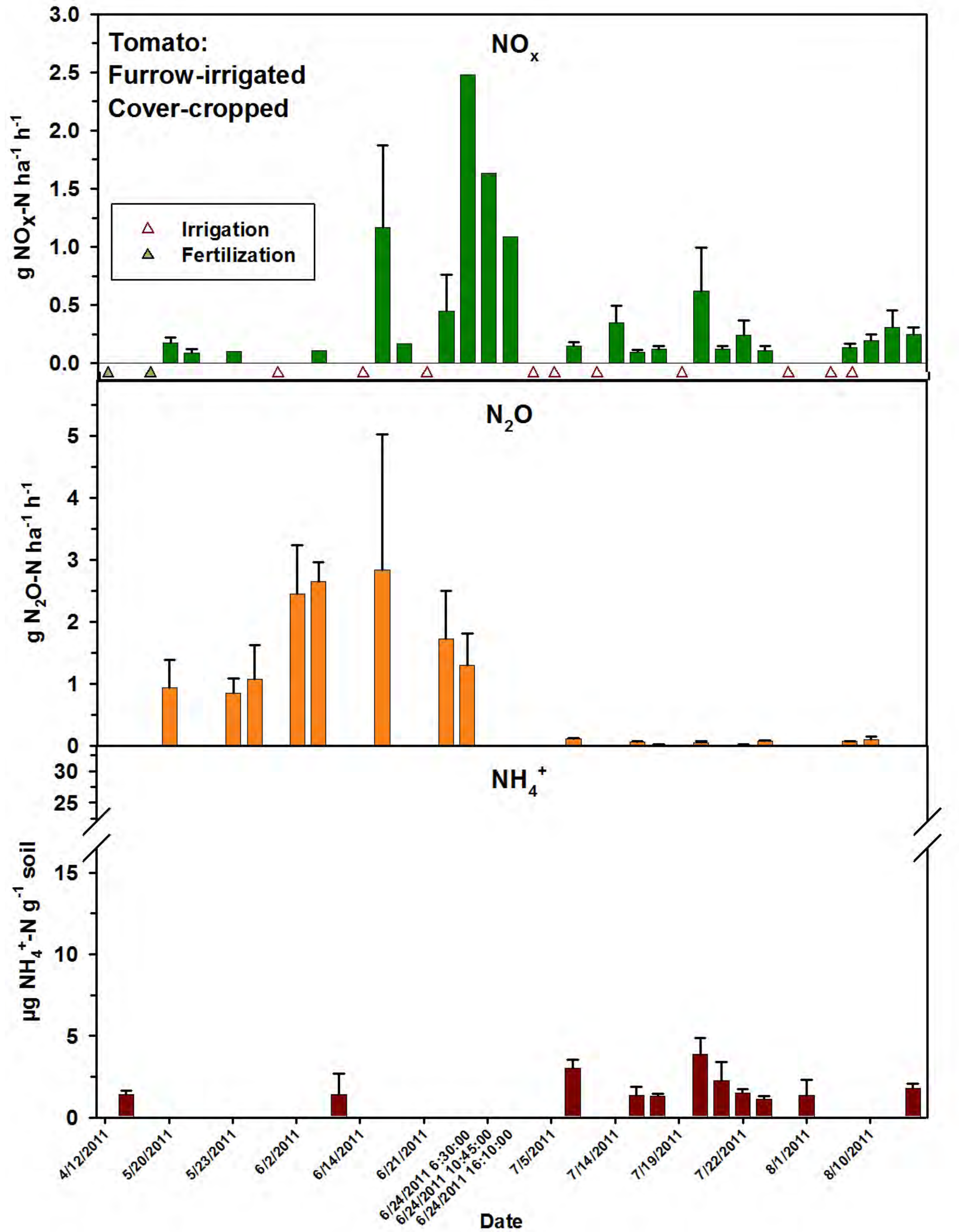


Figure 4. NO_x and nitrous oxide (N_2O) flux, soil temperature at 1 cm depth, water-filled pores space (WFPS), and soil ammonium (NH_4^+) concentrations in furrow-irrigated tomato fertilized at 300, 162 and 0 kg N ha^{-1}. Standard errors are shown as line bars. n=3. Triangles along the x-axis indicate inorganic fertilization (green) and irrigation (white) events.


Tomato:
Furrow-irrigated
Cover-cropped
NOx
Irrigation
Fertilization
g NOx-N ha-1 h-1
N2O
g N2O-N ha-1 h-1
NH4+
µg NH4+-N g-1 soil
4/12/2011
5/20/2011
5/23/2011
6/2/2011
6/14/2011
6/21/2011
6/24/2011 6:30:00
6/24/2011 10:45:00
6/24/2011 16:10:00
7/5/2011
7/14/2011
7/19/2011
7/22/2011
8/1/2011
8/10/2011
Date

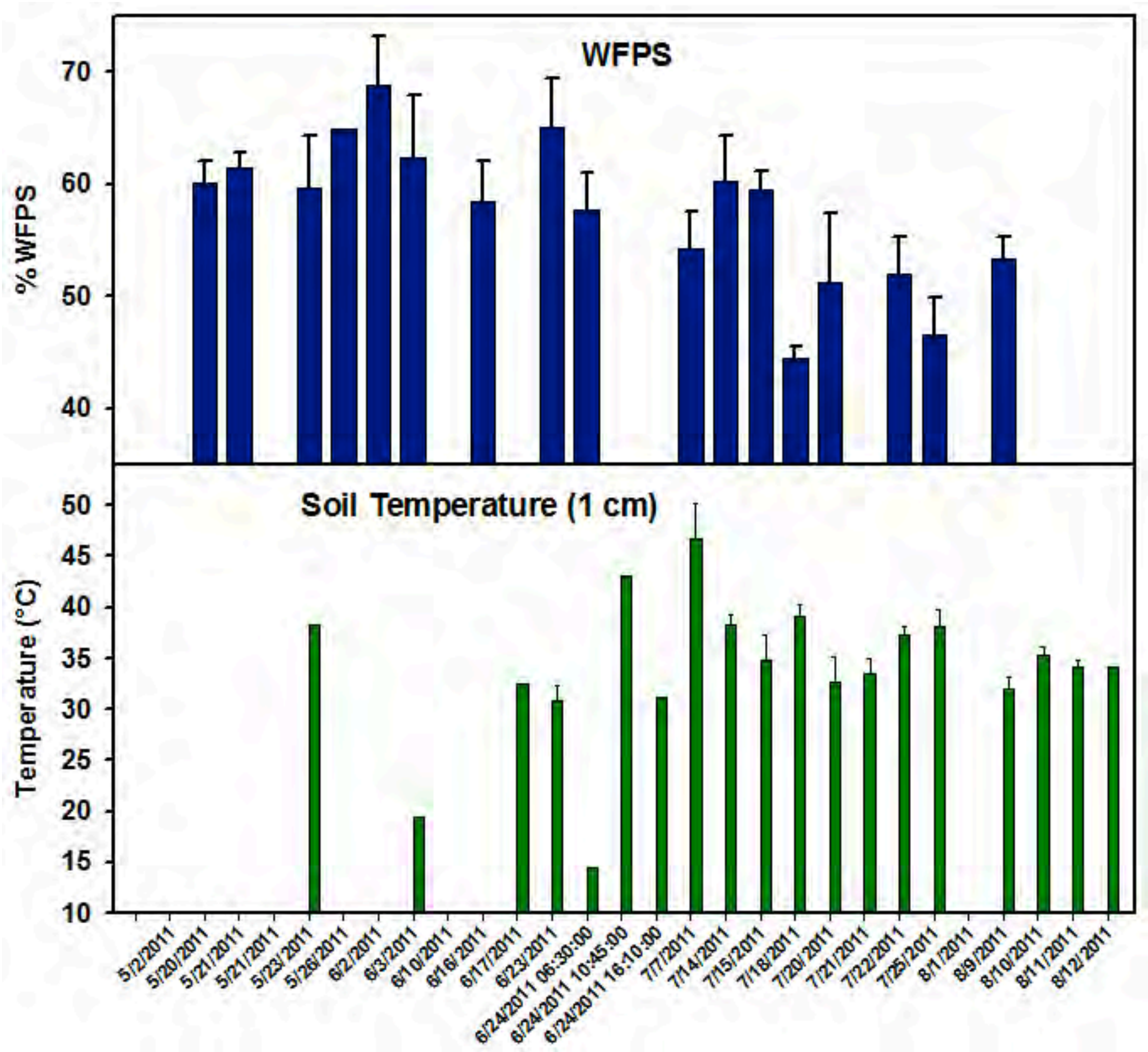
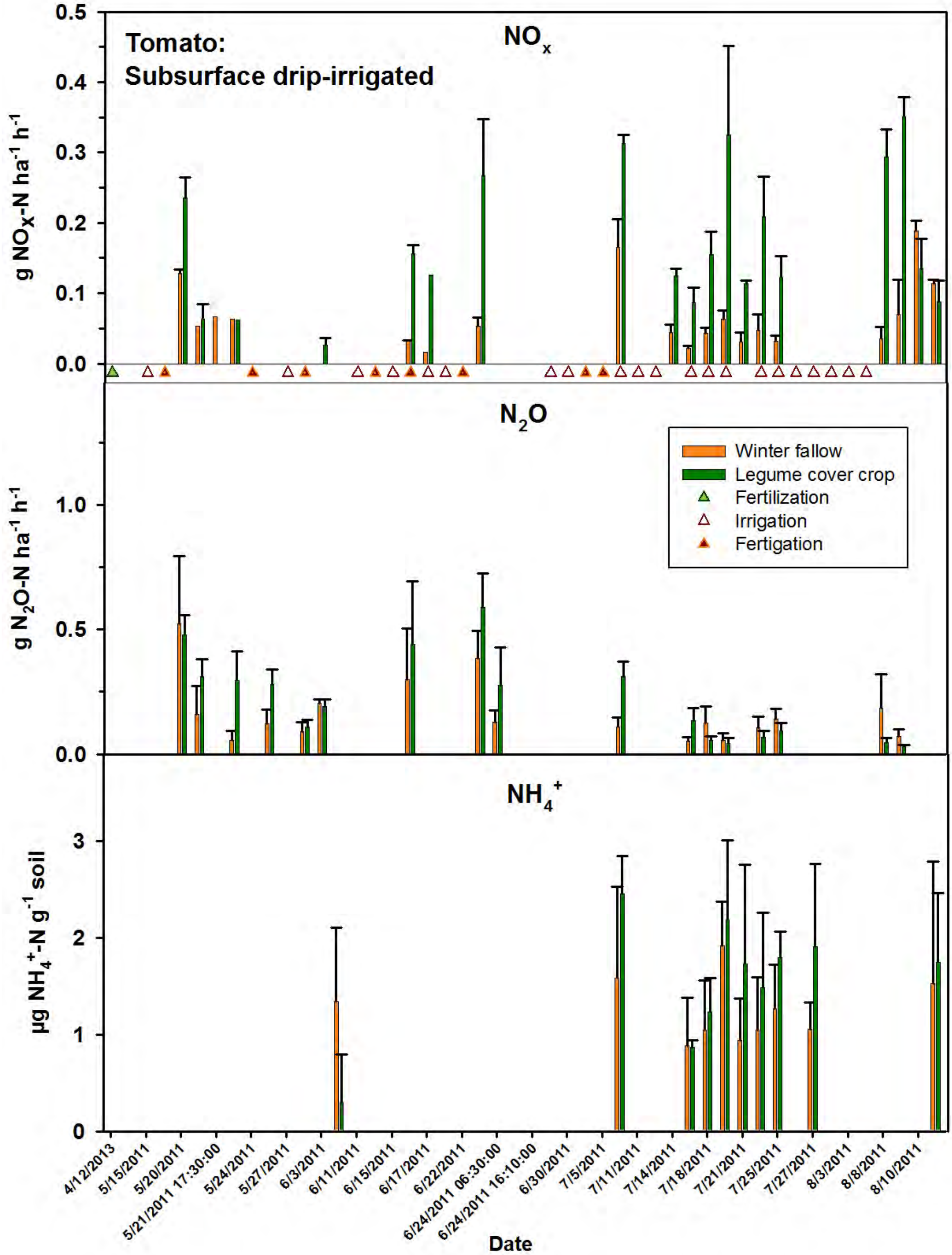


