

*Assessment of Nitrous Oxide Emissions in California's  
Dairy Systems*

FINAL REPORT

California Air Resources Board, Contract No. 09-325

Principal Investigators:  
William R. Horwath  
Martin Burger  
Stuart Pettygrove

Prepared for:  
California Air Resources Board

Prepared by:  
Martin Burger, Cristina Lazcano, 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**

The statements and conclusions in this Report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

## **Acknowledgements**

We would like to thank Alia Tsang, Karen Adler, Nick Monte, Travis Wilson, Matthew Ong, and three dairy farmers in the San Joaquin Valley 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 *Assessment of Baseline Nitrous Oxide Emissions in California's Dairy Systems* by the University of California, Davis, under the sponsorship of the California Air Resources Board. Work was completed as of November 27, 2013.

## TABLE OF CONTENTS

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

---

<b>Section</b>	<b>Page</b>
1. Introduction	1
2. Materials and Methods	2
2.1. Field sites description	2
2.2. Accounting of N inputs and outputs	3
2.3. Nitrous oxide flux measurements	5
2.4. Annual N <sub>2</sub> O emissions	6
2.5. Measuring environmental variables	6
3. Results	7
4. Discussion	21
4.1. Amounts of nitrogen inputs	22
4.2. Timing of nitrogen fertilization	23
4.3. Placement of nitrogen fertilizer	23
4.4. Nitrogen source	23
6. Recommendations	24
7. References	25
8. Glossary	28
APPENDIX A: Measurement Data	29
APPENDIX B: Flux Calculations	35

---

## List of Figures

1.	Daily N <sub>2</sub> O flux Farm A	9
2.	Daily N <sub>2</sub> O flux Farm B	10
3.	Daily N <sub>2</sub> O flux Farm C	11
4.	Soil ammonium and nitrate Farm A	13
5.	Soil ammonium and nitrate Farm B	14
6.	Soil ammonium and nitrate Farm C	15
7.	Water inputs and soil water content 2011	18
8.	Water inputs and soil water content 2012	19
9.	Soil and ambient air temperatures Farms A & B	20
10.	Soil and ambient air temperatures Farms C	21
	APPENDIX	
1A	Gas flux chamber in the field	34

## List of Tables

1.	Soil characteristics of the dairy forage production systems	2
2.	Management dates, water inputs, nitrogen inputs, and nitrogen outputs	8
3.	Nitrous oxide emissions summary and emission factors	12
4.	Pearson correlation coefficients Field 1, Farm A	16
5.	Pearson correlation coefficients Field 2, Farm A	16
6.	Pearson correlation coefficients Farm B	17
7.	Pearson correlation coefficients Farm C	17

## Abstract

The greenhouse gas (GHG) nitrous oxide ( $\text{N}_2\text{O}$ ) is produced by soil microorganisms. Nitrogen (N) inputs, soil moisture and carbon stimulate the production of this gas, which accounts for about one third of all GHGs from California's agriculture sector. Nitrogen inputs, crop N removal, and cumulative  $\text{N}_2\text{O}$  emissions were measured from spring 2011 to fall 2012 in three dairy forage production systems receiving liquid and solid manure, as well as synthetic N fertilizer. The annual  $\text{N}_2\text{O}$  emissions ranged from 4.8–7.4 kg  $\text{N}_2\text{O}$ -N (mass of N in the form of  $\text{N}_2\text{O}$ )  $\text{ha}^{-1}$  from sites with sandy soil (>70% sand) and from 11.4–16.5 kg  $\text{N}_2\text{O}$ -N  $\text{ha}^{-1}$  in clayey soils (>40% clay) and were comparable to those of similar systems in other regions (1.2–13.8 kg N loss as  $\text{N}_2\text{O}$ ) although the California systems received higher N inputs (694–1281 kg N  $\text{ha}^{-1}$ ) than those systems (150–225 kg N  $\text{ha}^{-1}$ ). The periods of  $\text{N}_2\text{O}$  release after irrigation events were longer (weeks) in a clayey than in sandy soils (days). Nitrous oxide fluxes up to 1.4 kg  $\text{N}_2\text{O}$ -N  $\text{ha}^{-1} \text{d}^{-1}$  were recorded after large applications of synthetic N fertilizer (>100 kg N  $\text{ha}^{-1}$ ) whereas moderate additions of liquid manure and/or synthetic N fertilizer supplied together with the irrigation water resulted in lower, albeit consistent,  $\text{N}_2\text{O}$  emissions of up to 100 g  $\text{N}_2\text{O}$ -N  $\text{ha}^{-1} \text{d}^{-1}$ . To lower  $\text{N}_2\text{O}$  emission potential, applying N incrementally in moderate doses with the irrigation water according to crop N demand is recommended.

## Executive Summary

### *Background*

Nitrous oxide ( $\text{N}_2\text{O}$ ) is produced by microorganisms that use inorganic, or mineral, forms of nitrogen (N) in soil. Nitrous oxide release from the soil is affected by  $\text{N}_2\text{O}$  production rates, which in turn depend on N substrate availability, carbon, and soil moisture, and production pathways (nitrification related and denitrification). All these factors are controlled by soil porosity (related to soil texture and organic matter content) and soil water content. Nitrous oxide emissions from agricultural soils contribute about one third of California agriculture's total net greenhouse gas (GHG) emissions [California Air Resources Board (CARB), 2011]. Research to quantify  $\text{N}_2\text{O}$  emissions from the great variety of California cropping systems and to understand the drivers of these emissions is essential to develop effective mitigation practices and strategies. The present study provides annual  $\text{N}_2\text{O}$  emission estimates and input-output N budgets for three forage production systems typical for about 400,000 acres of irrigated forage cropland receiving dairy manure and synthetic N as fertilizers in California.

### *Methods*

Nitrogen inputs and outputs (yields),  $\text{N}_2\text{O}$  emissions, and soil variables were measured during two summer growing seasons and one winter rainy growing season in the above three cropping systems over the years 2011 and 2012. The concentration of different N fractions in the liquid manure inputs was measured in samples collected either at the pumps transferring the manure from the storage lagoons before mixing with irrigation water or in samples of the mixtures of irrigation and manure water applied to fields. The N inputs were then calculated based on the pump rates and irrigation times. Synthetic N fertilizer input rates during different growing seasons were obtained from farmers. Nitrous oxide emissions were measured following irrigation or rainfall events. The measurements were made by placing a vented chamber on the

soil surface and sampling headspace at regular, timed intervals. The air samples were analyzed by gas chromatography and the flux of N<sub>2</sub>O was calculated from the change in N<sub>2</sub>O concentration over chamber deployment period. The annual and seasonal N<sub>2</sub>O emissions were calculated by converting the measured fluxes to daily fluxes and interpolating between daily fluxes. The emission factors were calculated by dividing the amount of annual N<sub>2</sub>O-N emissions by the amount of N inputs. Yields and crop N removal were measured to determine N outputs. Soil moisture and temperature were measured with each chamber deployment, and available soil N was determined during each irrigation event to obtain information on how soil, environmental factors and management affected N<sub>2</sub>O emissions.

### *Results*

The annual N<sub>2</sub>O emissions ranged from 4.7-7.4 kg N<sub>2</sub>O-N ha<sup>-1</sup> in sandy soils, and from 11.4-16.5 kg N<sub>2</sub>O-N ha<sup>-1</sup> in a clayey soil. The annual total N inputs ranged from 694-1281 kg N ha<sup>-1</sup>. The annual N outputs ranged from 282-571 kg N ha<sup>-1</sup>. Of the total N inputs, 509-984 kg N ha<sup>-1</sup> were considered available for crop uptake – or N<sub>2</sub>O production. The emission factors (EF) (the N<sub>2</sub>O-N expressed as percentage of the applied available N) ranged from 0.88 ±0.23 - 1.45 ±0.20% in the sandy soils and were 1.66 ±0.55% in the clayey soil. Because the clayey soil retained a higher water content for longer (days to weeks) than the sandy soils (1-2 days), the elevated N<sub>2</sub>O fluxes lasted longer than in the sandy soils. The total amount of N<sub>2</sub>O emitted was comparable to emissions from similar systems reported in the literature. However, the EFs in the present study tended to be lower than the EFs in comparable studies in the literature, not because the emissions in California were lower, but rather, because the N inputs in the California dairy forage systems were higher than those in comparable studies at other locations. The highest emissions, lasting several days in the sandy soils and several weeks in the clayey soil, followed applications of synthetic N fertilizer at rates of >100 to >200 kg N ha<sup>-1</sup>. The highest N<sub>2</sub>O losses (>10 kg N<sub>2</sub>O-N) were recorded after applications of anhydrous ammonia at a rate of >200 kg N ha<sup>-1</sup>. Applications of liquid manure and synthetic N fertilizer mixtures at moderate rates together with irrigation water produced lower N<sub>2</sub>O emissions than the applications of injected N fertilizers.

### *Conclusions*

This study provides important information on how N fertilizer and manure management in dairy forage production systems affects N<sub>2</sub>O emissions. The information provides the basis to reevaluate and develop recommendations to reduce N<sub>2</sub>O emissions in dairy forage production systems. The annual N<sub>2</sub>O emissions ranged from 4.8 – 7.4 kg N<sub>2</sub>O-N ha<sup>-1</sup> from sites with sandy soil (>70% sand) and from 11.4 – 16.5 kg N<sub>2</sub>O-N ha<sup>-1</sup> in clayey soils (>40% clay), which represents losses of 0.9 -1.5% of the applied available N as N<sub>2</sub>O for the sandy soils and of 1.7% for the clayey soil. The periods of N<sub>2</sub>O release after irrigation events were longer (weeks) in a clayey than in sandy soils (days), and this contributed to the overall higher emissions in the clayey soil. To extrapolate these results to other similar systems in California, more research on the effects of soil type on N<sub>2</sub>O emissions is needed. Applications of highly concentrated fertilizers, such as anhydrous ammonia applied in clayey soil at rates >200 kg N ha<sup>-1</sup>, resulted in N<sub>2</sub>O emissions accounting for up to 68% of total seasonal N<sub>2</sub>O emissions. Such large applications of concentrated N fertilizers are not recommended since they lead to greater annual N<sub>2</sub>O emissions than incremental moderate N additions applied together with the irrigation water. To apply N at adequate rates for forage crops, such as silage corn, more information on crop N



demand across soil types is needed. The approach centers on synchronizing N applications with crop N demand. Once the N requirement for each crop stage is known, the N applications can be adjusted accordingly. This strategy should lead to improved N use efficiency and likely lower N<sub>2</sub>O emissions.

## 1. Introduction

With the passage of the Global Climate Change Solution Act (AB 32), improved quantification of N<sub>2</sub>O emissions in California's agriculture sectors is essential. The GHG emission budgets, or baseline emissions, are needed to address the mandated reduction in GHG emissions by 2020. The greenhouse gas (GHG) nitrous oxide (N<sub>2</sub>O) contributes about one third to the total GHG emissions from California's agriculture sector. Of particular concern is the emission of N<sub>2</sub>O from agricultural fertilizer nitrogen (N) practices. According to the Intergovernmental Panel on Climate Change (IPCC) (2007), the main driver for increasing N<sub>2</sub>O emissions in North America is management of manure and manure application to soils. California is the number one dairy state in the U.S., and milk and cream is the state's most valuable farm commodity. Prior to this study, no research had been conducted to develop N<sub>2</sub>O inventories from California's 400,000 acres of irrigated forage cropland that receives dairy manure.

Increasing N inputs generally increases the potential for producing N<sub>2</sub>O emissions. Many studies have shown that high N inputs significantly increased N<sub>2</sub>O emissions (Bouwman et al. 2002; Eichner 1990; Stehfest and Bouwman 2006). Forage cropland land typically receives higher annual N inputs than other cropping systems. This is often the result of importing feed to maintain large herds for economic reasons. According to our previous research, the N inputs into these silage corn/winter forage cropping systems range from 500 to 1200 kg N ha<sup>-1</sup> yr<sup>-1</sup>, versus 350 to 600 kg N ha<sup>-1</sup> yr<sup>-1</sup> removed in the harvested crop (Geisseler et al. 2012). Our modeling results, generated by using the Root Zone Water Quality Model (Ma et al. 2000), suggest that management can be modified to reduce available N and potential for N<sub>2</sub>O production (Geisseler et al. 2012).

Nitrous oxide production occurs under oxygen (O<sub>2</sub>) limitation, typically when diffusion of O<sub>2</sub> from the atmosphere into the soil is limited at high soil water content, for many soils at a water-filled pore space (WFPS) >60% (Linn and Doran 1984). In addition to denitrification, which uses nitrate as substrate, N<sub>2</sub>O is also produced during nitrification, especially under low oxygen (O<sub>2</sub>) availability (Bremner and Blackmer 1978; Wrage et al. 2001; Zhu et al. 2013). The main driver of nitrification and production of N<sub>2</sub>O during nitrification is ammonium (NH<sub>4</sub><sup>+</sup>) availability. Both ammonical fertilizers (e.g. anhydrous ammonia, urea) and liquid manure water supply NH<sub>4</sub><sup>+</sup> to soils.