Figure 5. NO_x and nitrous oxide (N_2O) flux, soil ammonium (NH_4^+) concentrations, water-filled pores space (WFPS), and soil temperature in the furrow-irrigated, winter cover-cropped tomato system fertilized with 179 kg N ha^{-1} in cover cropped and winter-fallow tomato cropping systems. Standard errors are shown as line bars. n=3. Triangles along the x-axis indicate inorganic fertilization (green) and irrigation (white) events.



Tomato:
Subsurface drip-irrigated
NOx
g NOx-N ha-1 h-1
0.5
0.4
0.3
0.2
0.1
0.0
N2O
g N2O-N ha-1 h-1
1.0
0.5
0.0
Winter fallow
Legume cover crop
Fertilization
Irrigation
Fertigation
NH4+
μg NH4+-N g-1 soil
3
2
1
0
4/12/2013
5/15/2011
5/20/2011
5/21/2011 17:30:00
5/24/2011
5/27/2011
6/3/2011
6/11/2011
6/15/2011
6/17/2011
6/22/2011
6/24/2011 06:30:00
6/24/2011 16:10:00
6/30/2011
7/5/2011
7/11/2011
7/14/2011
7/18/2011
7/21/2011
7/25/2011
7/27/2011
8/3/2011
8/8/2011
8/10/2011
Date

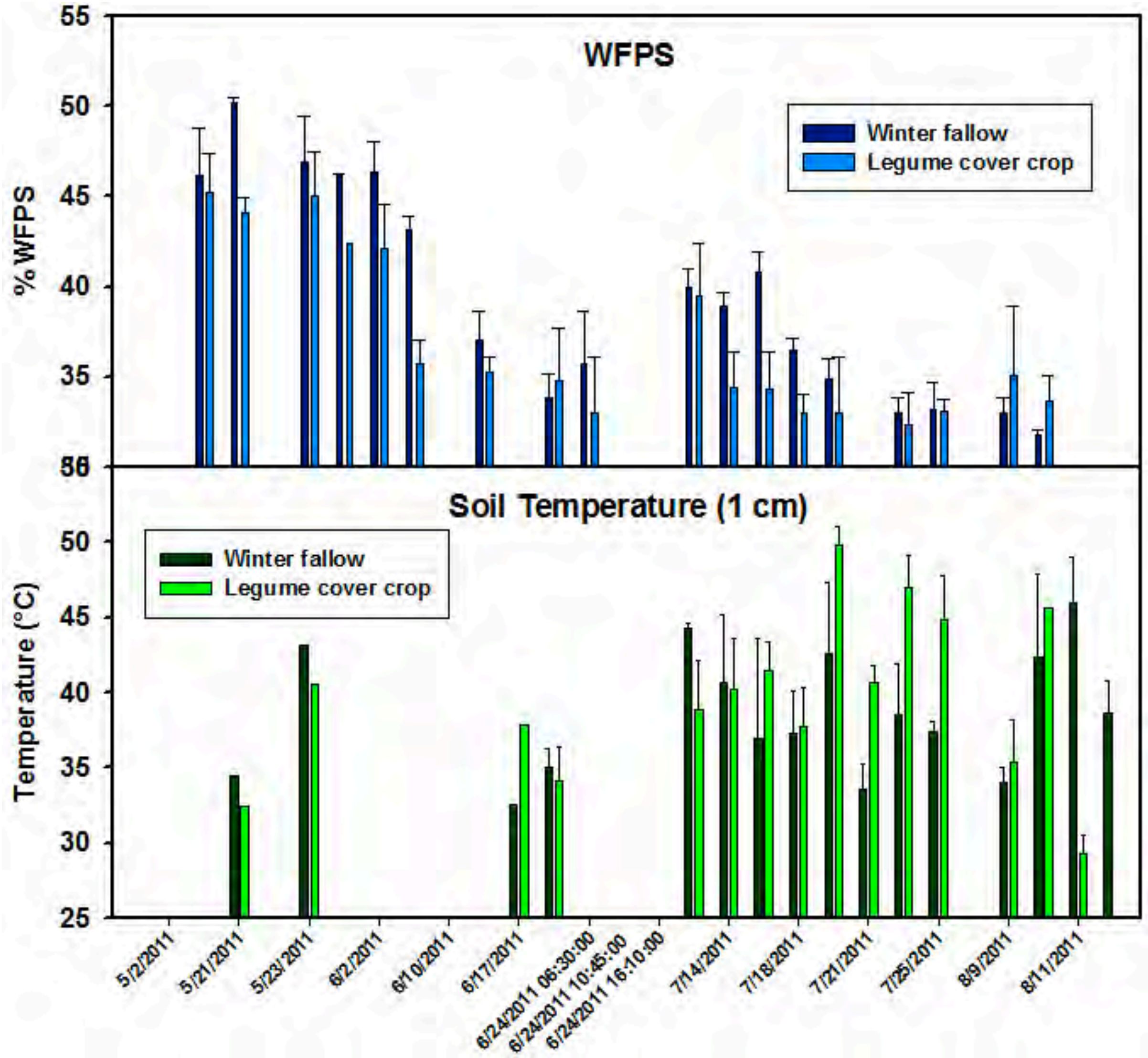


Figure 6. NO_x and nitrous oxide (N_2O) flux, soil ammonium (NH_4^+) concentrations, water-filled pores space (WFPS), and soil temperature in subsurface drip-irrigated tomato fertilized with 179 kg N ha^{-1} in cover cropped and winter-fallow tomato cropping systems. Standard errors are shown as line bars. n=3. Triangles along the x-axis indicate inorganic fertilizer application (green), irrigation (white) and fertigation (black) events.

3.4 *Wheat*

The NO_x fluxes measured in early summer in the wheat systems were between 9 and 70 mg NO_x-N ha^{-1} h^{-1} (Table 8). The N_2O-N fluxes in the N fertilized treatments were 10 to 40 times greater than the NO-N fluxes, and the NH_4^+ concentrations were between 1 and 2.5 μg NH_4^+-N g^{-1} soil.

Table 8. The NO_x and N_2O flux, soil ammonium concentrations, and water filled pore space in five wheat treatments at Dixon and Russell Ranch field sites.

Date	NOx (mg NO-N ha^{-1} h^{-1}	N_2O (mg N_2O-N ha^{-1} h^{-1})	NH_4^+ (µg NH_4^+-N g^{-1})	WFPS (%)
May 24, 2011				
Control	25.8 ± 7.7	10.0 ±3.5	1.6 ±1.2	46 ±4
AA & U	17.8 ±12.4	179.1 ±60.5	1.9 ±0.9	45 ±4
AS & U	9 ±10.9	108.5 ±60.7	0.9 ±0.2	46 ±4
May 30, 2012				
Wheat-T-fallow	69.5 ±22.7	1377 ±242	1.4 ±0.2	nd
Wheat-T-cc	55.4 ±4.8	2487 ±405	2.5 ±0.4	nd

Control = no N fertilizer applied; AA & U = 112 kg N ha^{-1} applied as anhydrous ammonia at planting and 98 kg N ha^{-1} applied as urea in February; AS & U = 112 kg N ha^{-1} applied as ammonium sulfate at planting and 98 kg N ha^{-1} applied in February; Wheat-T-fallow = wheat-tomato-fallow rotation; wheat-T-cc = wheat-tomato-cover crop rotation, wheat was fertilized with 112 kg N applied as urea at planting and 80 kg N ha^{-1} applied as foliar application in March.