In addition to N inputs, soil mineralization, soil moisture and carbon (C) substrate availability control N<sub>2</sub>O emissions. Two types of wastes are typically produced by California dairies. These include liquid manure from anaerobic storage ponds (lagoons) and dry scrape corral manure. Liquid manure with high concentrations of NH<sub>4</sub><sup>+</sup> is diluted with irrigation water. The added available organic C in the liquid manure may strongly affect the magnitude of N<sub>2</sub>O emissions. Manure stored in anaerobic lagoons contains volatile fatty acids, which have a high biochemical oxygen demand and likely provide an additional stimulus to promote N<sub>2</sub>O efflux *via* denitrification (Coyne 2008) and nitrifier denitrification (Zhu et al. 2013). Mineralization of soil organic matter both from solids in the manure inputs and native soil provide additional N potentially available for nitrification and denitrification.

The objective of this research is to determine N<sub>2</sub>O emissions in three forage production systems receiving dairy lagoon wastewater, solid manure, and synthetic N fertilizer and to develop a better understanding of the physical and chemical factors and sources of N that control

N<sub>2</sub>O emissions in these systems. Annual N<sub>2</sub>O budgets and N<sub>2</sub>O emission factors as a fraction of annual N inputs, as well as crop N uptake are presented.

## 2. Materials and Methods

### 2.1. Field sites description

It is characteristic of the dairy farms from the Central Valley in California to use the farmland surrounding the facilities to produce forage crops. Two to three crops are grown per year, including silage corn in summer and other forage crops (oat, alfalfa, Sudan grass, wheat, Triticale, and forage mixes) during fall and/or winter. In these systems irrigation is typically carried out through flooding of the fields. While corn relies almost entirely on water supplied through irrigation, fall and winter forage are only irrigated when precipitation is insufficient. The dairy farms generate a considerable amount of manure, which is used to fertilize the cropland surrounding the dairy farms.

Three dairy farms were used in this study. Farms A and B were located in the county of Stanislaus, whereas Farm C was located in the Sacramento County. Soils from each farm were characterized at the beginning of the study in four composite samples (6 individual 2.5 cm diameter cores from 0-30 cm depth) taken in the vicinity of the gas sampling chamber bases (see below). The main physicochemical properties are shown in Table 1.

**Table 1.** Soil characteristics (0-30 cm depth) of the three dairy forage systems.

	Farm A		Farm B	Farm C
	Field 1	Field 2		
Sand (%)	78	70	84	31
Silt (%)	16	23	12	28
Clay (%)	7	7	4	41
pH (H <sub>2</sub> O 1:1)	6.7	7.2	6.8	7.5
Bulk density 5-15 cm (Mg m <sup>-3</sup> )	1.67	1.43	1.37	1.51
Total C (g kg <sup>-1</sup> )	10.4	12.5	11.8	12.4
Total N (g kg <sup>-1</sup> )	1.0	1.2	1.1	1.3

#### 2.1.1. Farm A

On Farm A, no-till management has been practiced since 2005. During summer, silage corn was grown, followed by a forage mixture of grasses and legumes grown during the winter rainy season. Two separately irrigated 180 m long and 60 m fields with similar soil characteristics were used for the study. The soil of both fields was characterized as a coarse-loamy, mixed, active, thermic Typic Haploxeralf.

In 2011, corn was planted on April 15 and harvested on August 22, and the forage mix was planted on October 20 and harvested April 3, 2012. In 2012, corn planting was on May 6 and harvest on August 24. Corn was sown in double rows with plant rows separated 18 cm.

Separation between double rows was 70 cm. Except for the stubble, the entire biomass of the corn crop was harvested to produce silage.

### 2.1.2 *Farm B*

On Farm B, conventional tillage practices were employed, i.e. fields were ripped and disked twice in between crops. Assessment of N<sub>2</sub>O emissions was carried out in a 7.2 ha field. The 7.2 ha-field was irrigated by flood irrigation. The soil on Farm B was classified as a mixed, thermic Typic Xeropsamment. It was characterized by a high sand content (84%) (Table 1). Two crops were planted annually; silage corn during summer (2011, 2012) and Dirkman silage wheat during the fall/winter period. Corn was planted on May 15 and harvested on August 31, 2011. Wheat was planted on October 15, 2011, and harvested on April 16, 2012. In 2012, corn was planted in double rows spaced 76 cm apart on May 15 and harvested on September 3.

### 2.1.3 *Farm C*

Farm C followed conventional tillage practice with multiple disking operations in between crops. An 8-ha field, divided into 17 m wide and 400 m long checks (i.e. irrigation sectors), was monitored at this farm. The soil was classified as a fine, mixed, superactive, thermic Abruptic Durixeralf. It was characterized by relatively higher clay content than Farms A and B (Table 1). Two forage crops were grown annually in this field, silage corn as a summer crop and ryegrass during fall/winter. Corn was planted in single rows, 76 cm apart, on June 20 and harvested on October 14, 2011, and in 2012, corn planting occurred on June 18 and harvest on October 21. Two plant fractions were separated at harvest: (i) the upper part of the plant containing the earlets, part of the leaves and stalk, and (ii) the lower plant containing only stalks and leaves which later were chopped and compacted into bales. Ryegrass was planted on October 28, 2011, but due to the absence of rain, the ryegrass did not develop and was re-planted after a pre-irrigation on January 10, 2012. The ryegrass was harvested on April 8, and a second cutting occurred on May 10, 2012.

## 2.2 *Accounting of the N inputs*

### 2.2.1 *Manure and N management*

On all three farms, dairy manure management encompasses separation of solid and liquid fractions of the manure washed out from feed lanes and free stalls, i.e. the manure slurry is first passed through a screen to separate particles larger than a few millimeters from the liquid fraction. The solid fraction (“separator manure”) is composted in windrows and re-used as bedding or stored in piles and spread on the fields in spring and fall. The liquid fraction is stored in large open ponds (lagoons) and applied to crops together with irrigation water. In addition, solid, or dry scrape, manure (“corral manure”) is stored in piles and spread on the fields. All N inputs were categorized as either ‘soluble’ [NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, total dissolved N (TDN)] or ‘solids’ (not soluble organic N). The soluble N can be considered readily available for plant uptake and N<sub>2</sub>O production. The solids have to be mineralized before the N from this source becomes available for plant uptake or further N transformations. Only a fraction of the solid organic N can be expected to become available for plant uptake or N<sub>2</sub>O production during the growing season.

Each of the three farms followed distinct N fertilization practices:

Farm A applied liquid starter fertilizer in the form of urea, ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) (34 and 40 kg N  $\text{ha}^{-1}$  in 2011 and 2012, respectively), and additionally, lagoon water and inorganic fertilizer in the form of urea ammonium-nitrate (UAN32) together with irrigation water (approx. 7:1 freshwater: lagoon water) at almost every irrigation event once the corn plants were past the seedling stage, and this resulted, in general, in applications of 20 – 40 kg N  $\text{ha}^{-1}$  of available N with most irrigations. There were 10 and 11 irrigation events during the corn growing season in 2011 and 2012, respectively. Irrigation frequency was low after planting with only one event during the first month in 2011 (due to unseasonably low temperatures in early summer) and one irrigation during the first 16 days in 2012. Later on, corn was irrigated every 8 to 9 days until harvest. The fields were irrigated three times during fall/winter 2011/12 when irrigations took place at the end of October, in mid January, and at the end of March. All irrigations contained lagoon water.

Farm B: Corral manure (142 kg N  $\text{ha}^{-1}$ ), composted (159 kg N  $\text{ha}^{-1}$ ), and not-composted separator manure (283 kg N  $\text{ha}^{-1}$ ) were incorporated into the soil in spring 2011 after disking two weeks before corn planting. No solid manure was applied in 2012. Synthetic N fertilizer was applied to the corn crop by injecting UAN32 at a rate of 104 and 117 kg N  $\text{ha}^{-1}$  in 2011 and 2012, respectively, about four weeks after planting. Lagoon water was mixed into the irrigation water (approx. mixing rate 3:1 fresh water: lagoon water) and applied to the corn crop 6 and 7 times in 2011 and 2012, respectively. The applications of available N via irrigation ranged from 20 to 50 kg N per irrigation event. Corn was first irrigated between 20 and 30 days after planting and after that irrigation events took place every 15 to 20 days until harvest.

Farm C: One week before planting, 227 kg N  $\text{ha}^{-1}$  in the form of anhydrous ammonia was injected. Application of lagoon water through irrigation (mixing rate 1:1 freshwater: lagoon water) occurred on August 29, 2011 (159 kg available N  $\text{ha}^{-1}$ ), and on September 12 and 27, 2012 (115 and 89 kg available N  $\text{ha}^{-1}$ , respectively). The corn crop was flood-irrigated every 10 to 20 days during the cropping season with waste water from a fish farm and runoff from other fields (3-7 kg available N  $\text{ha}^{-1}$  at each irrigation event).

### 2.2.2. *Measuring N inputs and outputs*

In 2011, samples of lagoon water were collected at the lagoon water pumps (before mixing with fresh water) during irrigation events. In 2012, samples of the final irrigation mixture applied to the fields were collected directly from the hydrants at each irrigation event and stored at 4°C until analysis.

Irrigation/lagoon water samples were filtered through nominal 0.3  $\mu\text{m}$  glass fiber filters. The solids (TSS, total suspended solids) were dried and analyzed for total C and N by dry combustion (Costech ECS 4010, Valencia CA) (Dumas 1848). The filtrate was analyzed colorimetrically for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  (Doane and Horwath 2003). Total dissolved N was determined by the alkaline persulfate oxidation (Cabrera and Beare 1993), heated in a boiling water bath for 2 h, and analyzed for  $\text{NO}_3^-$  as described above. Total dissolved N (TDN), which includes dissolved organic N,  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  was considered available N, i.e. inorganic N or mineralizable N available for plant uptake within days. A subsample of the solid manures spread on the fields was dried for 48 h at 105°C to determine the moisture content and the total N content of separate samples was determined by the dry combustion method (same as for TSS of

the filtrate above). The  $\text{NH}_4^+$  content of the solid manure was determined by extracting subsamples of the manure with 1 M KCl, followed by colorimetric analysis of the extracts as above.

The amount of N applied as solid manures was calculated from estimates of total volume spread on each field (number of truck loads) and the N content in samples of this material. For each site, the N inputs of irrigation water and irrigation mixtures containing lagoon water were calculated based on the measured N concentrations of the different N fractions, the pump rates and the length of the irrigation events. At Farm C there was a substantial runoff with every irrigation. Runoff was measured by an area-velocity (AV) sensor, connected to a datalogger/autosampler (ISCO, Model 6700, Teledyne Technologies Inc, Thousand Oaks, CA). The AV sensor was installed in the pipe collecting the outflow from the field. Runoff samples were collected by the autosampler every hour, collected within six hours after the end of the runoff period, and stored at 4°C until analysis for TDN within 7d. The TSS in the runoff was analyzed as above. The total amount of N loss in runoff was calculated from the total amount of runoff and the average  $\text{NH}_4^+$ , TDN, and total N concentration of the samples collected. Thus, runoff was accounted for and subtracted from the N inputs.

Crop N removal was accounted for based on the crop yields provided by the farmers, the dry matter content of the harvested plant material, and the measured total plant N contents. To determine total N content, either subsamples of silage were obtained or, alternatively, five corn plants were randomly collected at each of the gas sampling locations before harvest. Plants were weighed and subsequently chopped using a garden shredder (Sears Craftsman). A subsample of the homogenized chopped material or silage was weighed and subsequently dried for one week at 60°C. Samples of ryegrass (Farm C) and the forage mixture (Farm A) were collected in the vicinity of the gas sampling locations and dried at 60°C. Dried corn subsamples were weighed to determine plant moisture. Plant biomass samples were ground and pulverized, and total N was determined by the dry combustion method as above.

### 3. *Measuring $\text{N}_2\text{O}$ emissions*

Nitrous oxide fluxes were measured from spring 2011 to fall 2012, thus comprising two corn growing seasons and one winter/rainy season. The  $\text{N}_2\text{O}$  fluxes were measured at high frequency (daily or every other day) before and after fertilization and irrigation events until the fluxes subsided to near background levels and less frequently (weekly or bi-weekly) in between these management events. In general, the sampling took place around mid-day (between 11 am and 3 pm) when soil temperatures are close to the daily mean temperature.

Nitrous oxide flux was measured, using a static chamber technique (Hutchinson and Livingston 1993). Rectangular stainless steel chambers were used. Chamber bases, 50 x 30 cm, 8 cm deep, with 2cm-wide horizontal flange at the top end were inserted into the soil in between and parallel to the rows of corn plants, so that the flange rested on the soil surface. The bases were left in place unless field operations required their temporary removal. During flux measurements, 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. Chamber tops were covered with reflective insulating material and equipped with sampling ports with butyl rubber septa and were vented (4.8 mm dia., 10 cm long tubes).

Four pairs of chambers were installed at regular intervals in the direction of the irrigation water flow starting near the head end (water input) of the field. At each of the four sampling locations, the chamber bases were installed both parallel and perpendicular to the plant rows in order to ensure representative sampling of the inter-row areas.

During sampling, the chambers were fitted onto the bases. To collect a gas sample from the chamber, headspace air was removed by inserting the needle of a polypropylene syringe (Monoject) through the septum of the sampling port and by slowly withdrawing 20 mL gas. Headspace gas was removed 0, 20 and 40 min after deploying the chamber tops onto the bases. When N<sub>2</sub>O fluxes were expected to be high, samples were taken from the chamber at shorter intervals (0, 15, and 30 min). The gas in the syringes was immediately transferred into evacuated 12-mL glass vials with grey butyl rubber septa (Exetainer, Labco Ltd., Buckinghamshire, UK). The gas samples were analyzed within two weeks of collection by a Shimadzu gas chromatograph (Model GC-2014) with a <sup>63</sup>Ni electron capture detector (ECD) linked to a Shimadzu auto sampler (Model AOC-5000). The autosampler uses a gas-tight syringe to remove 2 mL gas from the sample vials and injects it into the GC port. The GC uses as carrier gas a mixture of helium and P5 (mixture of 95% argon and 5% methane). The N<sub>2</sub>O is separated by a Haysep Q column at 80° C. The ECD is set at 320° C and the pressure of the carrier gas flowing into the ECD is 60 kPa. The minimum quantity of N<sub>2</sub>O detected by this GC system is 0.1 pg s<sup>-1</sup>. After the acquisition of the sample, the autosampler's syringe and the GC's sample loop are purged with helium to back flush water and other slow chromatographically resolved analytes. The GC system was calibrated daily using analytical grade N<sub>2</sub>O standards (Airgas Inc., Sacramento CA).

Gas fluxes were calculated from the rate of change in chamber N<sub>2</sub>O concentration, chamber volume, and soil surface area (Hutchinson and Mosier 1981) (see APPENDIX). Chamber gas concentrations determined by GC (volumetric parts per million) 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 flux calculations used an algorithm appropriate for curvilinear concentration data with time when N<sub>2</sub>O concentration in the chamber increased at a decreasing rate (Hutchinson and Livingston 1993; Hutchinson and Mosier 1981) and linear regression at all other times. The calculation compensates for the diffusion constraints imposed by the rapid increase in the partial pressure of certain gas species (e.g. N<sub>2</sub>O) within the chamber when the flux is high.

#### *4. Evaluation of the annual N<sub>2</sub>O emissions*

The total integrated annual N<sub>2</sub>O emissions from each chamber location were calculated under the assumption that the measured fluxes represented mean daily fluxes, and that mean daily fluxes changed linearly between measurements (trapezoidal integration) (Venterea et al. 2005). To calculate annual emissions, estimates of the average emissions of measured irrigation events bracketing not-monitored events were used. The emission factors (EFs) were calculated by dividing the annual mass of N<sub>2</sub>O-N emitted by the mass of fertilizer-N applied.

### 5. Measurement of environmental variables

During each sampling event, chamber air, soil and ambient air temperatures were measured. In addition, soil samples (0-30 cm) were collected in order to determine soil moisture and inorganic N. Soil samples were collected using a 1.83-cm steel corer close to the gas chamber bases. Gravimetric soil moisture was calculated from field-moist and oven-dry (105°C, 24h) mass of soil collected in the field. The gravimetric soil moisture values were converted to water-filled pore space (WFPS) values by using measured bulk density values in the 5-15 cm layer and calculated as follows:

$$\%WFPS = (w * \text{bulk density}) / [1 - (\text{bulk density}/2.65)] * 100\%$$

where w is gravimetric water content.

Inorganic soil N ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) was determined in the 0-30 cm layer by extracting 15 g of well-mixed soil with 80 mL of 1M potassium chloride solution, and by analyzing the extracts colorimetrically for ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) by a Shimadzu spectrophotometer (Model UV-Mini 1240). For determining  $\text{NH}_4^+$ , the phenate (indophenol blue) method was employed (Forster 1995). Nitrate in the extracts was reduced to nitrite ( $\text{NO}_2^-$ ) with vanadium chloride, and the  $\text{NO}_2^-$  was analyzed by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine-dihydrochloride (Doane and Horwath 2003). The total C and N in soil of the 0-30 cm layer and plant samples was measured by a C and N analyzer (Costech Analytical Technologies Inc., Valencia, CA) by the dry combustion method (Dumas 1848) after grinding air-dried representative soil and plant samples to a fine powder. The pH in the 0-30 cm layer of soil was measured in supernatant of soil slurries (soil/ $\text{H}_2\text{O}$  ratio 1:1) by a pH meter (Model 220, Denver Instrument Co., Arvada, CO). 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 of the cores to 105°C.

Multiple stepwise regression analysis was performed in order to assess the influence of the environmental variables measured at the sites at the time of sampling (%WFPS, soil temperature at 5 cm, air temperature,  $\text{NH}_4^+$ -N,  $\text{NO}_x$ -N,  $\text{NO}_3^-$ -N,  $\text{NO}_2^-$ -N) on daily  $\text{N}_2\text{O}$  flux at each of the sampling locations within the fields. In stepwise regression, the predictor variables are entered into a regression equation one at a time as long as the multiple correlation ( $r^2$ ) of the equation is increased. Thus, predictor variables are only added if they statistically improve the regression equation. Relationships between all environmental variables and gas fluxes including  $\text{N}_2\text{O}$ ,  $\text{NO}_x$  and  $\text{CO}_2$  were assessed through Pearson's correlations. The Kolmogorov-Smirnov test was used to test whether the data were normally distributed, and log-transformations were carried out if necessary. Data analysis was carried out using SAS version 9.1 (SAS Inc., Cary, NC).

### 3. Results

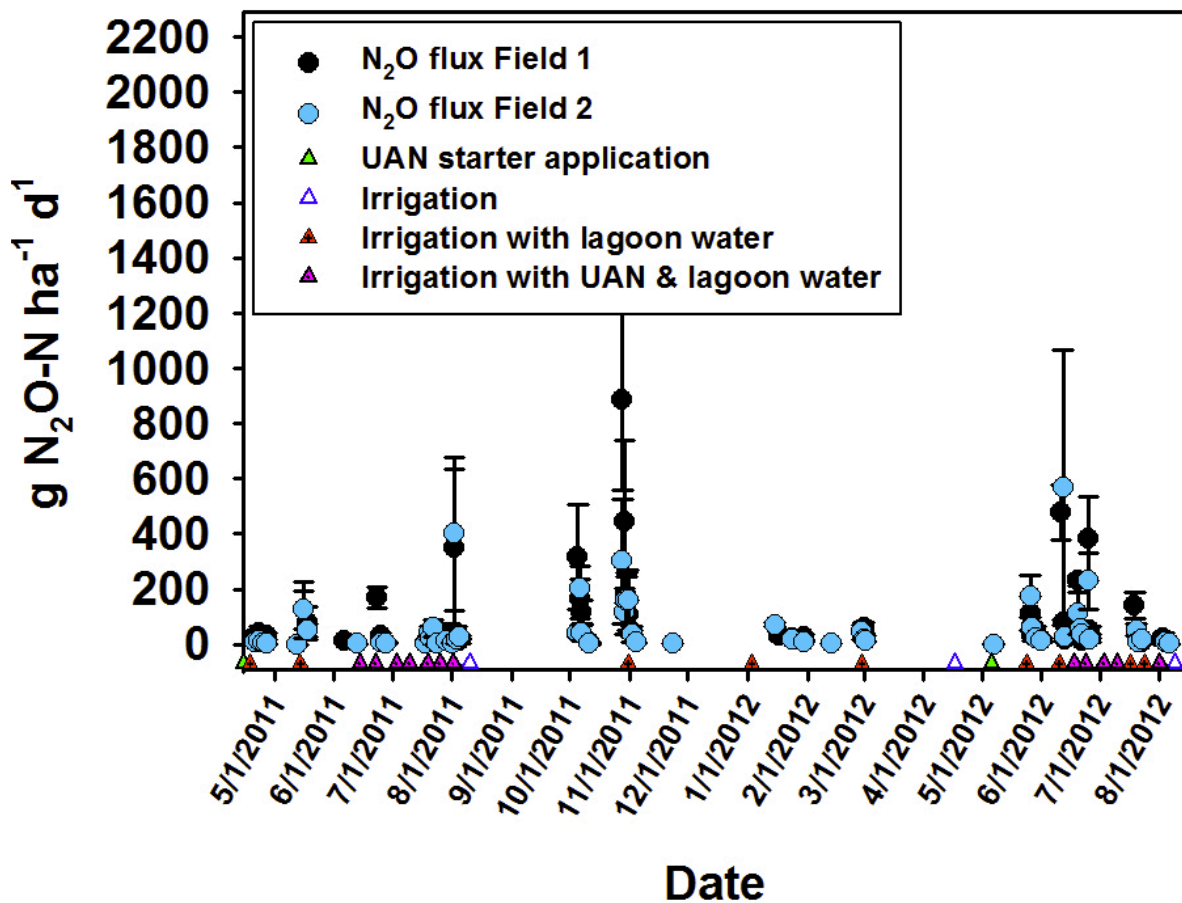
Farm management dates, water and N inputs, as well as N outputs via the crops are shown in Table 2. The solids of the applied N applied ranged from 8-24% during the corn growing season, and from 19-40% during the winter forage growing season, except for Farm B in 2011, when the solids made up 67% of all N applications.



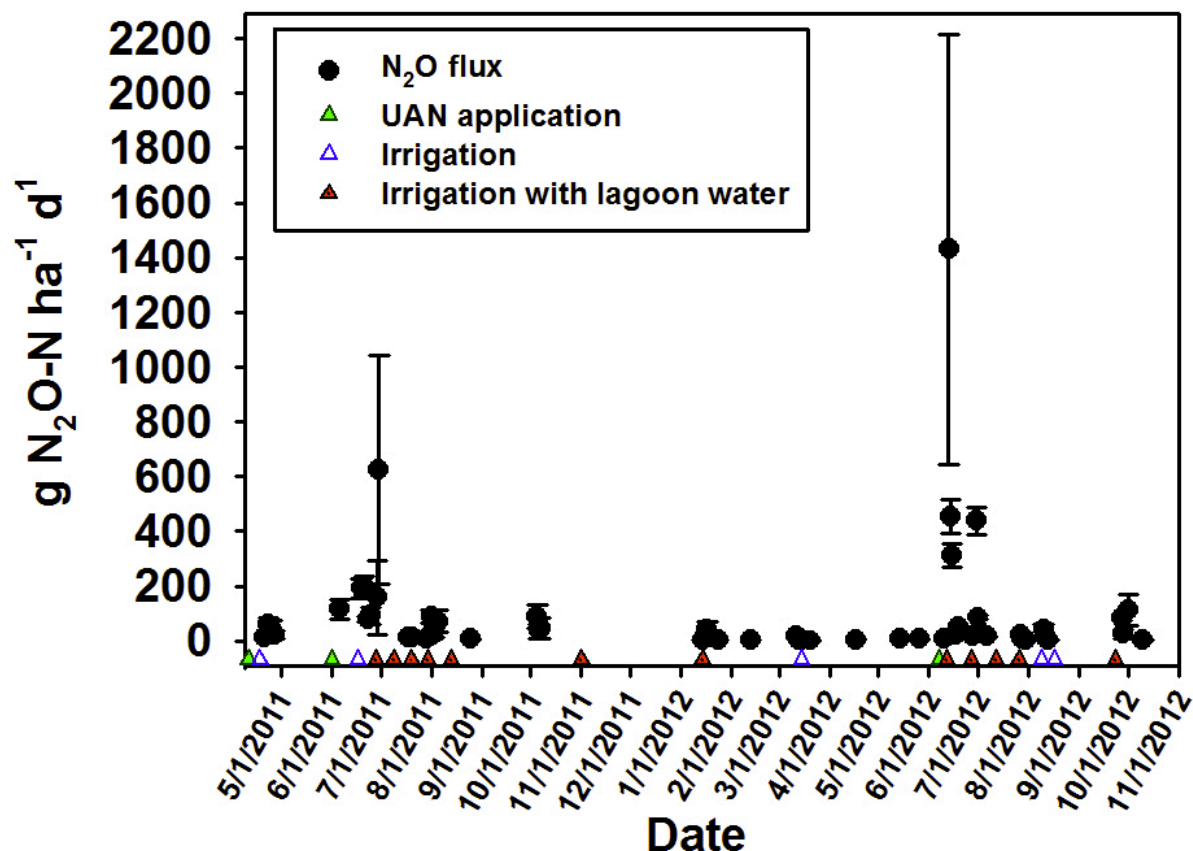
**Table 2.** Crop management dates, water and nitrogen inputs, and N outputs at the three dairy farms.