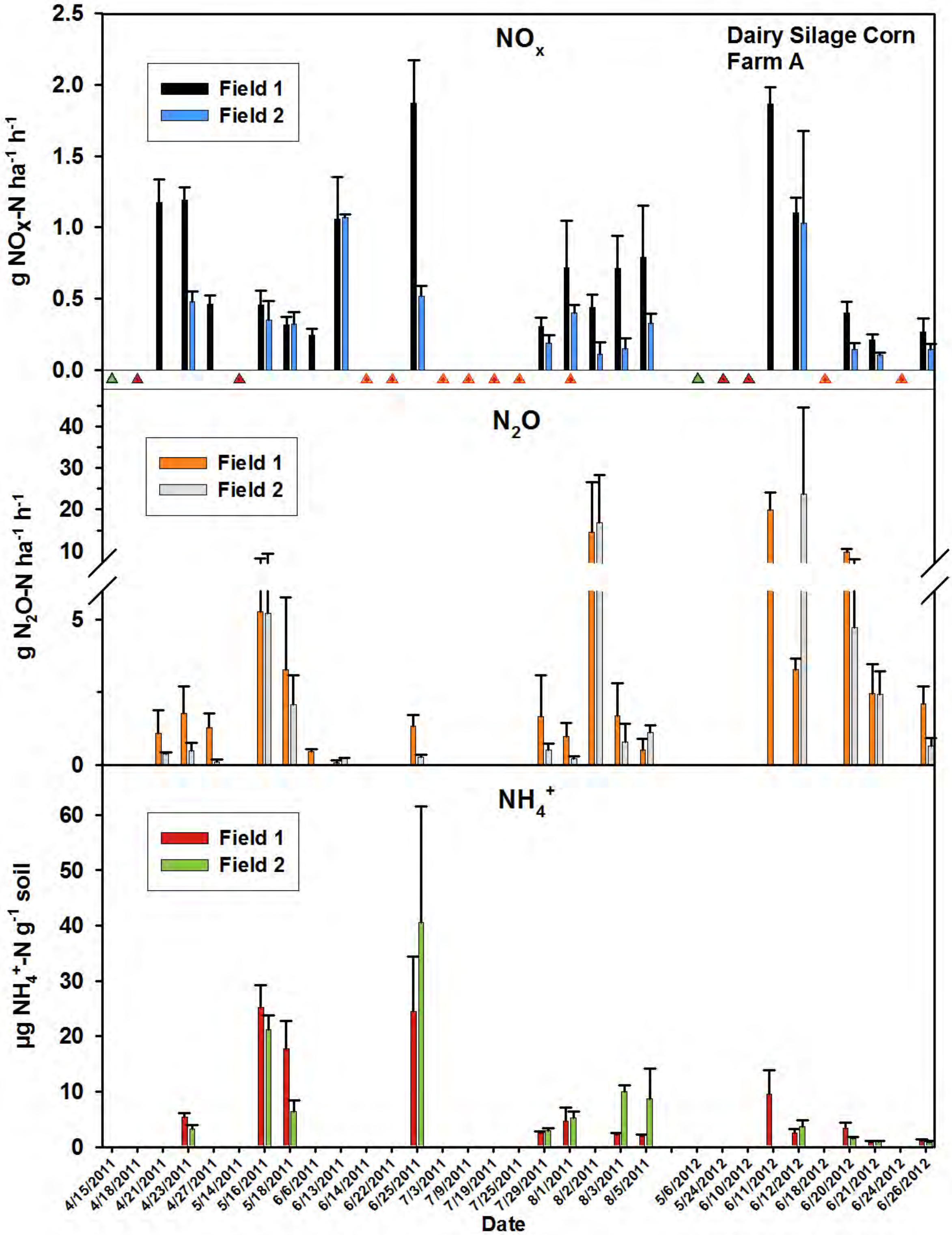
3.5 *Dairy silage corn*

The soil temperatures (1 cm depth) during measurements at all the sites were 25-40°C (Figures 7, 9, 10). The WFPS ranged from 50-80% at Farm A and from 40-80% at Farm B, but on Farm C, all WFPS measurements were >70% and sometimes reaching 100%.

In the fields of Farm A, the NO_x flux was mostly ≤1 g NO_x-N ha^{-1} h^{-1}, except for two days when NO_x flux reached about 2 g NO_x-N ha^{-1} h^{-1} (Figure 7). The soil NH_4^+ concentrations on one of those days was 25 µg NH_4^+-N g^{-1} (June 25, 2011), and 10 µg NH_4^+-N g^{-1} on the other (June 11, 2012). Soil NO_2^- concentrations were low on most days, and there was no correlation of NO_x flux with NO_2^- concentration in the soil. Nevertheless, the highest NOx flux occurred when NO_2^- was at the highest concentration (Figure 8). The N_2O fluxes were mostly <5 g N_2O-N ha^{-1} h^{-1}, reaching up to 20 g N_2O-N ha^{-1} h^{-1} on some days.

In two fields of Farm B, the NO_x fluxes were mostly <2 g NO_x-N ha^{-1} h^{-1}, but on two occasions (June 19, 2011 and June 15, 2012), NO_x fluxes reached >14 g NO_x-N ha^{-1} h^{-1} (Figure 8). On those two occasions the soil NH_4^+ concentrations were 140 and 50 µg NH_4^+-N g^{-1} soil.

At Farm C, the NO_x flux was mostly <1 g NO_x-N ha^{-1} h^{-1}, except between June 22 and 27, 2011, when NO_x fluxes reached up to 3.3 g NO_x-N ha^{-1} h^{-1} and between Sept 18 and 21, 2012, when NO_x fluxes up to 41 g NO-N ha^{-1} h^{-1} were recorded (Figure 10). At Farm C, NO_x fluxes in 2011 were mostly <0.5 g NO_x-N ha^{-1} h^{-1} except for three days (June 22 – June 27, 2011) when fluxes peaked at 3.3 g NO_x-N ha^{-1} h^{-1} (Figure 9). During that period, soil NH_4^+ concentrations were 7 µg NH_4^+-N g^{-1} and the WFPS was 96%. Soil NO_2^- concentrations during this period were about 4 µg NO_2^--N g^{-1} (Figure 11). In June 2012, the NO_x flux exceeded 1 g NO_x-N ha^{-1} h^{-1} on only one day (June 27) when soil NH_4^+ concentrations were 24 µg NH_4^+-N g^{-1} and the WFPS was 76%. In September 2012, the NO_x fluxes peaked at 42 g NO_x-N ha^{-1} d^{-1} (September 21) when soil NH_4^+ concentrations were 8 µg NH_4^+-N g^{-1} and the WFPS was 88%. The N_2O flux at Farm C in both years was elevated in June, with fluxes up to 30-40 g N_2O-N ha^{-1} h^{-1}, but in September 2012, peak N_2O fluxes were lower than the NO_x fluxes.



NOx
Dairy Silage Corn
Farm A
Field 1
Field 2
g NOX-N ha-1 h-1
N2O
Field 1
Field 2
g N2O-N ha-1 h-1
NH4+
Field 1
Field 2
µg NH4+-N g-1 soil
Date
4/15/2011
4/18/2011
4/21/2011
4/23/2011
4/27/2011
5/14/2011
5/16/2011
5/18/2011
6/6/2011
6/13/2011
6/14/2011
6/22/2011
6/25/2011
7/3/2011
7/9/2011
7/19/2011
7/25/2011
7/29/2011
8/1/2011
8/2/2011
8/3/2011
8/5/2011
5/6/2012
5/24/2012
6/10/2012
6/11/2012
6/12/2012
6/18/2012
6/20/2012
6/21/2012
6/24/2012
6/26/2012

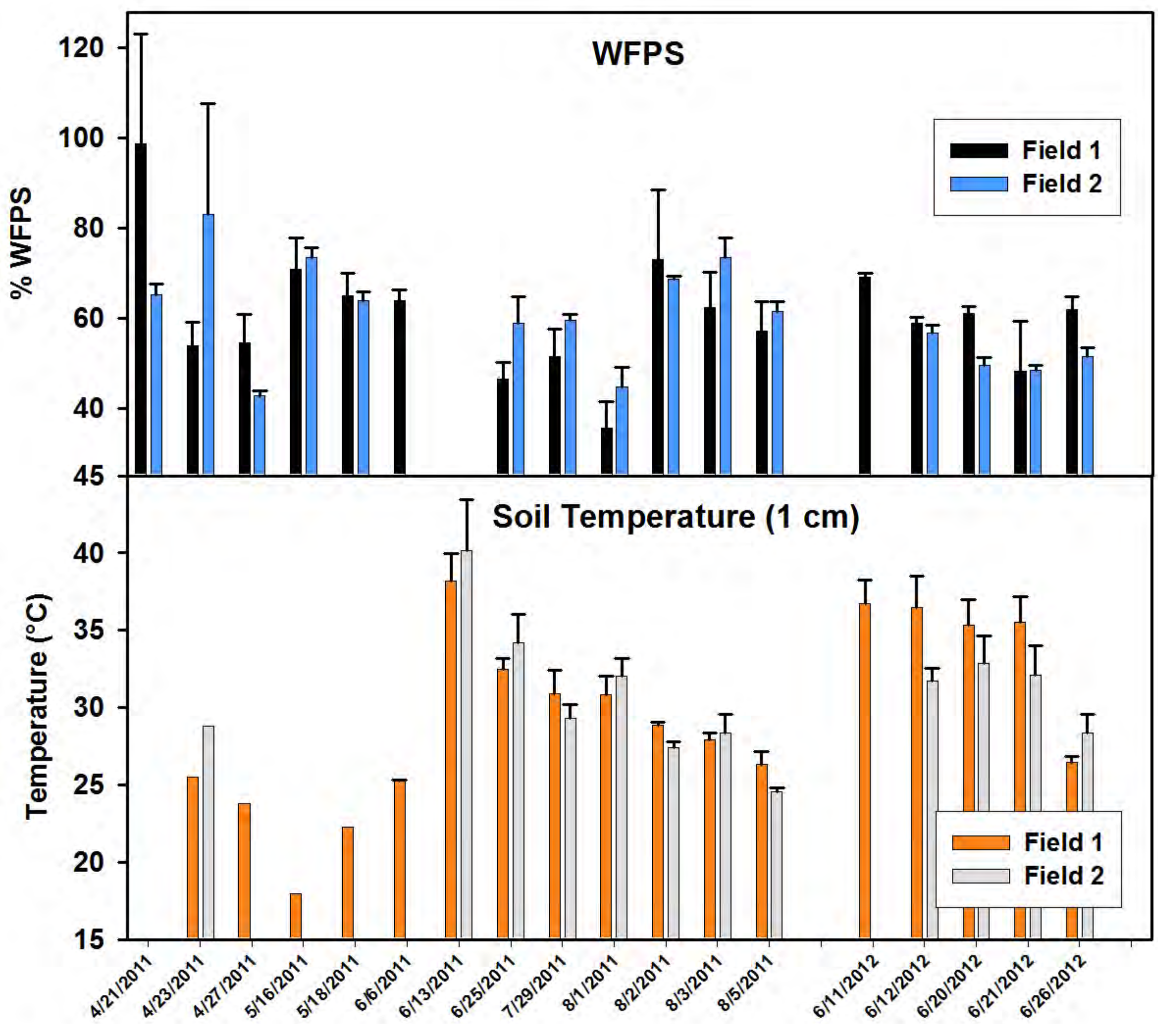


Figure 7. NO_x and nitrous oxide (N_2O) flux, soil ammonium (NH_4^+) concentrations, water-filled pores space (WFPS), and soil temperature in the dairy silage corn systems of Farm A. Standard errors are shown as line bars. n=4. Triangles along the x-axis indicate inorganic fertilization (green), irrigation with lagoon water (red), and irrigation with lagoon water and inorganic fertilizers (orange) events.