Crop	Dates		Water input (cm)		Synthetic Fertilizer	N inputs (kg ha <sup>-1</sup> )			N outputs (kg ha <sup>-1</sup> )
	Planting	Harvest	Irrigation	Rainfall		Manure		Total	
						Soluble	Solids		
<b><i>Farm A</i></b>									
Corn 2011	15 April	22 Aug.	74	5.3	298	198	69	565	218
Triticale 2011	20 Oct.	3 April	29	2.6		155	37	192	194
Corn 2012	6 May	24 Aug.	88	0.2	182	172	114	468	356
<b><i>Farm B</i></b>									
Corn 2011	15 May	31 Aug.	65	5.0	104	245	713	1062	275
Wheat 2011	15 Oct.	16 April	43	6.0		162	75	237	223
Corn 2012	15 May	3 Sept.	86	0.2	118	268	72	458	348
<b><i>Farm C</i></b>									
Corn 2011	20 June	14 Oct.	49	0.7	227	159	35	421	212
Ryegrass 2011	28 Oct.	8 Apr. & 10 May	33	21.8		300	197	497	70
Corn 2012	18 June	21 Oct.	65	0.2	224	460	100	784	243

The N<sub>2</sub>O fluxes were measured during the corn growing seasons 2011 and 2012, and during the winter rainy season 2011-2012, when other forage crops were grown. The daily N<sub>2</sub>O fluxes on **Farm A** ranged from a few mg N<sub>2</sub>O-N ha<sup>-1</sup> to almost 600 g N<sub>2</sub>O-N ha<sup>-1</sup> during the corn growing season (Figure 1). Such high fluxes seldom lasted more than one day although somewhat elevated fluxes persisted for up to a week. On Farm A, the highest N<sub>2</sub>O fluxes were recorded after fall irrigations following the corn harvest, when the soils had been dry for about two months. However, for the remainder of the winter season, daily N<sub>2</sub>O fluxes were <100 g N<sub>2</sub>O-N ha<sup>-1</sup>. On **Farm B**, the daily N<sub>2</sub>O fluxes during the corn growing season were generally less than 200 g N<sub>2</sub>O-N ha<sup>-1</sup>, except for a few very high emissions in June both years when daily N<sub>2</sub>O emissions of almost 1 kg N<sub>2</sub>O-N were recorded (Figure 2). The N<sub>2</sub>O fluxes were <50 g N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup> during winter. On **Farm C**, elevated N<sub>2</sub>O fluxes lasting two to four weeks occurred at the beginning of the corn growing season (June), and then again towards the end of the growing season in (September), lasting about 10 d in 2011 and about one month in 2012 (Figure 3). Daily N<sub>2</sub>O fluxes were <30g N<sub>2</sub>O-N ha<sup>-1</sup> during the rainy season.

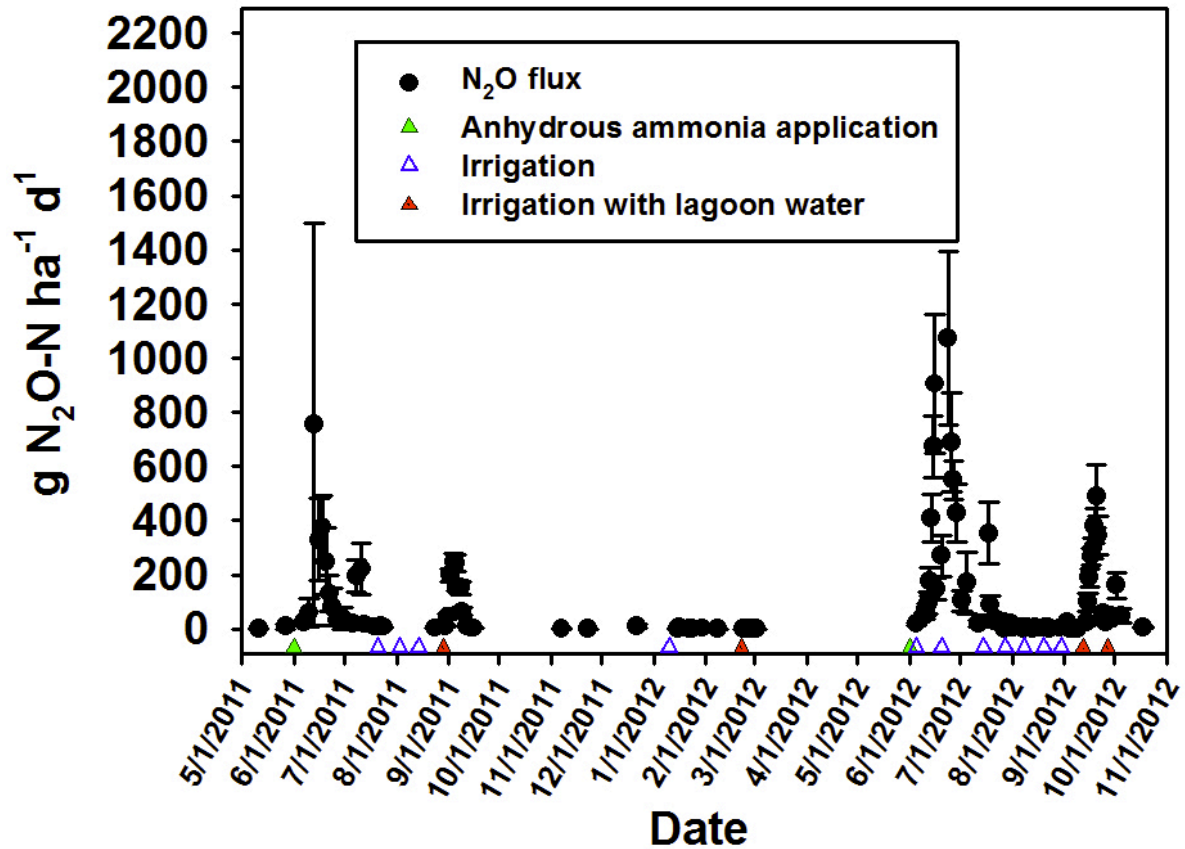


**Figure 1.** Mean daily N<sub>2</sub>O flux on Farm A. Standard errors shown as line bars (n=4). Triangles indicate dates of urea ammonium-nitrate (UAN) fertilizer application and irrigation.



**Figure 2.** Mean daily N<sub>2</sub>O flux on Farm B. Standard errors shown as line bars (n=4). Triangles indicate dates of urea ammonium-nitrate fertilizer application and irrigation.

On Farm B, the total N<sub>2</sub>O emissions during the corn growing season were greater in 2011 than 2012, whereas on Farm C, these emissions were comparable between the two years (Table 3). The N<sub>2</sub>O emissions during the winter rainy season were lower by an order of magnitude than those during the summer growing seasons on Farm B and C, but on Farm A, N<sub>2</sub>O emissions during winter were similar in magnitude in summer and winter. The total N<sub>2</sub>O emissions during the 2011 corn growing season on Farm A could not be reliably calculated because we missed several key measurements of N<sub>2</sub>O fluxes due to communication glitches (e.g., we did not collect data during three irrigation events).



**Figure 3.** Mean daily N<sub>2</sub>O flux on Farm C. Standard errors shown as line bars (n=4). Triangles indicate dates of anhydrous ammonia fertilizer application and irrigation.

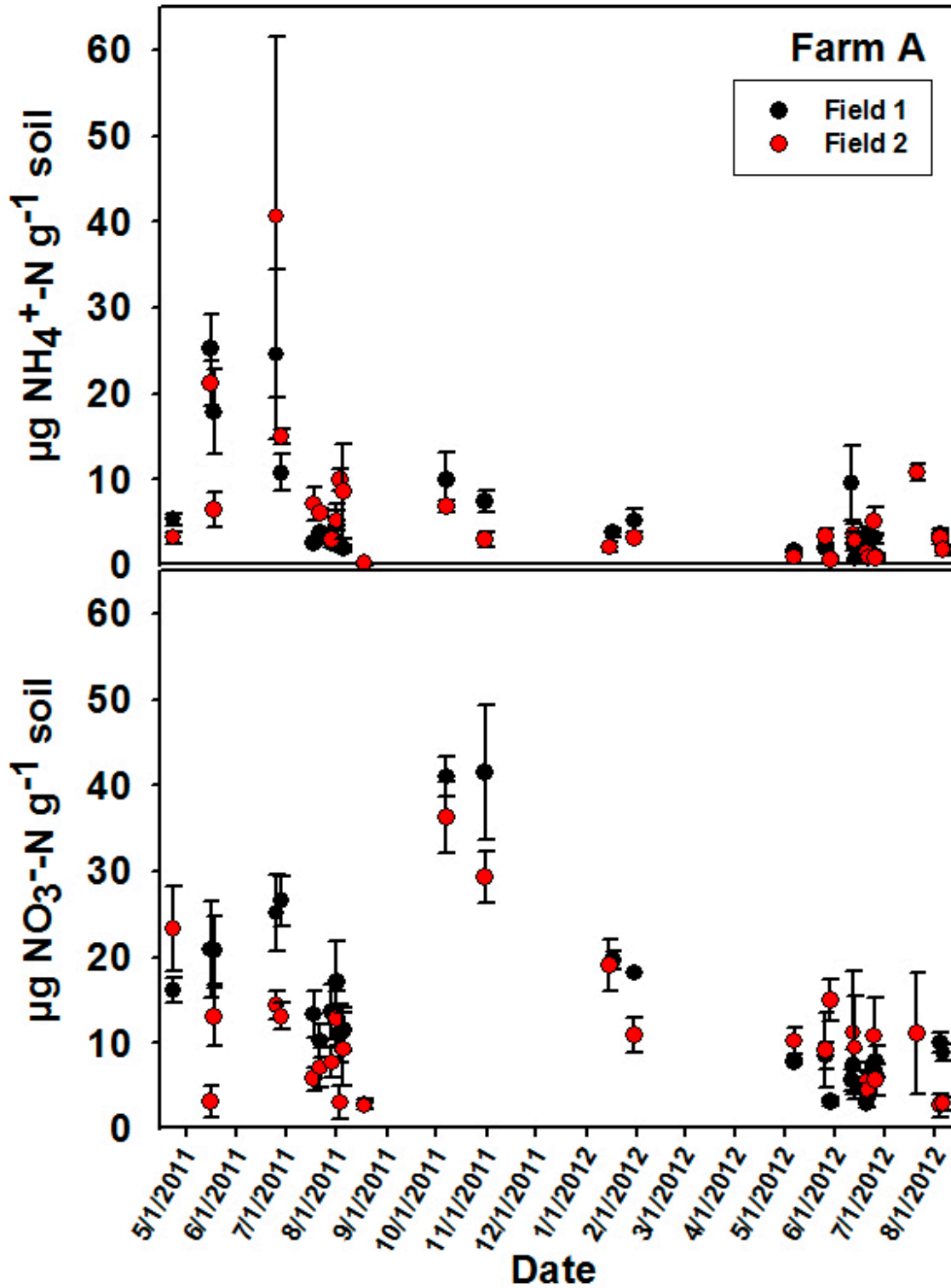
**Table 3.** Nitrogen inputs, cumulative and seasonal N<sub>2</sub>O emissions and emission factors (EF) and standard errors for the three dairy forage production systems.

	N inputs (kg N ha <sup>-1</sup> )		N <sub>2</sub> O-N (kg ha <sup>-1</sup> )	EF 1* (%)	EF 2 (%)
	Available N	Total N			
<b>Farm A</b>					
<i>Field 1</i>					
Oct 2011 – April 2012	155	192	3.33 ±0.97	2.15±0.62	1.73 ±0.51
Corn growing season 2012	388	502	3.16 ±0.38	0.81±0.10	0.63 ±0.08
<b>Annual estimate</b>	509	694	<b>6.49 ±0.12</b>	<b>1.28±0.02</b>	0.98 ±0.02
<i>Field 2</i>					
Oct 2011 – April 2012	155	192	2.20 ±0.64	1.41 ±0.41	1.15 ±0.33
Corn growing season 2012	388	502	2.51 ±1.03	0.65 ±0.27	0.50 ±0.21
<b>Annual estimate</b>	509	694	<b>4.71 ±0.60</b>	<b>0.93 ±0.12</b>	0.71 ±0.09
<b>Farm B</b>					
Corn growing season 2011	349	1062	6.62 ±1.12	1.90 ±0.32	0.62 ±0.11
Nov 2011 – April 2012	162	237	0.78 ±0.15	0.48 ±0.09	0.28 ±0.06
Corn growing season 2012	386	458	3.82 ±0.61	0.99 ±0.16	0.83 ±0.13
<b>Annual estimate</b>					
(May 2011 – April 2012)	511	1299	<b>7.40 ±1.00</b>	<b>1.45 ±0.20</b>	0.57 ±0.08
(Nov 2011 – Oct 2012)	548	695	<b>4.83 ±1.28</b>	<b>0.88 ±0.23</b>	0.70 ±0.18
<b>Farm C</b>					
Corn growing season 2011	386	421	11.14 ±3.81	2.89 ±0.99	2.65 ±0.90
Nov 2011 – April 2012	300	497	0.23 ±0.05	0.08 ±0.02	0.05 ±0.01
Corn growing season 2012	684	784	16.24 ±1.63	2.37 ±0.24	2.07 ±0.21
<b>Annual estimate</b>					
(May 2011 – April 2012)	686	918	<b>11.37 ±3.80</b>	<b>1.66 ±0.55</b>	1.24 ±0.41
(Nov 2011 – Oct 2012)	984	1281	<b>16.47 ±3.81</b>	<b>1.67 ±0.39</b>	1.29 ±0.30