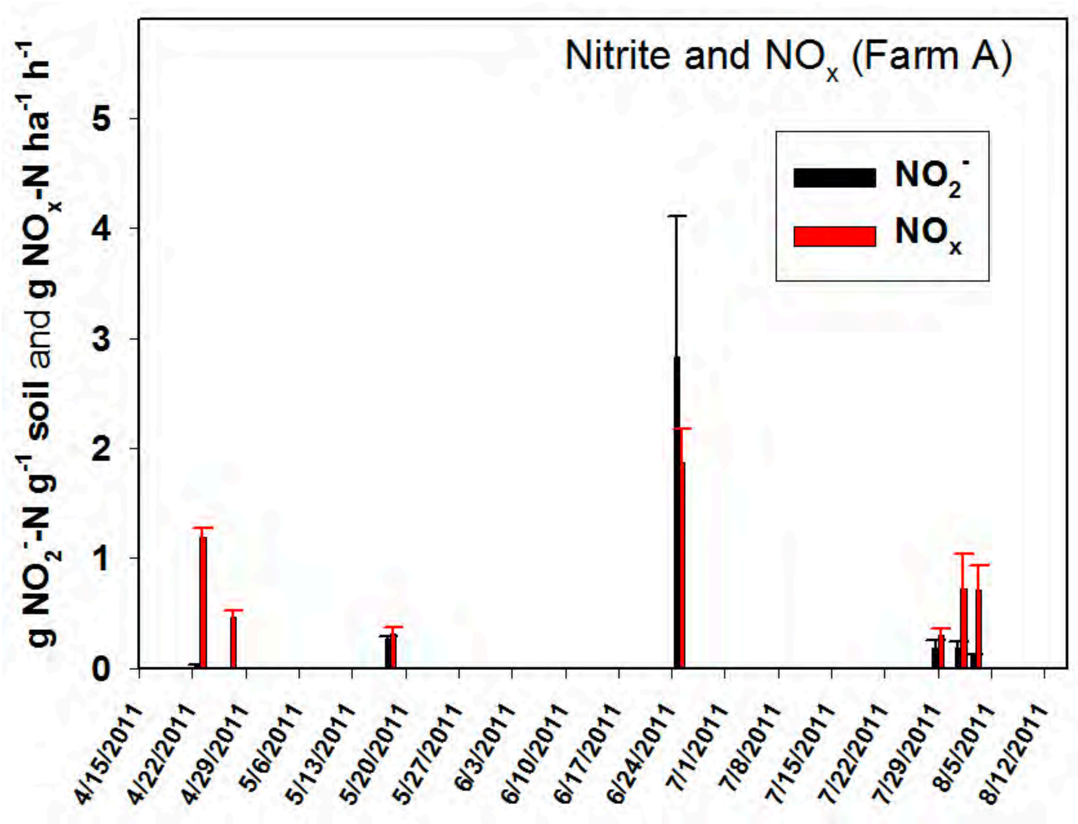
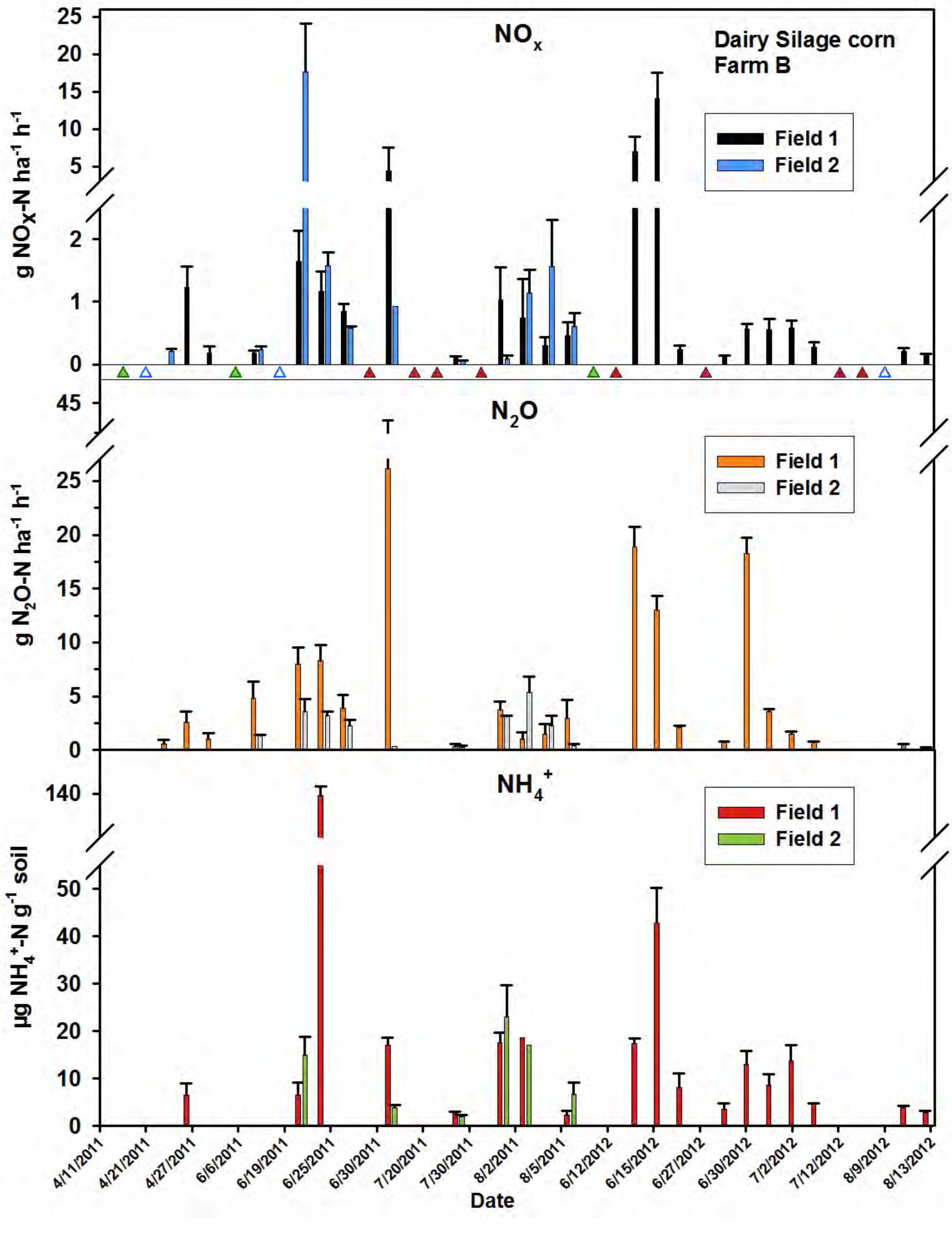


Figure 8. Soil nitrite concentrations and NO_x flux at Farm A. Standard errors shown as line bars. n=4.


NO$_x$
Dairy Silage corn
Farm B
Field 1
Field 2
g NO$_X$-N ha^{-1} h^{-1}
N$_2$O
g N$_2$O-N ha^{-1} h^{-1}
NH$_4^+$
µg NH$_4^+$-N g^{-1} soil
4/11/2011
4/21/2011
4/27/2011
6/6/2011
6/19/2011
6/25/2011
6/30/2011
7/20/2011
7/30/2011
8/2/2011
8/5/2011
6/12/2012
6/15/2012
6/27/2012
6/30/2012
7/2/2012
7/12/2012
8/9/2012
8/13/2012
Date