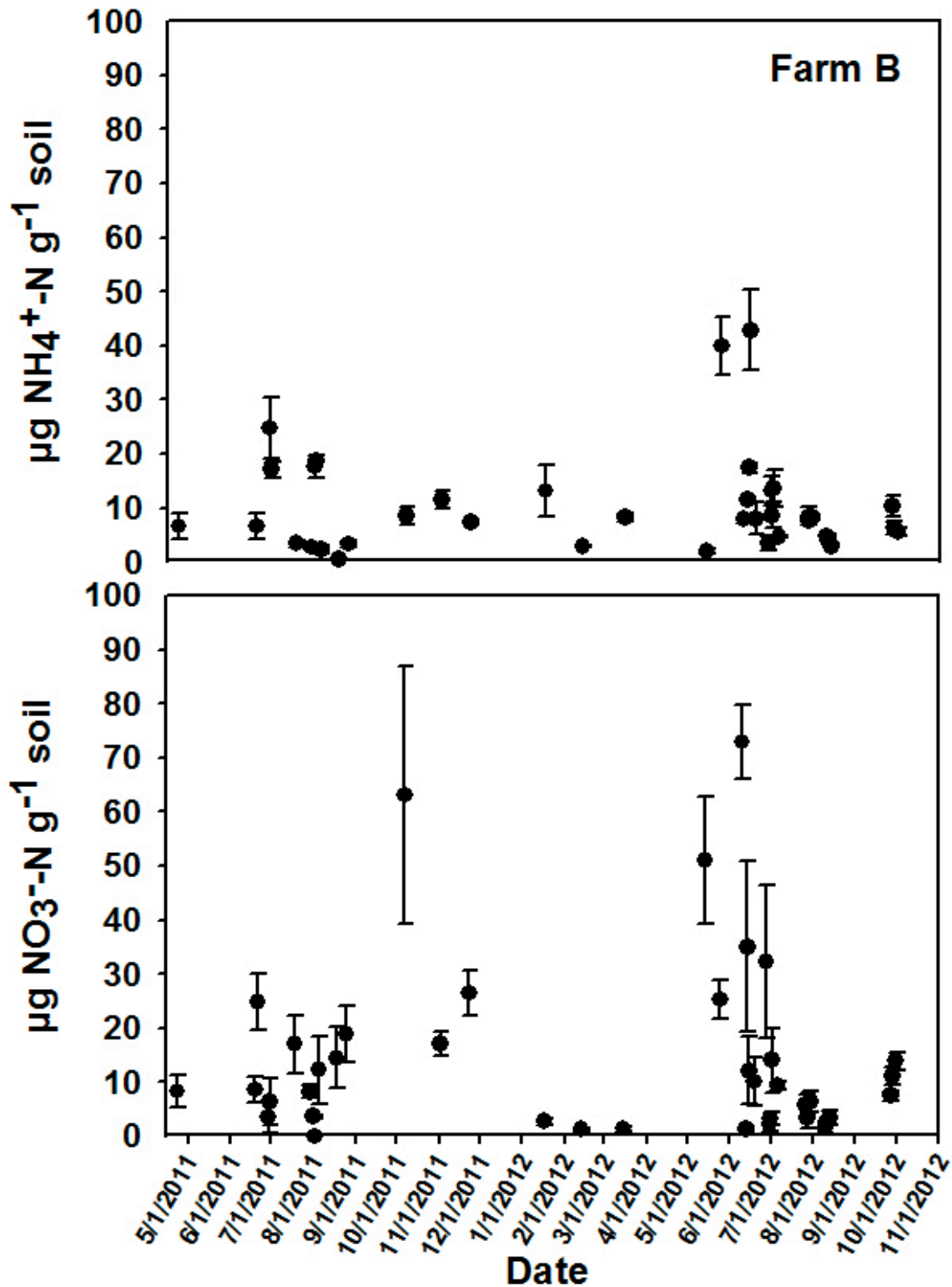
\* EF 1 = Percentage of the available applied N emitted as N<sub>2</sub>O. EF 2 = Percentage of the total applied N emitted as N<sub>2</sub>O.

The annual emission factors (EF) calculated as percentage of the applied available N emitted as N<sub>2</sub>O-N (EF 1) ranged from 0.87 to 1.66% with Farm A having the lowest and Farm C the highest value (Table 3). Calculated for the corn growing season only, the EFs ranged from 0.65-3.53%. The EFs for the winter rainy seasons were <1 on Farm B and C, but for Farm A, the EFs for this period were between 1.42 and 2.15. The EFs calculated as percentage of the applied total N emitted as N<sub>2</sub>O-N (EF 2) followed similar trends as the EF 1 values.

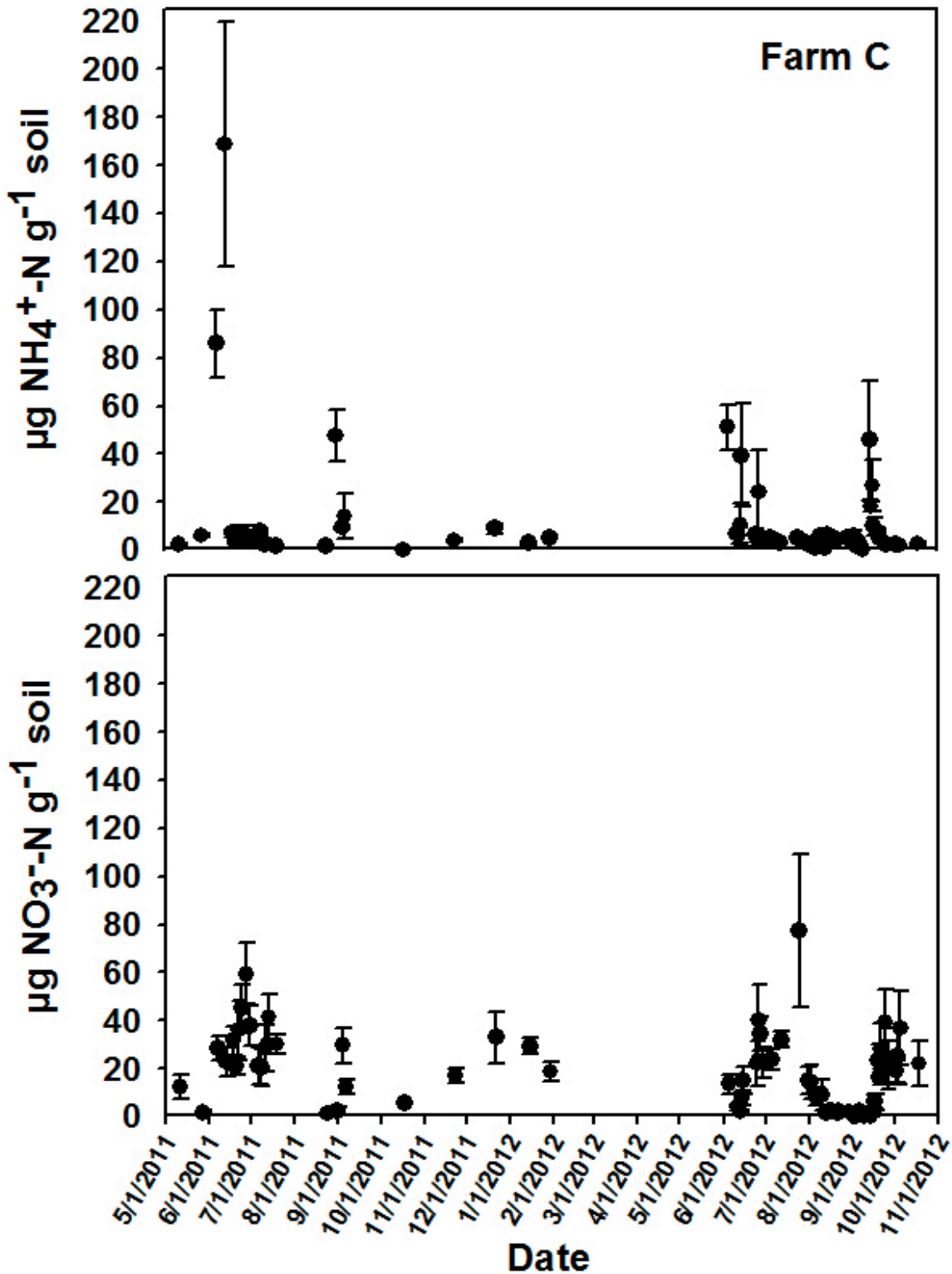
The concentration of NH<sub>4</sub><sup>+</sup> in the 0-30 cm layer in all the soils of the three farms were almost all the time >10 µg NH<sub>4</sub><sup>+</sup>-N g soil, equivalent to about 45 kg NH<sub>4</sub><sup>+</sup>-N ha<sup>-1</sup> (Figures 4-6). On Farm A, NH<sub>4</sub><sup>+</sup> levels ranged from 10-40, on Farm B from 10-20, and on Farm C from 10-180 in early summer to 5-50 µg NH<sub>4</sub><sup>+</sup>-N g in the fall. The concentrations of NO<sub>3</sub><sup>-</sup> ranged from 30-50 µg NO<sub>3</sub><sup>-</sup>-N ha<sup>-1</sup> on Farm A, from 10-70 on Farm B, and from 10-50 on Farm C with no particular pattern among growing seasons.



**Figure 4.** Mean soil ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) concentrations on Farm A. Standard errors shown as line bars (n=4).



**Figure 5.** Mean soil ammonium (NH<sub>4</sub><sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) concentrations on Farm B. Standard errors shown as line bars (n=4).



**Figure 6.** Mean soil ammonium ( $\text{NH}_4^+$ ) and nitrate ( $\text{NO}_3^-$ ) concentrations on Farm C. Standard errors shown as line bars (n=4).



On Farm A, the WFPS in the 0-30 cm layer reached 70-80% immediately following irrigations and then subsided to 50% within 2-3 days (Figure 7). On Farm B, WFPS after irrigations was between 70 and 90%, and receded to 60% within a few (3-5) days (Figure 7). On Farm C, the WFPS during the irrigation season ranged from 70-100%. The decline from 100-70% after the irrigation events usually took about 10 days (Figure 8).

### 3.1. Regression analyses

For **Field 1 on Farm A**, stepwise regression analysis showed that 43% of the variability in the N<sub>2</sub>O daily flux could be explained by changes in soil WFPS and temperature at 5 cm depth (R<sup>2</sup>= 0.43; p<0.001). The best multiple regression model could be expressed as

$$\log N_2O = 1.16 + (0.05 * WFPS) + (0.14 * \text{Temp. 5cm}).$$

Correlation analysis showed that N<sub>2</sub>O emissions were positively correlated with WFPS (Table 4). Soil WFPS was also positively correlated to NH<sub>4</sub><sup>+</sup>-N and negatively to NO<sub>3</sub><sup>-</sup>-N, meaning that at high soil moisture content, NH<sub>4</sub><sup>+</sup> concentrations were high while NO<sub>3</sub><sup>-</sup> concentrations were low. Soil temperature was negatively correlated with soil NH<sub>4</sub><sup>+</sup>-N.

**Table 4.** Pearson correlation coefficients for the different environmental variables measured in Field 1 of Farm A. Coefficients increase with increasing correlation. Asterisks indicate significant correlations at p ≤ 0.05.

	logN <sub>2</sub> O	logNO <sub>x</sub>	NO <sub>3</sub> <sup>-</sup> -N	NH <sub>4</sub> <sup>+</sup> -N	WFPS(%)	Temp. 5cm
logN <sub>2</sub> O	1	0.142	0.015	0.167	0.564*	0.165
logNO <sub>x</sub>	0.142	1	0.184	0.201	0.134	0.375*
NO <sub>3</sub> <sup>-</sup> -N	0.015	0.184	1	0.156	-0.259*	-0.225
NH <sub>4</sub> <sup>+</sup> -N	0.167	0.201	0.156	1	0.206*	-0.246*
WFPS (%)	0.564*	0.134	-0.259*	0.206*	1	-0.155
Temp. 5cm	0.165	0.375*	-0.225	-0.246*	-0.155	1

Regarding **Field 2**, the multiple regression model was not significant (P>0.26). No significant correlation was found in Field 2 between WFPS and gas fluxes (Table 5).

**Table 5.** Pearson correlation coefficients for the different environmental variables measured in Field 2 of Farm A. Asterisks indicate significant correlations at p ≤ 0.05.

	logN <sub>2</sub> O	logNO <sub>x</sub>	NO <sub>3</sub> <sup>-</sup> -N	NH <sub>4</sub> <sup>+</sup> -N	WFPS(%)	Temp. 5cm
logN <sub>2</sub> O	1	0.017	0.124	-0.054	0.112	-0.084
logNO <sub>x</sub>	0.017	1	0.263	-0.008	0.067	0.057
NO <sub>3</sub> <sup>-</sup> -N	0.124	0.263	1	0.039	-0.138	-0.126
NH <sub>4</sub> <sup>+</sup> -N	-0.054	-0.008	0.039	1	0.146	-0.309*
WFPS (%)	0.112	0.067	-0.138	0.146	1	-0.324*
Temp. 5cm	-0.084	0.057	-0.126	-0.309*	-0.324*	1

On **Farm B**, 37% of the variability of the N<sub>2</sub>O daily flux was explained by changes in WFPS, soil temperature, and NH<sub>4</sub><sup>+</sup>-N according to the following stepwise multiple regression analysis, with R<sup>2</sup>= 0.37; p< 0.001:

$$\log N_2O = 2.70 + (0.01 * NH_4^+ - N) + (0.02 * WFPS) + (0.14 * Temp. 5cm)$$

According to the Pearson correlation analysis, the daily N<sub>2</sub>O flux was significantly and positively correlated to NO<sub>x</sub> flux, soil NH<sub>4</sub><sup>+</sup>-N, and soil temperature at 5cm depth (Table 6).

**Table 6.** Pearson correlation coefficients for the different environmental variables measured on Farm B. Asterisks indicate significant correlations at P<0.05.

	logN <sub>2</sub> O	logNO <sub>x</sub>	NO <sub>3</sub> <sup>-</sup> -N	NH <sub>4</sub> <sup>+</sup> -N	WFPS (%)	Temp. 5cm
log N <sub>2</sub> O	1	0.699*	-0.066	0.382*	0.130	0.574*
log NO <sub>x</sub>	0.699*	1	0.025	0.396*	0.198	0.265
NO <sub>3</sub> <sup>-</sup> -N	-0.066	0.025	1	-0.021	-0.505*	0.209*
NH <sub>4</sub> <sup>+</sup> -N	0.382*	0.395*	-0.021	1	0.101	0.352*
WFPS (%)	0.130	0.198	-0.505*	0.101	1	-0.320*
Temp. 5cm	0.574*	0.265*	0.209*	0.352*	-0.320*	1

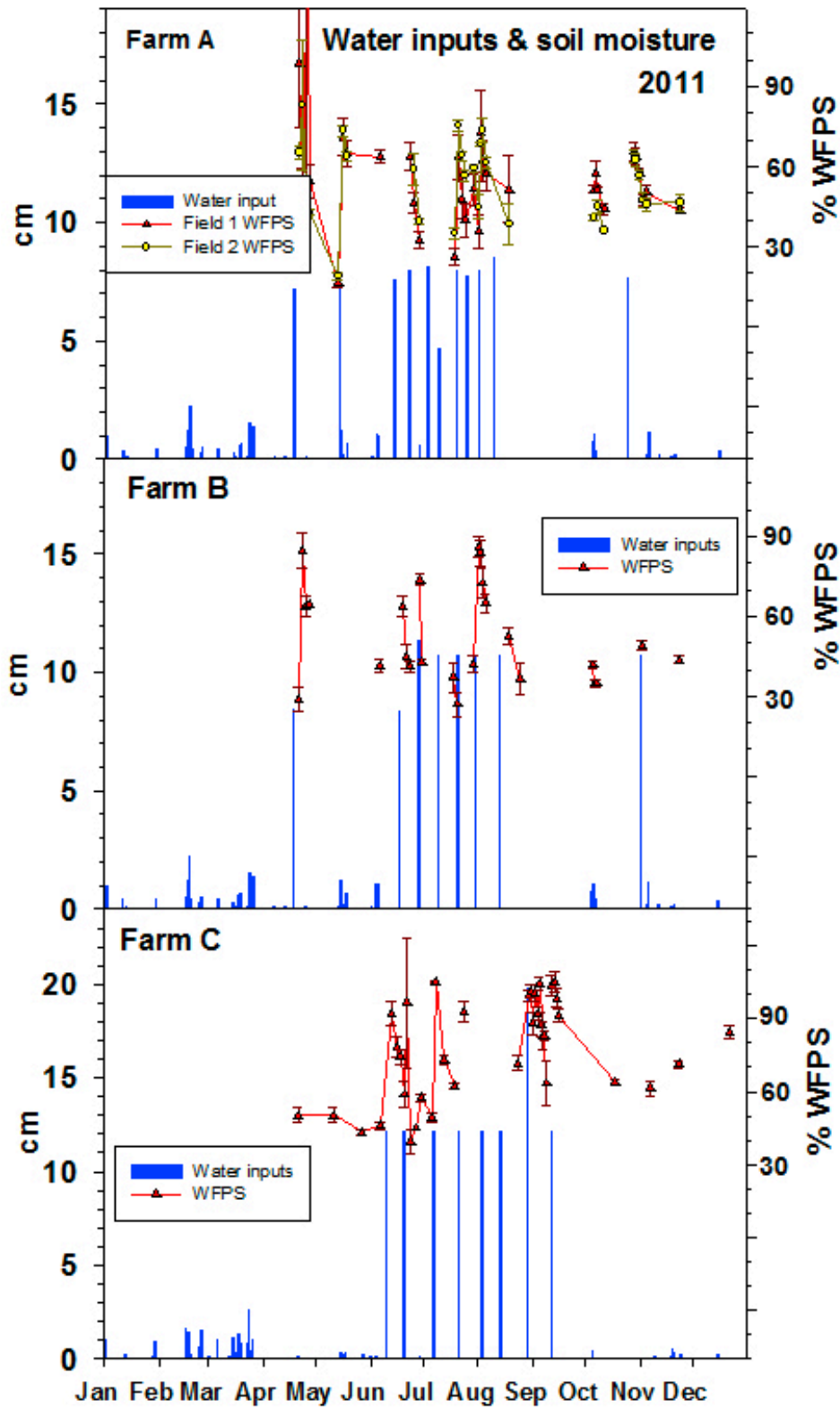
On **Farm C**, multiple regression analysis with step-wise selection of variables showed that soil NO<sub>2</sub><sup>-</sup>-N, WFPS and soil temperature were the soil characteristics with the highest predictive value of the N<sub>2</sub>O daily flux. These variables predicted N<sub>2</sub>O flux according to the following regression equation with R<sup>2</sup>=0.43, p<0.001:

$$N_2O = -0.63 + (0.25 * NO_2^- - N) + (0.03 * WFPS) + (0.17 * Temp. 5cm)$$

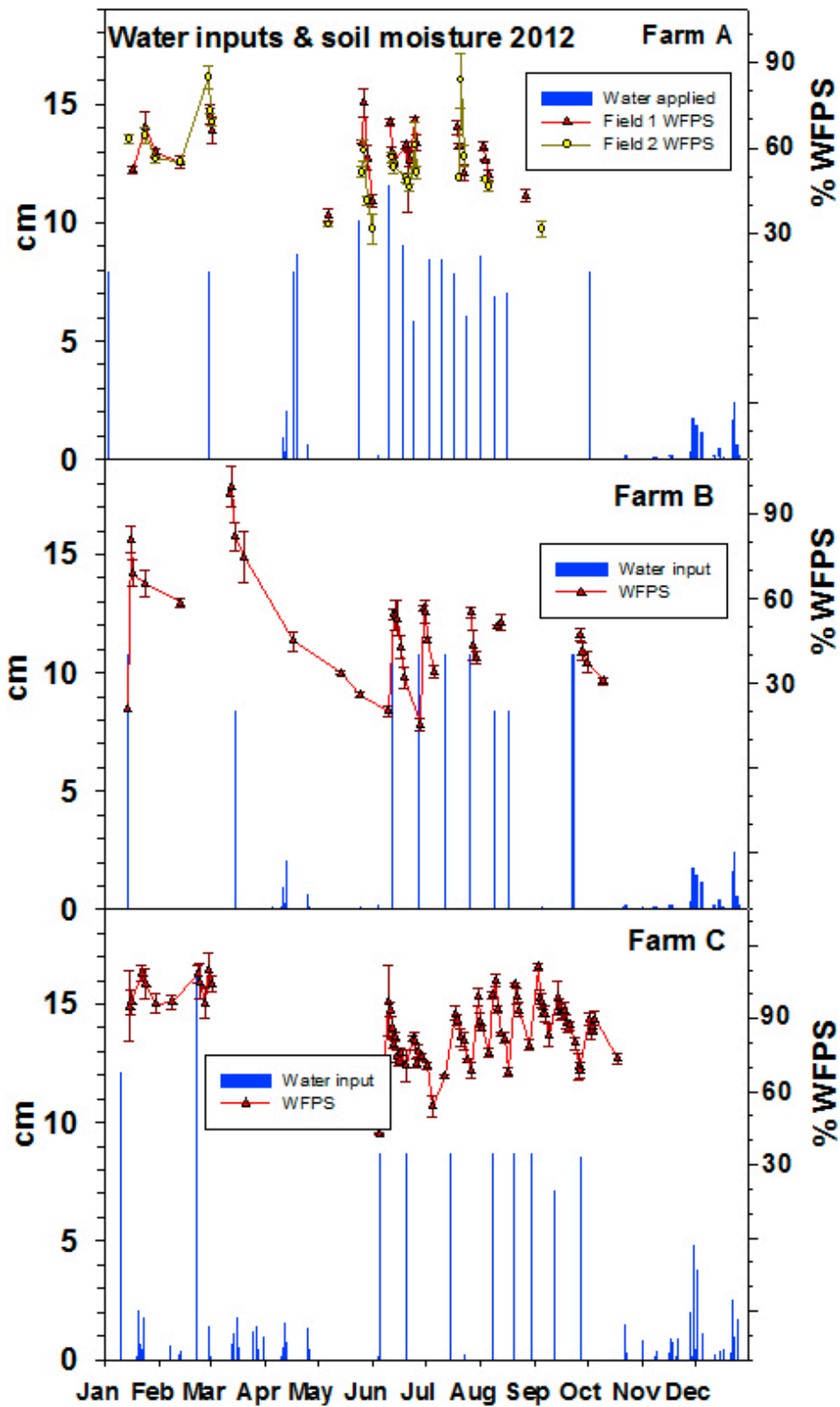
The correlation analysis showed that N<sub>2</sub>O flux was significantly and positively correlated to NO<sub>x</sub> flux (Table 7). The flux of N<sub>2</sub>O increased also with soil NH<sub>4</sub><sup>+</sup>-N, NO<sub>3</sub><sup>-</sup>-N, soil temperature at 5cm depth, but no significant correlation was found with NO<sub>2</sub><sup>-</sup>-N.

**Table 7.** Pearson correlation coefficients for the different environmental variables measured on Farm C. Asterisks indicate significant correlations at P<0.05.

	logN <sub>2</sub> O	logNO <sub>x</sub>	NO <sub>2</sub> <sup>-</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	NH <sub>4</sub> <sup>+</sup> -N	%WFPS	Temp.
log N <sub>2</sub> O	1	0.556*	0.195	0.217*	0.229*	0.101	0.342*
log NO <sub>x</sub>	0.556*	1	0.186	0.210*	0.030	-0.064	0.077
NO <sub>2</sub> <sup>-</sup> -N	0.195	0.186	1	0.220	-0.018	-0.181	0.127
NO <sub>3</sub> <sup>-</sup> -N	0.217*	0.210*	0.220	1	0.033	-0.207*	0.165*
NH <sub>4</sub> <sup>+</sup> -N	0.229*	0.030	-0.018	0.033	1	0.006	-0.026
%WFPS	0.101	-0.064	-0.181	-0.207*	0.006	1	-0.245*
Temp.	0.342*	0.077	0.127	0.165*	-0.026	0.245*	1



**Figure 7.** Water inputs as rainfall and irrigation (cm) and mean soil water content as water-filled pore space (WFPS) with standard errors shown as line bars (n=4) at the three sites in 2011.



**Figure 8.** Water inputs as rainfall and irrigation (cm) and mean soil water content as water-filled pore space (WFPS) with standard errors shown as line bars (n=4) at the three sites in 2012.

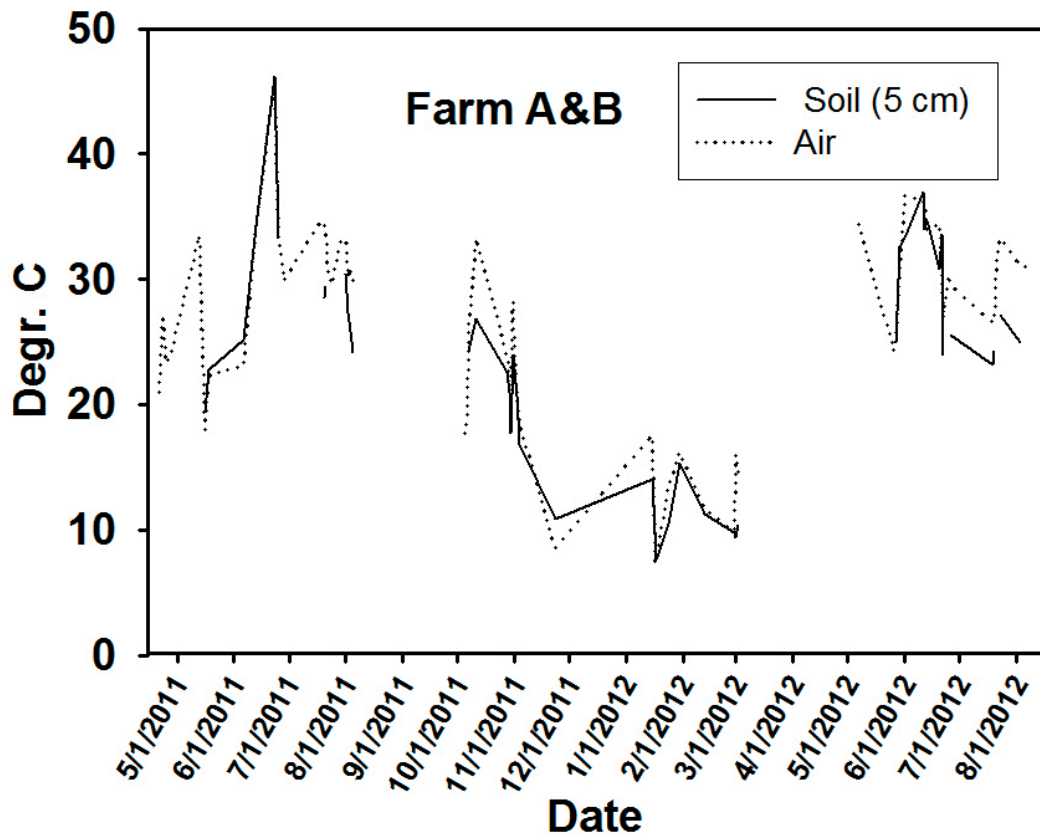


Figure 9. Soil and ambient air temperature at the field sites in Stanislaus County (Farm A & B).