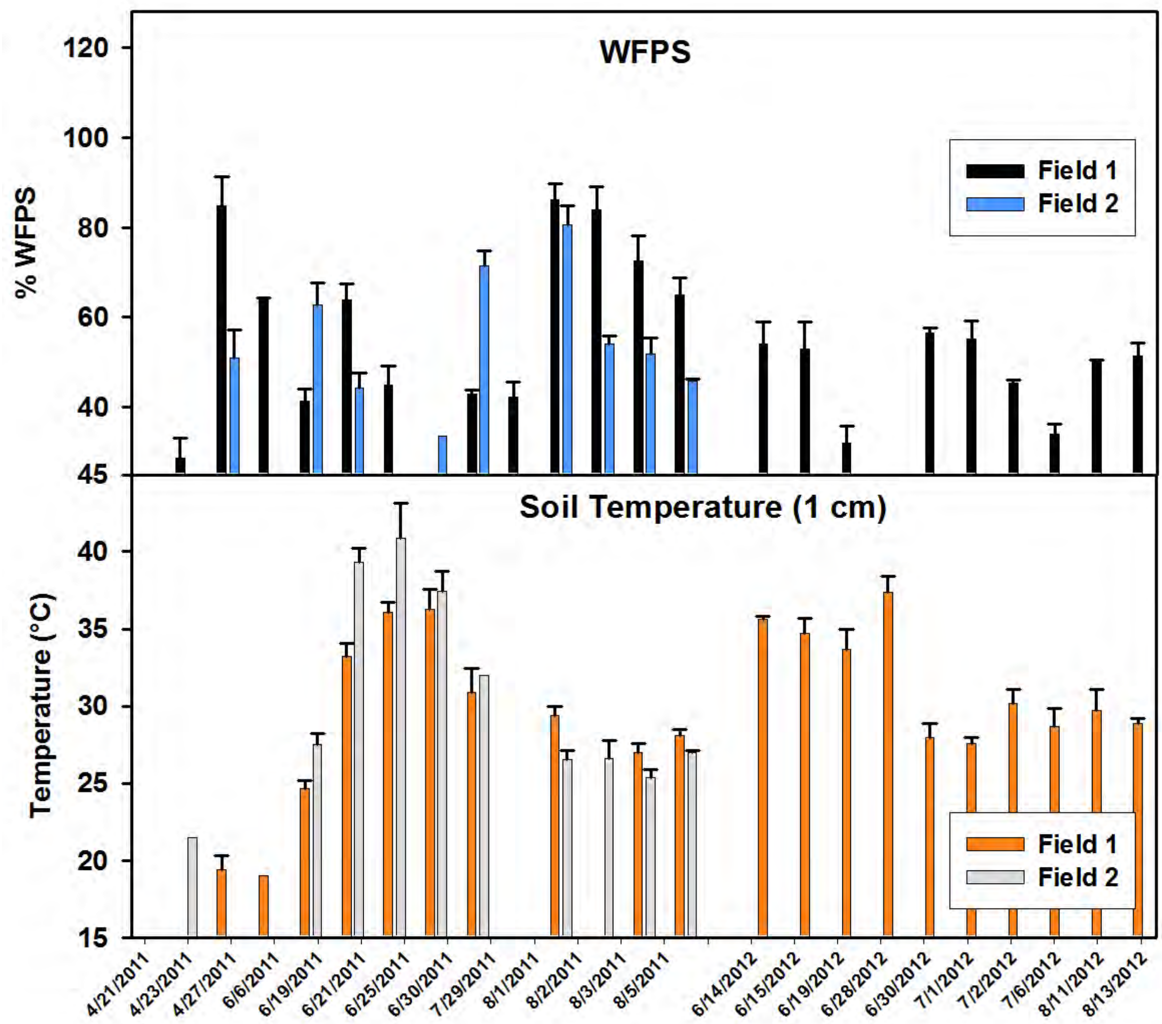
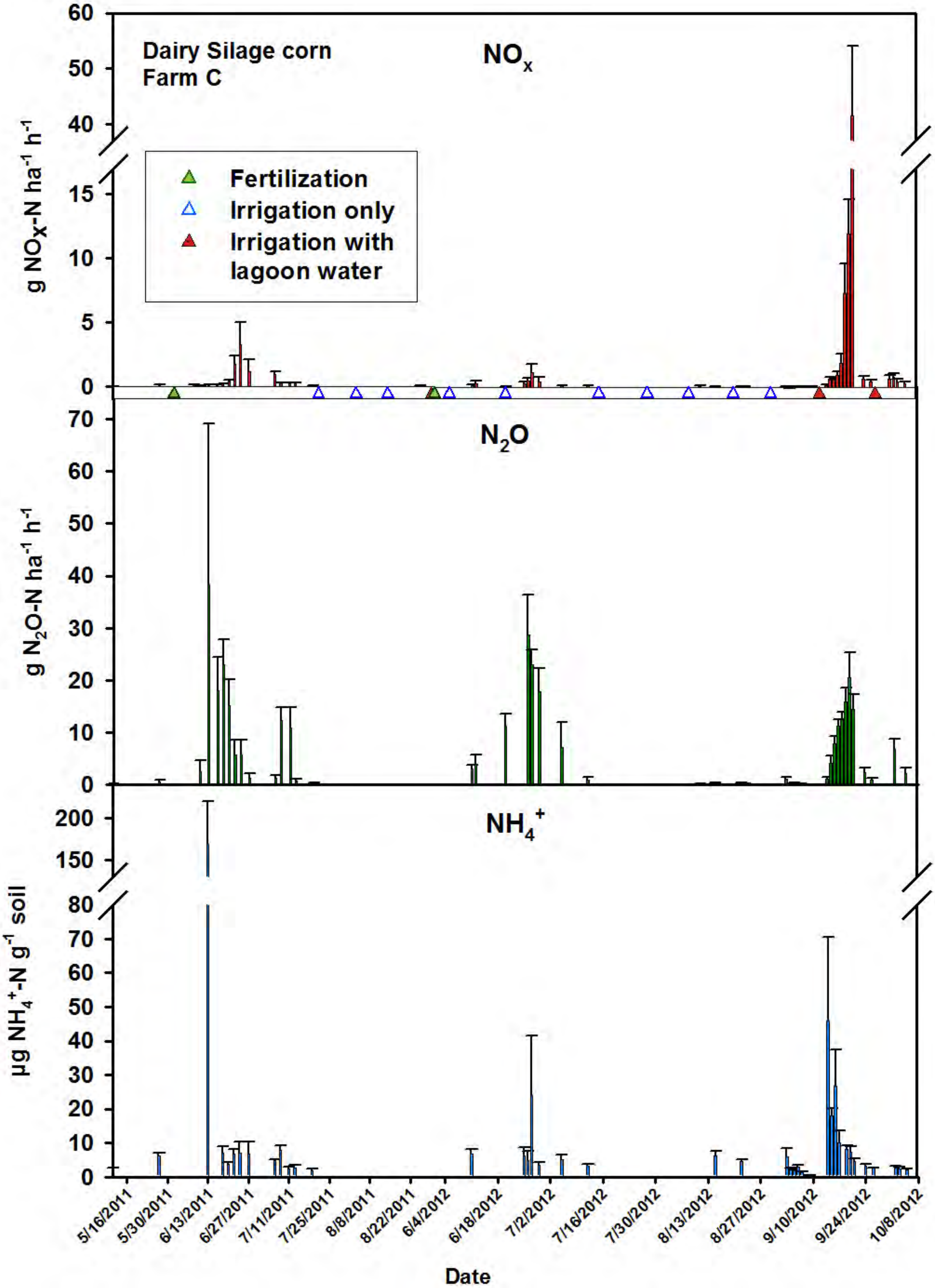


Figure 9. NO_x and nitrous oxide (N_2O) flux, soil ammonium (NH_4^+) concentrations, water-filled pore space (WFPS), and soil temperature in the dairy silage corn systems of Farm B. Standard errors are shown as line bars. n=4. Triangles along the x-axis indicate inorganic fertilization (green), irrigation (white), and irrigation with lagoon water (red) events.


Dairy Silage corn
Farm C
NO_x
Fertilization
Irrigation only
Irrigation with lagoon water
g NO_x-N ha^{-1} h^{-1}
N_2O
g N_2O-N ha^{-1} h^{-1}
NH_4^+
µg NH_4^+-N g^{-1} soil
5/16/2011
5/30/2011
6/13/2011
6/27/2011
7/11/2011
7/25/2011
8/8/2011
8/22/2011
6/4/2012
6/18/2012
7/2/2012
7/16/2012
7/30/2012
8/13/2012
8/27/2012
9/10/2012
9/24/2012
10/8/2012
Date

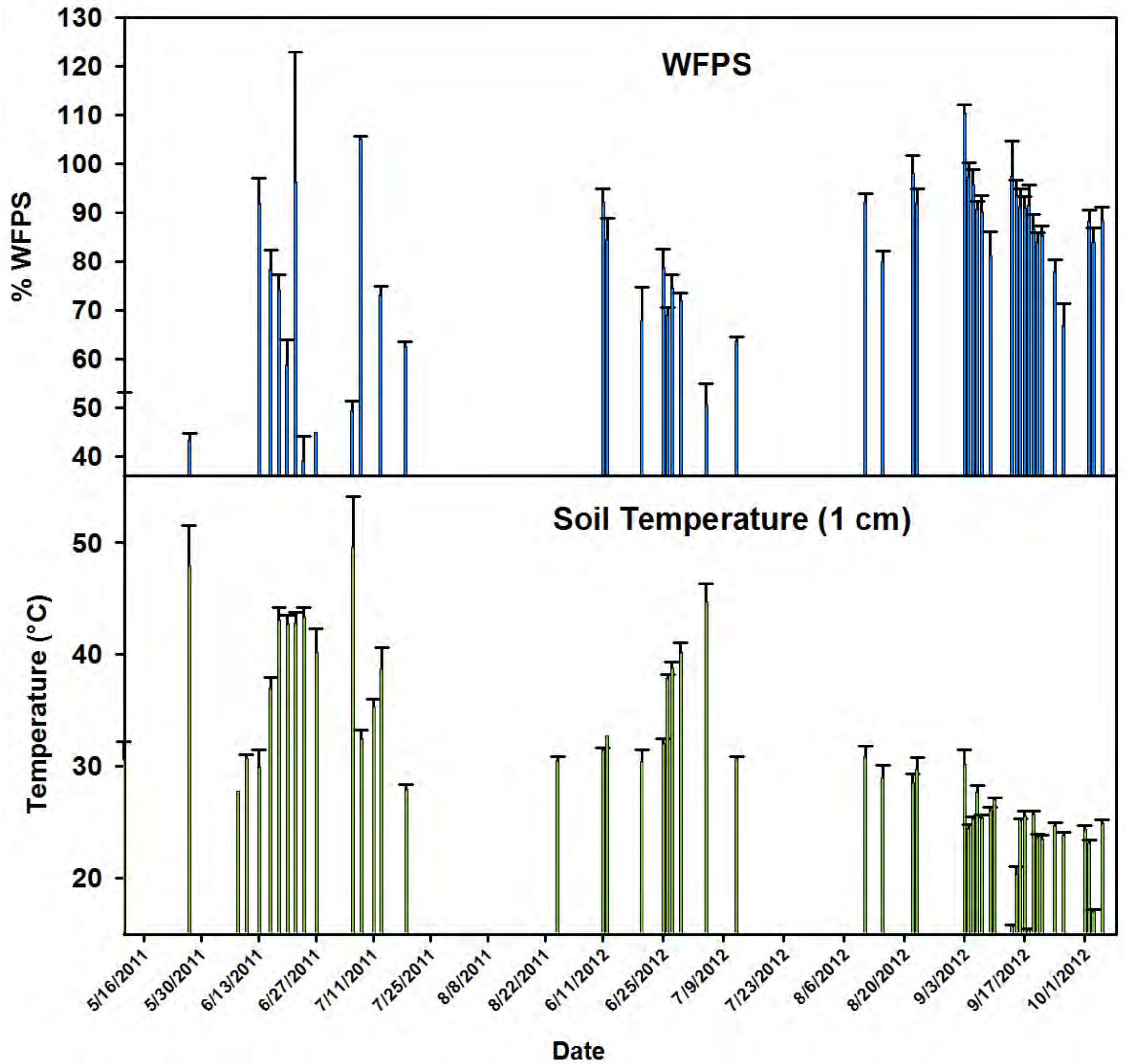


Figure 10. NO_x and nitrous oxide (N_2O) flux, soil ammonium (NH_4^+) concentrations, water-filled pore space (WFPS), and soil temperature in the dairy silage corn systems of Farm C. Standard errors shown as line bars. n=4. Triangles along the x-axis indicate inorganic fertilization (green), irrigation (white), and irrigation with lagoon water (red) events.