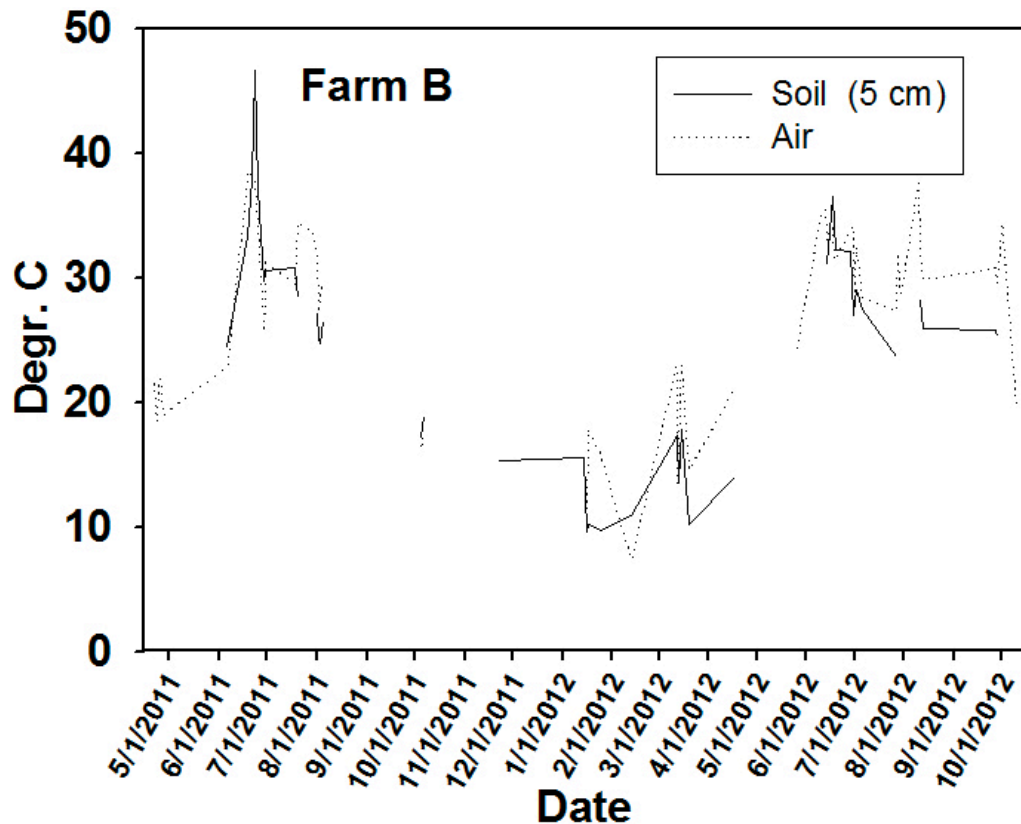


Figure 10. Soil and ambient air temperature at Farm C.

#### 4. Discussion

This study compared N fertility management and use of manures and their effect on N<sub>2</sub>O emissions in the forage production systems of three dairy farms typical for the Sacramento and San Joaquin Valleys. We discuss how the different management strategies affected N<sub>2</sub>O emissions and what the most likely explanations for the observed emission patterns are, taking into consideration the measured environmental parameters, N inputs, and agronomic variables. Furthermore, we compare the magnitude of the N<sub>2</sub>O emissions and the emission factors derived in this project with those of published studies.

All three farms used the same type of irrigation (flood irrigation) and similar crop rotations, and planting and harvesting of summer and winter crops occurred within the same time frame. However, the soil at two of the sites was characterized by high sand content, not uncommon for dairies in the San Joaquin Valley (Stuart Pettygrove, personal communication), whereas the soil of the third site had a high clay content. Soil texture influences N<sub>2</sub>O emissions, with finer texture soils emitting more N<sub>2</sub>O than coarse-textured soils (Bouwman et al. 2002). The N<sub>2</sub>O emissions could therefore be expected to be inherently higher from the clayey than from the sandy soils and differences in emissions and other variables among the three farms are unlikely due solely to differences in management practices.

To summarize N inputs and to calculate emission factors, we considered two N fractions in the manures: (1) the readily available soluble (organic and mineral) N and (2) the solid fraction of the organic N inputs. Only a small fraction (about 15%) of the solid N in lagoon water is mineralized within a growing season (Heinrich and Pettygrove 2012), whereas N mineralized from the organic fraction of dry scrape manure varies depending on the initial composition, processing and storage. For relatively fresh solid cattle manure, N mineralization within 6 months of 22% of the organic fraction has been reported (Burger and Venterea 2008). Most of the solid manure applied to one of the fields in this study had been passed through a screen to separate solids (separator manure) and liquids and some of the applied manure had been composted. The mineralization kinetics of the solid manures has not been determined. Because the much greater part of the solid fraction of applied manures did not undergo N transformations within the time frame of this study, the soluble N likely played a much greater role in influencing N<sub>2</sub>O production and crop N uptake than the solid N. The long-term effects of the manure inputs (both soluble and solid fractions) into these fields in terms of N<sub>2</sub>O emissions are not known. Determining the N mineralization rates in the different fields was beyond the scope of this study.

There are few studies in the literature, in which N<sub>2</sub>O emissions were measured year-round. Most N<sub>2</sub>O emission values are reported for a single or multiple growing seasons. In a recent meta-analysis including 19 studies, an average of 3.01 kg N<sub>2</sub>O-N ha<sup>-1</sup> was emitted per corn growing season resulting, on average, in an EF of 1.1% (Linguist et al. 2012). Among maize crops fertilized with >200 kg N ha<sup>-1</sup> (31 observations), the average seasonal N<sub>2</sub>O emissions were 3.9 kg N<sub>2</sub>O-N ha<sup>-1</sup> (Linguist et al. 2012). Rochette et al. (2008) compared seasonal N<sub>2</sub>O emissions in Canadian corn silage systems following applications of liquid or solid cattle manure or synthetic fertilizer during two years. The total N<sub>2</sub>O emissions from liquid and solid manures did not differ and were ≥ than from synthetic fertilizer. Nitrous oxide following liquid cattle manure applications ranged from 1.25-7.31 kg N<sub>2</sub>O-N ha<sup>-1</sup> in clay and from 2.12-4.66 kg N<sub>2</sub>O-N ha<sup>-1</sup> in loam soil. The corresponding EFs in those studies ranged from 0.8-4.9% and from 1.4-3.1%. In another area (Pennsylvania, U.S.), fields under continuous maize fertilized for 20 years with manures emitted on average 5.5 kg N<sub>2</sub>O-N ha<sup>-1</sup> per maize growing season after applications of 225 kg manure-N ha<sup>-1</sup>, and this resulted in an EF of 2.4% (Adviento-Borbe et al. 2010). The N<sub>2</sub>O emissions on Farm C, where 224 kg N ha<sup>-1</sup> was applied as anhydrous ammonia, were similar in magnitude as the loss of 13.8 kg N<sub>2</sub>O-N ha<sup>-1</sup> reported for a corn system fertilized with anhydrous ammonia at the rate of 168 kg N ha<sup>-1</sup>, resulting in an EF of 7.3% (Thornton et al. 1996). Compared with the above annual or seasonal N<sub>2</sub>O emissions, the N<sub>2</sub>O emissions in the selected California dairy forage systems are similar in magnitude in absolute values. However, the EFs calculated for the California locations are somewhat lower because the N inputs in the California systems were higher.

#### *4.1 Amount of N inputs*

The greatest N<sub>2</sub>O emissions were measured in the field with the highest N inputs (Farm C). In 2012, inputs of available N in this field were almost twice as high (684 kg N ha<sup>-1</sup> during the corn growing season) as those in 2011 (386 kg N ha<sup>-1</sup>) or at the other farms (349-496 kg N ha<sup>-1</sup>). However, the N<sub>2</sub>O emissions at this site were of similar magnitude in 2011 when N inputs were lower. One of the reasons for the generally higher emissions at this site is likely the soil texture. The high soil water content and WFPS following irrigation events persisted longer at this than at the other Farm sites, and this may have stimulated microbial activity and N<sub>2</sub>O production.

#### 4.2 Timing of N inputs

The timing of the N inputs, which varied greatly among the three farms, clearly affected the N<sub>2</sub>O emissions. Both Farm B and C applied a substantial amount of synthetic N fertilizer at the beginning of the cropping season. On Farm B, >100 kg N ha<sup>-1</sup> in the form of UAN32 was applied, and in June of both years, this resulted in N<sub>2</sub>O fluxes of 0.62 (2011) and 1.43 kg N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup> (2012) shortly after the fertilizer applications. On Farm C, in both years, 227 kg of N ha<sup>-1</sup> was injected as anhydrous ammonia (NH<sub>3</sub>) before planting. This resulted in a loss of >5 kg N<sub>2</sub>O-N ha<sup>-1</sup> during a three-week period in June 2011. No other N sources were applied before or during this time. In 2012, during a five week-period starting on June 5, in which no other N sources were applied, >11 kg N<sub>2</sub>O-N ha<sup>-1</sup> were released. Following applications of 159 and 167 kg lagoon water-N (available N) ha<sup>-1</sup> in late August/September of 2011 and 2012, emissions of 1.6 and 2.6 kg N<sub>2</sub>O-N ha<sup>-1</sup> occurred during periods lasting about two weeks. Unusually high soil NH<sub>4</sub><sup>+</sup> concentrations were recorded at Farm C following the NH<sub>3</sub> application in 2011, and also on Farm B following the UAN32 applications in 2011 and 2012.

On the other farms, the remaining N applications were not as great as those mentioned above except for one lagoon-water application of 170 kg available N ha<sup>-1</sup> at Farm A on July 7, 2012. On Farm A, none of the N<sub>2</sub>O fluxes seemed clearly related to a particular N input, and this was shown by the stepwise regression model for Field 1, which identified only WFPS and soil temperature at 5 cm depth as variables influencing N<sub>2</sub>O flux. For Field 2, WFPS may have played less of a role in influencing the magnitude of N<sub>2</sub>O emissions than in Field 1 because the lower soil bulk density in Field 2 may have limited the occurrence of low O<sub>2</sub> concentrations in that soil. Higher bulk density in Field 1 may have been an important reason for the somewhat higher emissions in Field 1 than in Field 2. Soil temperature and WFPS were included as significant in the multiple regression models of the other Farms too. In addition, the stepwise regression model also identified NH<sub>4</sub><sup>+</sup> as a variable that could explain N<sub>2</sub>O flux on Farm B, but for Farm C, only NO<sub>2</sub><sup>-</sup>, but not NH<sub>4</sub><sup>+</sup>, was included as significant variable influencing N<sub>2</sub>O flux.

#### 4.3 Placement of N inputs

All but the above-mentioned N inputs of synthetic N fertilizers, which were banded at a depth of 20 cm, were applied with the irrigation water. With regard to the high N<sub>2</sub>O emissions following the synthetic N fertilizer applications, the effects of timing and placement on N<sub>2</sub>O emissions are therefore partly confounded. It is well known that banding of NH<sub>3</sub> leads to greater N<sub>2</sub>O emissions than dispersal of other types of fertilizer (Breitenbeck and Bremner 1986; Fujinuma et al. 2011; Thornton et al. 1996; Venterea et al. 2005; Venterea et al. 2010). This study shows that applying UAN32 in concentrated form (banded) may also lead to unusually high N<sub>2</sub>O emissions compared to less concentrated applications, such as additions via the irrigation water.

#### 4.4 N source as substrate of N<sub>2</sub>O

In this study, the relative importance of the different N sources – salt-based NH<sub>4</sub><sup>+</sup> and dissolved organic N in lagoon water, UAN32 in irrigation water, mineralized N from solid manures, and NO<sub>3</sub><sup>-</sup> – to N<sub>2</sub>O emissions, could not be unequivocally determined. Previous studies have shown that manure from anaerobic storage ponds has high potential for N<sub>2</sub>O production because the high labile carbon compounds, such as volatile fatty acids, can easily lead to oxygen



depletion (Patni and Jui 1985; Paul and Beauchamp 1989) promoting N<sub>2</sub>O production via ammonia oxidation and denitrification pathways (Heinrich and Pettygrove 2012; Zhu et al. 2013). It is possible that the presence of manure contributed to enhancing N<sub>2</sub>O production from synthetic N fertilizer sources.

## 5. Summary and conclusions

Nitrogen inputs and emissions of the greenhouse gas (GHG) N<sub>2</sub>O were measured from spring 2011 to fall 2012 in three forage production systems surrounding dairy farms in the Sacramento and San Joaquin Valley. The study was undertaken to improve the statewide estimates of GHG emissions, derive EFs, and obtain data for the calibration and validation of models. These baseline N<sub>2</sub>O emission estimates from agricultural activities are needed to design strategies to meet the goal of the legislatively mandated reduction in GHG emissions by 2020. The ancillary measurements taken, such as crop N uptake, availability of inorganic N, and soil water content were used to better understand the drivers of N<sub>2</sub>O emissions in these systems and to develop recommendations for best management practices having the potential to mitigate the emissions.