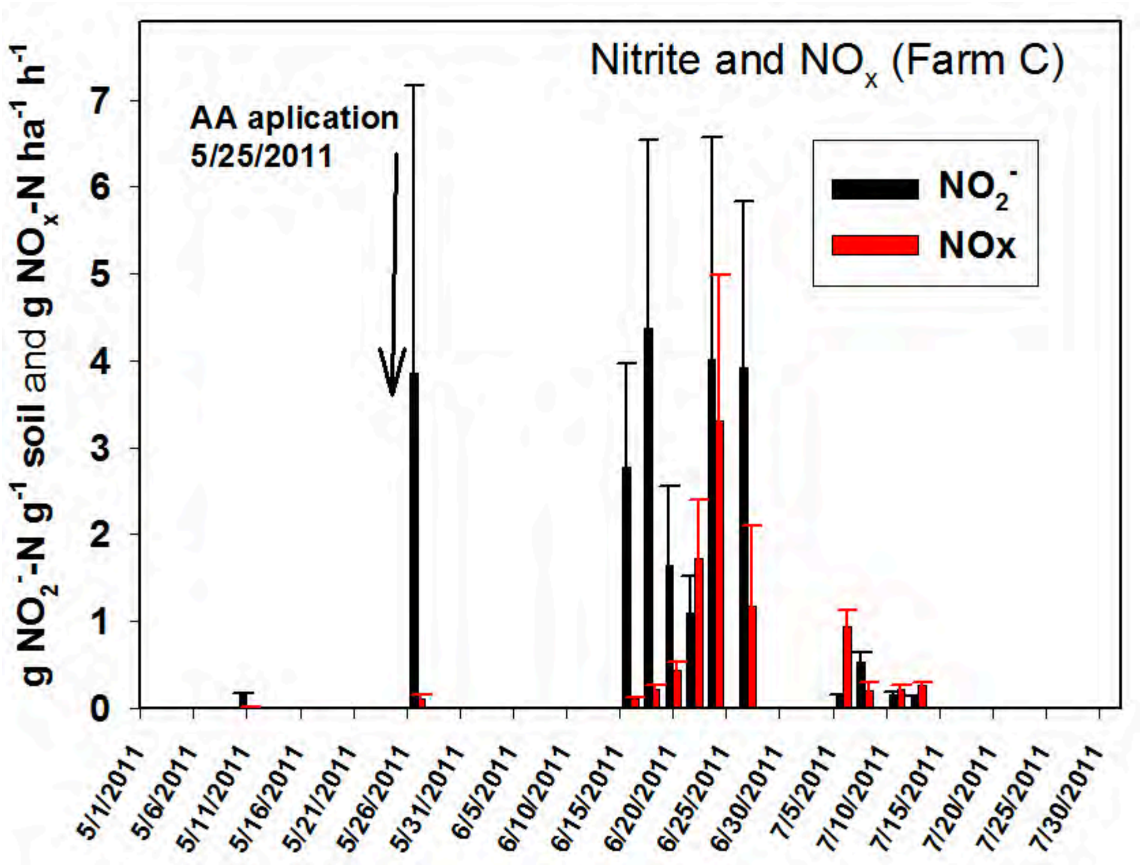


Figure 11. Soil nitrite concentrations vs. NO_x flux at Farm C. The date of the anhydrous ammonia (AA) application is also shown. Standard errors shown as line bars. n=4.

3.6 *Relationship between NOx flux and soil temperature*

The NO_x-flux in response to temperature change, expressed as the change in rate per 10°C change in soil temperature (Q_{10}) at 1 and 5 cm depth, was determined in 8 experiments at some of the field sites. The Q_{10} ranged from 1.2-3.8 with a mean of 2.5 based on soil temperature changes at 1 cm depth, and from 1.3-5.2 with a mean of 3.4 based on soil temperature changes at 5 cm depth (Table 9). Figure 12 shows data from three sites adjacent to and inside a corn field. Each data point shown represents an individual measurement.

Table 9. Q_{10} of NO_x-flux based on the change in soil temperature at 1 and 5 cm depths.

Location	Date	Min. T. 1 cm (°C)	Max. T. 1 cm (°C)	Min. T. 5 cm (°C)	Max. T. 5 cm (°C)	Q_{10} 1 cm	Q_{10} 5 cm
C1	7/21/12	18.8	45.8	21.2	42.2	1.8	2.0
C2	7/21/12	18.2	49.9	21.7	46.8	2.4	3.0
C3	7/21/12	17.1	32.5	18.2	32.5	3.8	4.4
FB	8/10/12	19.8	29.2	20.4	27.6	1.6	2.1
FC	9/15/12	15.6	25.3	17.5	23.5	3.0	4.2
FC	9/16/12	15.3	25.0	16.0	23.2	1.9	2.5
FC	9/26/12	16.8	24.9	16.9	23.0	1.2	1.3
FC	10/3/12	15.9	25.2	17.2	23.6	3.0	5.2
Median						2.2	2.8
Mean						2.5	3.4

C1-C3 = Campbell Tract, UC Davis; FB = Farm B; FC = Farm C

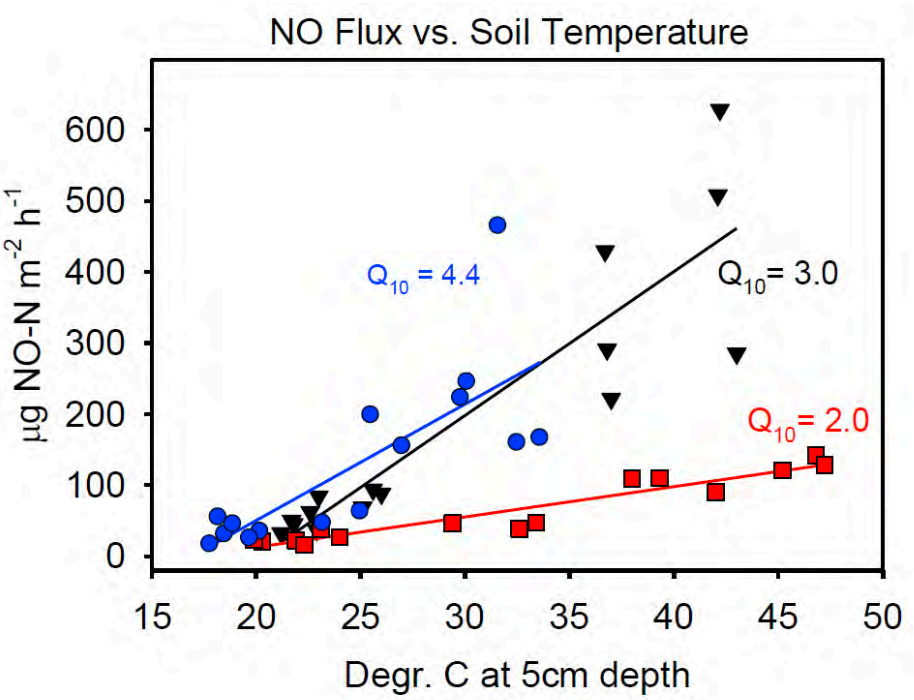


Figure 12. NO_x-flux in relation to soil temperature at 5 cm during the course of one day at three locations. The fluxes represented by the red and black symbols were measured at the edge of a corn field (WFPS 43%), the fluxes represented by the blue symbols were measured within the same corn field (WFPS 46%).

4. Discussion

We measured NO_x fluxes under varied soil moisture conditions in five different cropping systems receiving N inputs at different rates and in varied forms, and we calculated average hourly fluxes for each treatment and system. The average hourly fluxes provide information on the general trends in emissions among the different systems studied (Table 7). The lowest fluxes were observed in the wheat systems, the tractor rows of the almond orchard, the furrow-irrigated tomato control treatment (no N fertilizer applied this season) and the two SDI treatments of the tomato systems (Table 7). Somewhat greater average hourly NO_x fluxes were measured in alfalfa, the tree rows of the almond orchard, and the FI treatments of the tomato systems fertilized at recommended N rates. Our results are in agreement with those of earlier studies in California cropping systems. For alfalfa, except for one day, the measured fluxes in this study ranged from 0.07-0.6 g NO_x-N ha^{-1} h^{-1}, which is very similar to earlier reported ranges of 0.1-0.6 (Matson and Firestone, 1995). Likewise, the range of emissions in the sprinkler irrigated almond orchard in our study was 0.02-1.09 vs. 0.1-0.9 g NO_x-N ha^{-1} h^{-1} in the previous study, and for FI tomatoes the corresponding ranges are 0.04-1.2 vs. 0.1-1.2 g NO_x-N ha^{-1} h^{-1} (Matson and Firestone, 1995). In the systems receiving high N inputs, such as FI tomatoes fertilized with 300 kg N ha^{-1} and the dairy silage corn systems, the average NO_x fluxes were between 0.4 and 2.8 g NO_x-N ha^{-1} h^{-1} and higher than in the other systems studied here. There are not many field data of NO_x emissions resulting from liquid manure applications in the literature. Although on most days the range of fluxes measured by us in corn systems was similar as in a previous study (0.01-5.2 g NO_x-N ha^{-1}

h^{-1}) (Matson and Firestone, 1995), we also recorded some fluxes that exceeded those values by a wide margin and were comparable to those reported for fertilized (184 kg N as urea and 63 kg N as anhydrous ammonia) irrigated wheat systems in Sonora, Mexico (peak fluxes of 20-55 g NO_x-N ha^{-1} h^{-1})(Matson *et al.*, 1998), and with the fluxes measured above an injection band of anhydrous ammonia (120 kg N ha^{-1}) in a California tomato system (5-10 g NO_x-N ha^{-1} h^{-1}, with peak values of up to 100 g NO_x-N ha^{-1} h^{-1})(Venterea and Rolston, 2000b).

Nitric oxide flux is highly dependent on temperature, with a predicted doubling of NO production for each 10°C increase in temperature between 15° and 35°C (Williams *et al.*, 1995). Most of our NO_x flux measurements were made in the afternoons. The recorded fluxes therefore represent values close to the maximum of those days. The fluxes, soil temperatures, and times of measurements are compiled in the Appendix (Tables 1A-6A). If the reported NO_x emission values will be used as modeling inputs, the fluxes need to be adjusted for diel fluctuations in temperature. We derived Q_{10} factors under field conditions in three different corn cropping systems. The lowest NO_x flux of the day was always measured early in the morning when soil temperatures typically are at their daily minimum. The ranges of Q_{10} varied from 1.2 to 3.8 with a mean of 2.5 and a median value of 2.2 based on soil temperature dynamics at a depth of 1 cm. Based on soil temperature at 5 cm, the range was 1.3-5.2 with a mean of 3.5 and a median of 2.8 (Table 15). The Q_{10} obtained based on soil temperature at 1 cm may have been lower because nitrifying bacteria have been reported to stop growing >40°C (Focht and Verstraete, 1977). Temperatures at 1 cm depth were approaching or exceeding this temperature on some of the days and were higher than at 5 cm depth.

Besides temperature, availability of the substrate NH_4^+ and NO_2^-, as influenced by the amount, form, and placement of N inputs, controls NO_x flux. For example, on Farm B, NO_x-fluxes of 10-15 g NO_x-N ha^{-1} h^{-1} were measured shortly after UAN32 fertilizer applications on June 15, 2011 and June 7, 2012, and an irrigation with lagoon water. The high NO_x emissions also coincided with NH_4^+ concentrations >100 μg NH_4^+-N g^{-1}. In the tomato system, the application of 300 kg N ha^{-1} as UAN32 – almost twice the recommended N rate for furrow-irrigated tomato crops – lead to sustained high NO_x emissions lasting about 6 weeks. It is possible that in the dairy silage corn systems the liquid manure enhanced NO_x emissions due to the availability of carbon which stimulates O_2 consumption in the soil. Nitric oxide and N_2O production increase with decreasing O_2 levels in the soil (Zhu *et al.*, 2013). Nitrite, the intermediate during ammonia oxidation to NO_3^-, is a precursor of NO and N_2O in the soil (VanCleemput and Samater, 1996; Venterea and Rolston, 2000a, b; Zhu *et al.*, 2013). We detected NO_2^- after application of anhydrous ammonia (Farm C) and after application of liquid manure and UAN in the irrigation water at Farm A, and in both cases enhanced NO_x emissions coincided with high NO_2^- levels in the soil (Figures 8 and 11). There was also a weak correlation of NO_x flux with NO_2^- levels in the almond orchard (Figure 2).

Since most NO produced in soil is consumed to produce N_2O (Venterea and Rolston, 2000b; Venterea *et al.*, 2004), the placement of the substrate can be expected to affect the magnitude NO_x emissions. Diffusion of gases at high WFPS is low, and consumptive processes of NO are likely favored over the release of this reactive gas to the atmosphere. In general, during the periods when high NO_x emissions occurred, the WFPS was ≤60%, but there were some noteworthy exceptions. For example, in September 2012, NO_x fluxes on the order of 7-42 g NO_x-N ha^{-1} h^{-1} occurred at Farm C while WFPS was >90%. The high NO_x emissions took place in spite of high WFPS most likely because the liquid manure, which was applied via flood irrigation, provided the substrate (NH_4^+) for nitrification and NO_x

production near the soil surface. It is interesting that in June, 2011, substantial NO_x flux following the anhydrous ammonia application at Farm C did not occur until WFPS declined to <50% (Figure 10) even though NO_2^- concentrations were elevated as soon as the anhydrous ammonia was applied (Figure 11).

The NO_x emissions were related to N inputs and NH_4^+ availability, and most NO_x emitted was likely due to nitrification. Once most of the applied NH_4^+ was converted to NO_3^- or taken up by the crops, the NO_x fluxes subsided. This was particularly evident at Farm C, where lower NH_4^+ concentrations in the soil coincided with tapering off of NO_x flux. Similarly, as soil NH_4^+ concentrations decreased from >100 μg NH_4^+-N g^{-1} on Farm B, the NO flux subsided to more moderate levels. In the almond orchard, following four fertigation events, there were four distinct peaks of NO_x emissions, which declined over the course of 10 days probably because the NH_4^+ was taken up by the trees or nitrified although the decrease in NH_4^+ concentrations was not clearly shown. It appears, therefore, that in general NO_x fluxes decrease with time since N fertilization, which has been observed earlier (Williams *et al.*, 1992; Matson and Firestone, 1995).

The relationship between N_2O and NO_x fluxes varied, depending on the system. Average hourly NO_x fluxes were similar (SDI-irrigated and wheat systems, as well as Field 2 on Farm B) or lower than average hourly N_2O fluxes, except for furrow-irrigated tomatoes fertilized with an excessive N rate, which had higher average NO_x than N_2O fluxes (Table 7). Differences between NO_x and N_2O fluxes in the different systems may be explained by soil water content and ultimately by irrigation systems. While N_2O production can be expected to be related to NO_x production, the opportunity for the consumption of NO_x is greater at high than low and intermediate soil water content. Therefore, when WFPS is high, N_2O tend to be greater than NO_x emissions. The flood-irrigated alfalfa and silage corn systems, where average N_2O fluxes were 2 to 16 times higher than average NO_x fluxes in six of the seven fields, reached high WFPS with every irrigation, and this likely explains the larger differences between N_2O and NO_x fluxes in the flood- than drip- and furrow-irrigated systems.

To compare the contribution of NO_x from agricultural soil to overall statewide NO_x emissions, the average values measured in the present study were used to calculate a rough estimate of total NO_x emissions from agricultural soil during summer. There are many caveats to deriving such an estimate. First, the NO_x fluxes were measured in only 16 fields in five major cropping systems whereas >300 different crops are grown in California. Notably absent in the present study were measurements in grapevine, rice, citrus, cotton, pasture land, and others. Second, the measured NO_x fluxes were highly variable, generally decreasing with time since fertilizer applications, and the average hourly NO_x fluxes of this study are not necessarily representative for certain days when the actual fluxes could potentially be much higher or lower than the average fluxes. Third, site-specific differences due to management practices and soil types were not considered when extrapolating the results of the present study to other cropping systems. The approximate estimates of NO_x emissions (in Mg NO_x d^{-1}, or tonnes NO_x per day) (Table 10) were derived in two ways. Either the hourly NO_x fluxes measured in this study were assumed to represent the daytime fluxes (12 hours) and the night-time fluxes (12 hours) were assumed to be 50% of the daytime fluxes ('low' estimate), or the hourly fluxes were considered representative for the total daily (24 hours) emissions ('high' estimate). The average NO_x fluxes in furrow-irrigated tomato were assumed to be representative for all vegetable, field & seed, and rice cropping systems, whereas all fluxes in fruit & nut cropping systems were assumed to be similar as the ones measured in the almond orchard. Average fluxes in alfalfa were assumed to be representative for all alfalfa and forage crops, and those in corn systems of the dairy farms were considered representative for all silage corn acreage.

Table 10. Estimates of daily NO_x emissions from agricultural land in California.

Cropping systems	Area (ha)¶	Hourly NO_x flux*	Daily NO_x flux (low est.)	Daily NO_x flux (high est.)
		g NO_x-N ha^{-1} h^{-1}	Mg NO_x d^{-1}	Mg NO_x d^{-1}
Vegetables	517,004	0.32 [1]	9.8	13.0
Fruits & nuts	989,069	0.35 [2]	20.5	27.3
Field & seed crops	332,794	0.32 [1]	6.3	8.4
Rice	234,818	0.32 [1]	4.4	5.9
Wheat	319,838	0.04 [3]	0.8	1.0
Alfalfa & forage	724,696	0.54 [4]	23.1	30.9
Silage corn	192,308	1.35 [5]	15.3	20.5
Total	8,177,000		80.3	107.0

¶ Based on California Department of Food & Agriculture 2011 data, * estimated from hourly NO_x flux in [1]furrow-irrigated tomato fertilized with 162 kg N ha^{-1}, [2] microjet sprinkler-irrigated almond, [3]wheat, [4]flood-irrigated alfalfa, and [5]flood-irrigated corn fertilized with mineral fertilizer and liquid dairy manure.

The total NO_x emissions in California have declined from about 4,900 Mg d^{-1} in 1990 to 3,000 Mg d^{-1} in 2010 and are projected to decrease to 2,200 Mg d^{-1} by 2020 (CARB). Therefore, based on the above estimate, NO_x emissions from agricultural soil account for <4% of total NO_x emitted, but the contribution of NO_x from agricultural land could increase to about 5% within this decade if further reductions of NO_x from mobile and stationary sources will be attained.

Summary and Conclusions

Emissions of NO_x were measured in almond, alfalfa, tomato, wheat, and silage corn cropping systems during summer months (June-September) in California's Central Valley. The study was undertaken to estimate the contribution of NO_x from agricultural soil in order to improve the predictive power of ozone (O_3) models for the San Joaquin Valley because NO_x availability under certain circumstances (e.g. when the availability of volatile organic compounds is high) controls O_3 formation. The NO_x fluxes were measured in 17 different fields or treatments representing varied soil moisture conditions, nitrogen availability, and management practices, such as irrigation and nitrogen inputs.

The average NO_x fluxes were lowest in wheat, the non-irrigated sections of an almond orchard and in subsurface drip-irrigated tomato (average flux <0.1 g NO_x-N ha^{-1} h^{-1}), and intermediate in alfalfa, the irrigated sector of an almond orchard, and furrow-irrigated tomato N fertilized at recommended rates (average flux ≤0.5 g NO_x-N ha^{-1} h^{-1}). The highest NO_x emissions were measured in furrow-irrigated tomato fertilized at an excessive N rate and in silage corn systems receiving high N inputs in the form of synthetic N fertilizers and manure from dairy farms (average flux up to 3 g NO_x-N ha^{-1} h^{-1}). The ranges of emissions near their daily maximum were comparable to those measured in earlier studies in the different systems, but following high N inputs, the emissions were higher (by an order of magnitude) for short periods (days).

The emissions at each location varied over time, depending on soil moisture, time since N fertilization, and soil temperature. In the present study, field experiments showed that NO_x emissions increase on average 2.5- and 3.5-fold with each increase of 10°C in soil temperature at 1 and 5 cm depth, respectively. Enhanced NO_x fluxes occurred under intermediate soil water contents (water-filled pore space 30-60%), whereas in relatively dry soils or at high water content, NO_x-fluxes were low. The results suggest that NO_x emissions are related to ammonium availability and nitrification rates, hence the decline of NO_x flux with time since N fertilizer applications.

Based on this relatively limited data set given the great variety of cropping systems in the San Joaquin Valley, it appears that N fertilization at recommended N rates does lead to fairly predictable NO_x emissions. However, the magnitude and duration of enhanced NO_x emissions (increased by an order of magnitude or more), are not necessarily predictable because they are event-based (e.g. date of N fertilization) and depend on complex interactions among NO production, gas transport and NO consumption in the soil, as well as other variables such as soil temperature at different depths.

Recommendations

The objective of this study was to provide field estimates of NO_x emissions from agricultural land. Because NO_x flux varies depending on farm management events (e.g. N fertilization, irrigation), day-by-day, or hourly, regional quantification of NO_x emissions from agricultural sources would require elaborate models including the mosaic of cropping systems and their associated management. The average NO_x emissions or ranges of emissions generated in this study might be extrapolated according to crop acreages and compared to known estimates of NO_x production from mobile and other NO_x sources as a rough estimate assessing the relative importance of NO_x emissions from agricultural land under current conditions.

References

Blanchard, C.L., Fairley, D., 2001. Spatial mapping of VOC and NO_x-limitation of ozone formation in central California. Atmos. Environ. 35, 3861-3873.

Doane, T.A., Horwáth, W.R., 2003. Spectrophotometric determination of nitrate with a single reagent. Anal. Lett. 36, 2713-2722.

Focht, D.D., Verstraete, W., 1977. Biochemical ecology of nitrification and denitrification. Advances in Microbiology and Ecology 1, 135-214.

Forster, J.C., 1995. Soil nitrogen. In: K., A., P, N. (Eds.), Methods in Applied Soil Microbiology and Biochemistry. Academic Press, San Diego, pp. 79-87.

Geisseler, D., Lazicki, P.A., Pettygrove, G.S., Ludwig, B., Bachand, P.A.M., Horwath, W.R., 2012. Nitrogen Dynamics in Irrigated Forage Systems Fertilized with Liquid Dairy Manure. Agron. J. 104, 897-907.

Lee, J., Hopmans, J.W., van Kessel, C., King, A.P., Evatt, K.J., Louie, D., Rolston, D.E., Six, J., 2009. Tillage and seasonal emissions of CO2, N2O and NO across a seed bed and at the field scale in a Mediterranean climate. Ag. Ecosyst. Env. 129, 378-390.

Matson, P., Firestone, M.K., 1995. Agricultural Systems in the San Joaquin Valley: Development of Emissions Estimates for Nitrogen Oxides. Technical Report prepared for CA Air Resources Board and CA EPA. . University of California Berkeley.

Matson, P.A., Naylor, R., Ortiz-Monasterio, I., 1998. Integration of environmental, agronomic, and economic aspects of fertilizer management. Science (Washington D C) 280, 112-115.

Olivier, J.G.J., Bouwman, A.F., Van Der Hoek, K.W., Berdowski, J.J.M., 1998. Global air emission inventories for anthropogenic sources of NOX, NH3 and N2O in 1990. Environ. Pollut. 102, 135-148.

VanCleemput, O., Samater, A.H., 1996. Nitrite in soils: Accumulation and role in the formation of gaseous N compounds. Fert. Res. 45, 81-89.

Venterea, R.T., Groffman, P.M., Verchot, L.V., Magill, A.H., Aber, J.D., 2004. Gross nitrogen process rates in temperate forest soils exhibiting symptoms of nitrogen saturation. Forest Ecology and Management 196, 129-142.

Venterea, R.T., Rolston, D.E., 2000a. Mechanisms and kinetics of nitric and nitrous oxide production during nitrification in agricultural soil. Global Change Biol. 6, 303-316.

Venterea, R.T., Rolston, D.E., 2000b. Nitric and nitrous oxide emissions following fertilizer application to agricultural soil: Biotic and abiotic mechanisms and kinetics. J. Geophys. Res. Atmos. 105, 15117-15129.

Williams, E.J., Guenther, A., Fehsenfeld, F.C., 1992. An inventory of nitric oxide emissions from soils in the United States. J. Geophys. Res. Atmos. 97, 7511-7519.

Williams, E.J., Hutchinson, G.L., Fehsenfeld, F.C., 1995. NO_x and N2O emissions from soil. Global Biogeochem. Cycl. 6, 351-388.

Zhu, X., Burger, M., Doane, T.A., Horwath, W.R., 2013. Ammonia oxidation pathways and nitrifier denitrification are significant sources of N2O and NO under low oxygen availability. P Natl Acad Sci USA.

Glossary of Terms, Abbreviations and Symbols

AB32	Assembly Bill 32
banded	Concentrated line of material in soil, such as fertilizer applied by injection into the soil
CARB	California Air Resources Board
C	Carbon
°C	Degree(s) Celsius
cc	Cover crop
CrO_3	Chromium trioxide
est.	estimated
Fertigation	Application of fertilizer dissolved in irrigation water
FI	Furrow irrigation
h	Hour(s)
ha	Hectare
H_2O	Water
N	Nitrogen
NH_4^+	Ammonium
NO	Nitric oxide
NO_2^-	Nitrite
NO_3^-	Nitrate
NO_x	Nitric oxide and nitrogen dioxide
N_2O	Nitrous oxide
O_2	Oxygen
O_3	Ozone
PTFE	Teflon
PVC	Poly-vinyl chloride
SDI	Subsurface drip irrigation
SE	Standard error
UAN32	Urea ammonium-nitrate
UC	University of California
VOC	Volatile organic compounds
WFPS	Water-filled pore space

yr	Year

APPENDIX

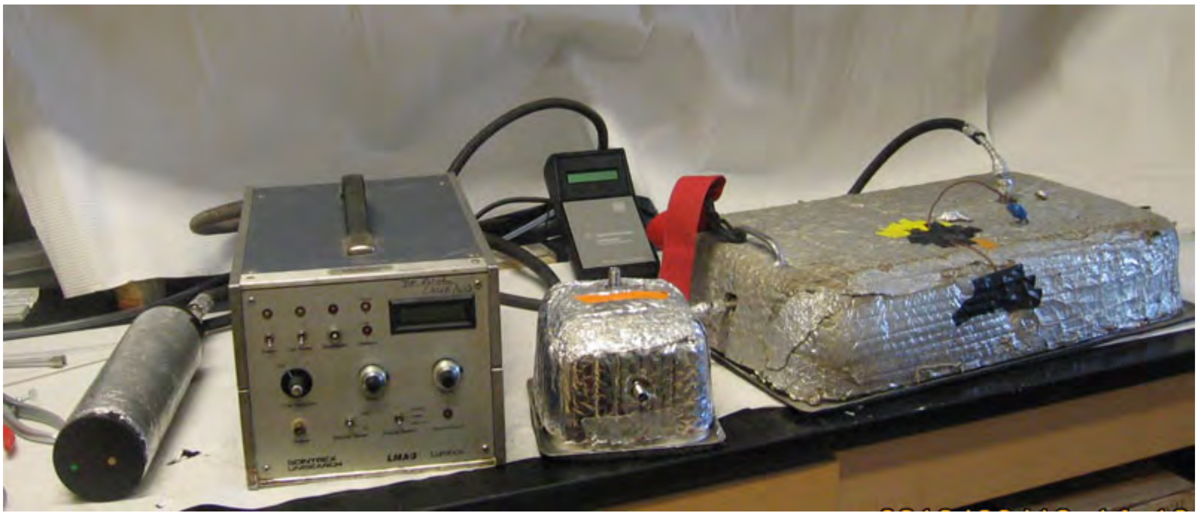


Figure 1A. Paraphernalia to measure NOx flux in the field. From left, vessel containing drying agent and Nafion™ tubing to remove air humidity, battery-powered Scintrex (LMA-3) NO_x analyzer, chamber used in alfalfa fields, chamber used in corn, tomato, and wheat systems.

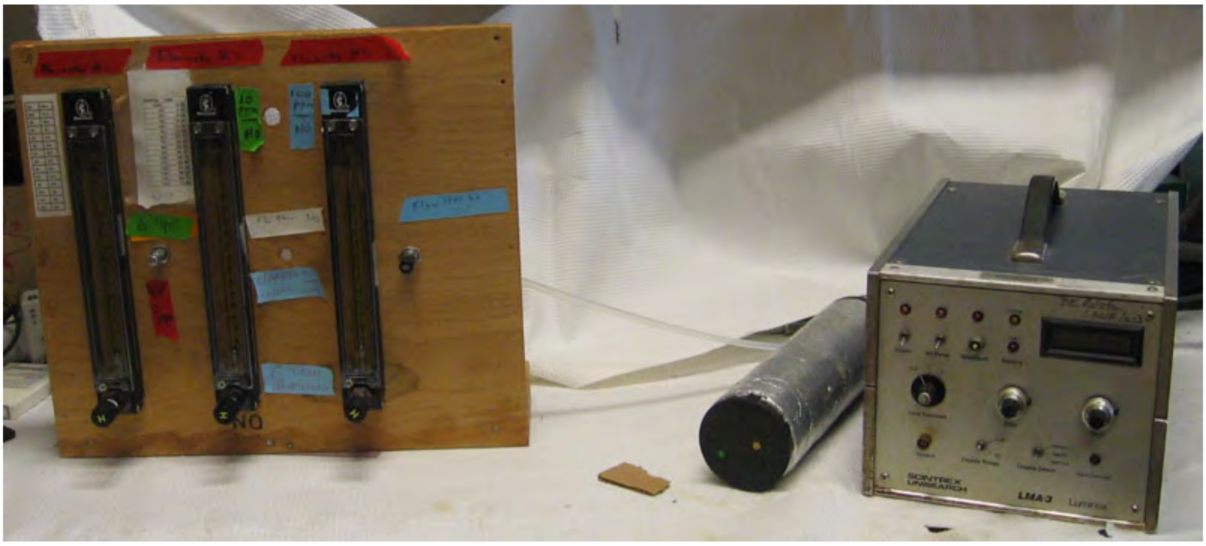


Figure 2A. Floating ball flowmeters (Manostat) used to measure the flow rates of NO standard gas and NO_x-free air during calibration of the NO_x analyzer.