The N<sub>2</sub>O emissions were related to the amount of available N applied in the fields under study with highest emissions following the greatest additions of available N. We identified several periods of high N<sub>2</sub>O emissions that followed large additions of concentrated N fertilizer material. The concentrated fertilizer material was anhydrous ammonia (80%N) and urea ammonium-nitrate (32%N) that was injected into the soil in bands at rates of >200 and >100 kg N ha<sup>-1</sup>, respectively. The N<sub>2</sub>O emissions following these applications of synthetic N fertilizer accounted for 68% of total seasonal N<sub>2</sub>O emissions in the case of anhydrous ammonia, but only for 11% in the case of UAN32. Incremental applications of available N as lagoon water or relatively low doses of synthetic fertilizer in the irrigation water did not lead to N<sub>2</sub>O emissions that were as high as those following the more concentrated, banded N applications. Although the results suggested that the high emissions were mainly caused by these concentrated N applications, the effect of N source on N<sub>2</sub>O emissions could not be clearly identified in these on-farm studies. In addition to N application rates and N sources and placement, soil type affected the N<sub>2</sub>O emissions, i.e. elevated N<sub>2</sub>O emissions lasted only for a few days in sandy soils (≥70% sand) vs. several weeks in clayey soils (>40% clay). The annual and seasonal (growing season) N<sub>2</sub>O emissions were comparable to published values from similar systems. The N application rates in the California systems were higher than those at the sites of the published studies. Since the emissions factors (EF) are calculated as the fractions of the applied N, the California EFs were greater than previously published EFs from similar systems.

## 6. Recommendations

The first recommendation concerns N management at the farms: To lower the N<sub>2</sub>O emission potential from California dairy forage systems, applying N incrementally at low to moderate doses, depending on crop stage, is recommended. This would entail applying most N via the irrigations to spread out N applications. In some cases, the facilities to measure and mix irrigation and lagoon water may need to be improved to allow for more accurate metering of N additions to accommodate spreading out the N additions over time. It is necessary to determine crop N demand and actual crop N uptake for each growth stage in order to generate a tool

growers could use to apply N in adequate quantities to meet crop demand, thereby avoiding excessive N application without affecting yield potential. Once actual crop N demand is known and lagoon N applications properly metered, synthetic N fertilizer applications could be adjusted accordingly.

The second recommendation concerns improving the statewide inventory of N<sub>2</sub>O emissions: The results suggest that soil texture may have had a strong impact on N<sub>2</sub>O emissions. However, in this study it was not possible to separate the effects of soil type on N<sub>2</sub>O emissions from those of management, and therefore, extrapolating the results of the present study to the entire dairy sector would be questionable. A more reliable estimate of statewide of N<sub>2</sub>O emissions from dairy systems can probably only be made if the effects of soil type on N<sub>2</sub>O are better understood. We recommend that such research is undertaken.

## 7. References

- Adviento-Borbe MAA, Kaye JP, Bruns MA, McDaniel MD, McCoy M, Harkcom S (2010) Soil Greenhouse Gas and Ammonia Emissions in Long-Term Maize-Based Cropping Systems. *Soil Sci. Soc. Am. J.* 74: 1623-1634
- Bouwman AF, Boumans LJM, Batjes NH (2002) Emissions of N<sub>2</sub>O and NO from fertilized fields: Summary of available measurement data. *Global Biogeochem. Cycl.* 16
- Breitenbeck GA, Bremner JM (1986) Effects of various nitrogen fertilizers on emission of nitrous-oxide from soils. *Biol. Fert. Soils* 2: 195-199
- Bremner JM, Blackmer AM (1978) Nitrous oxide emission from soils during nitrification of fertilizer nitrogen. *Science (Washington DC)* 199: 295-296
- Burger M, Venterea RT (2008) Nitrogen Immobilization and Mineralization Kinetics of Cattle, Hog, and Turkey Manure Applied to Soil. *Soil Sci. Soc. Am. J.* 72: 1570-1579
- Cabrera ML, Beare MH (1993) Alkaline persulfate oxidation for determining total nitrogen in microbial biomass extracts *Soil Sci. Soc. Am. J.* 57: 1007-1012
- Coyne MS (2008) Biological denitrification. In: Schepers JS, Raun WR (eds) *Nitrogen in agricultural systems*. American Society of Agronomy, Madison, WI
- Doane TA, Horwath WR (2003) Spectrophotometric determination of nitrate with a single reagent. *Anal. Lett.* 36: 2713-2722
- Dumas JB (1848) Sur les procédés de l'analyse organique. *Ann. Chim.* : 195-213
- Eichner MJ (1990) Nitrous oxide emissions from fertilized soils: Summary of available data. *J. Environ. Qual.* 19: 272-280
- Forster JC (1995) Soil nitrogen. In: K. A, P N (eds) *Methods in Applied Soil Microbiology and Biochemistry*. Academic Press, San Diego, pp 79-87
- Fujinuma R, Venterea RT, Rosen C (2011) Broadcast Urea Reduces N<sub>2</sub>O but Increases NO Emissions Compared with Conventional and Shallow-Applied Anhydrous Ammonia in a Coarse-Textured Soil. *J. Environ. Qual.* 40: 1806-1815

- Geisseler D, Lazicki PA, Pettygrove GS, Ludwig B, Bachand PAM, Horwath WR (2012) Nitrogen Dynamics in Irrigated Forage Systems Fertilized with Liquid Dairy Manure. *Agron. J.* 104: 897-907
- Heinrich AL, Pettygrove GS (2012) Influence of Dissolved Carbon and Nitrogen on Mineralization of Dilute Liquid Dairy Manure. *Soil Sci. Soc. Am. J.* 76: 700-709
- Hutchinson GL, Livingston GP (1993) Use of chamber systems to measure trace gas fluxes. In: Rolston DE (ed) *Agricultural Ecosystem Effects on Trace Gases and Global Climate Change*. ASA Special Publication no. 55, Madison, WI
- Hutchinson GL, Mosier AR (1981) Improved soil cover method for field measurement of nitrous oxide fluxes. *Soil Sci. Soc. Am. J.* 45: 311-316
- IPCC (2007) *Mitigation of Climate Change*. Chapter 8: Agriculture. Intergovernmental Panel on Climate Change, New York
- Linn DM, Doran JW (1984) Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. *Soil Sci. Soc. Am. J.* 48: 1267-1272
- Linquist B, van Groenigen KJ, Adviento-Borbe MA, Pittelkow C, van Kessel C (2012) An agronomic assessment of greenhouse gas emissions from major cereal crops. *Global Change Biol.* 18: 194-209
- Ma L, Ahuja LR, Ascough JC, Shaffer MJ, Rojas KW, Malone RW, Cameira MR (2000) Integrating system modeling with field research in agriculture: Applications of the root zone water quality model (RZWQM). *Advances in Agronomy* 71: 233-292
- Patni NK, Jui PY (1985) Volatile Fatty-Acids in Stored Dairy-Cattle Slurry. *Agricultural Wastes* 13: 159-178
- Paul JW, Beauchamp EG (1989) Effect of Carbon Constituents in Manure on Denitrification in Soil. *Can J Soil Sci* 69: 49-61
- Rochette P, Angers DA, Chantigny MH, Gagnon B, Bertrand N (2008) N<sub>2</sub>O fluxes in soils of contrasting textures fertilized with liquid and solid dairy cattle manures. *Can J Soil Sci* 88: 175-187
- Stehfest E, Bouwman L (2006) N<sub>2</sub>O and NO emission from agricultural fields and soils under natural vegetation: summarizing available measurement data and modeling of global annual emissions. *Nutr. Cycl. Agroecosyst.* 74: 207-228
- Thornton FC, Bock BR, Tyler DD (1996) Soil emissions of nitric oxide and nitrous oxide from injected anhydrous ammonium and urea. *J. Environ. Qual.* 25: 1378-1384
- U.S. Dept. of Agriculture (1992) Burt R (ed.) *Soil Survey Laboratory Methods Manual*. Investigations Report no. 42. Washington DC: USDA.
- Venterea RT, Burger M, Spokas KA (2005) Nitrogen oxide and methane emissions under varying tillage and fertilizer management. *J. Environ. Qual.* 34: 1467-1477
- Venterea RT, Dolan MS, Ochsner TE (2010) Urea Decreases Nitrous Oxide Emissions Compared with Anhydrous Ammonia in a Minnesota Corn Cropping System. *Soil Sci. Soc. Am. J.* 74: 407-418

Wrage N, Velthof GL, van Beusichem ML, Oenema O (2001) Role of nitrifier denitrification in the production of nitrous oxide. *Soil Biol. Biochem.* 33: 1723-1732

Zhu X, Burger M, Doane TA, Horwath WR (2013) Ammonia oxidation pathways and nitrifier denitrification are significant sources of N<sub>2</sub>O and NO under low oxygen availability. *P Natl Acad Sci USA*

## 8. Glossary of Terms, Abbreviations and Symbols

AB32	Assembly Bill 32
CARB	California Air Resources Board
C	Carbon
°C	Degree(s) Celsius
d	Day(s)
ECD	Electron capture detector (in gas chromatographs)
EF	Emission factor, the percentage of fertilizer N emitted as N <sub>2</sub> O
GHG	Greenhouse gas
h	Hour(s)
ha	Hectare
IPCC	Inter-governmental panel of climate change
KCl	Potassium chloride
kg	Kilogram
M	Molar
Mg m <sup>-3</sup>	Megagrams per cubic meter
N	Nitrogen
NH <sub>4</sub> <sup>+</sup>	Ammonium
NO <sub>3</sub> <sup>-</sup>	Nitrate
NO <sub>2</sub> <sup>-</sup>	Nitrite
N <sub>2</sub> O	Nitrous oxide
O <sub>2</sub>	Oxygen
pg	Picograms
P5	Mixture of 95% argon and 5% methane used as carrier gas in gas chromatographs
TDN	Total dissolved nitrogen
TSS	Total suspended solids
UAN32	Urea-ammonium nitrate

APPENDIX A

Measurement Data and Root Mean Squared Error Calculation:

Calculation of root mean squared error (RMSE) of standard curves used to analyze air samples for nitrous oxide concentrations by gas chromatography. The RMSE is the average distance of a predicted value from the fitted regression line.

ppm N2O	10/5 -10/18/12	predicted	error	error^2
0.321	35526	0.270	0.051	0.003
0.321	33128	0.233	0.088	0.008
0.321	33054	0.231	0.090	0.008
0.998	90045	1.130	-0.132	0.017
0.998	90961	1.144	-0.146	0.021
0.998	86647	1.076	-0.078	0.006
3.17	223850	3.240	-0.070	0.005
3.17	204770	2.939	0.231	0.053
3.17	221581	3.204	-0.034	0.001
	1.57667E-05		Msq error	0.0137
	-0.28978673		<b>RMSE (ppm)</b>	<b>0.117</b>
	0.990757964			

ppm N2O	5/7/12	predicted	error	error^2
0.321	37672	0.279	0.042	0.002
0.321	37117	0.271	0.050	0.002
0.321	37161	0.272	0.049	0.002
0.998	93612	1.070	-0.072	0.005
0.998	94377	1.081	-0.083	0.007
0.998	94162	1.078	-0.080	0.006
3.17	227016	2.957	0.213	0.045
3.17	237166	3.101	0.069	0.005
3.17	255326	3.358	-0.188	0.035
slope	1.41435E-05		Msq error	0.0123
intercept	-0.253706837		<b>RMSE (ppm)</b>	<b>0.111</b>
rsquare	0.991688559			

ppm N2O	6/21-6/25/13	predicted	error	error^2
0.321	25903	0.244	0.077	0.006
0.321	25463	0.235	0.086	0.007
1.123	76480	1.256	-0.133	0.018
1.123	75740	1.241	-0.118	0.014
3.171	170864	3.146	0.025	0.001
3.171	168970	3.108	0.063	0.004

slope	2.00199E-05	Msq error	0.0083
intercept	-0.274868292	<b>RMSE (ppm)</b>	<b>0.0911</b>
rsquare	0.994237415		

ppm N2O	5/7/12	predicted	error	error^2
0.321	37672	0.279	0.042	0.002
0.321	37117	0.271	0.050	0.002
0.321	37161	0.272	0.049	0.002
0.998	93612	1.070	-0.072	0.005
0.998	94377	1.081	-0.083	0.007
0.998	94162	1.078	-0.080	0.006
3.17	227016	2.957	0.213	0.045
3.17	237166	3.101	0.069	0.005
3.17	255326	3.358	-0.188	0.035

slope	1.41435E-05	Msq error	0.0123
intercept	-0.253706837	<b>RMSE (ppm)</b>	<b>0.111</b>
rsquare	0.991688559		

ppm N2O	4/27/11	predicted	error	error^2
1.123	83821	1.239	-0.116	0.013
1.123	82653	1.218	-0.095	0.009
1.123	83475	1.233	-0.110	0.012
0.27	25656	0.203	0.067	0.005
0.27	25665	0.203	0.067	0.005
0.27	25657	0.203	0.067	0.005
3.171	195200	3.223	-0.052	0.003
3.171	184704	3.036	0.135	0.018
3.171	190265	3.135	0.036	0.001
slope	1.78158E-05		Msq error	0.0078
intercept	-0.254498612		<b>RMSE (ppm)</b>	<b>0.0884</b>
rsquare	0.994731289			

ppm N2O	7/6-7/13/11	predicted	error	error^2
0.321	24105	0.248	0.073	0.005
0.321	23784	0.242	0.079	0.006
1.123	73643	1.247	-0.124	0.015
1.123	73581	1.246	-0.123	0.015
3.171	172476	3.240	-0.069	0.005
3.171	160844	3.006	0.165	0.027
slope	2.01663E-05		Msq error	0.0124
intercept	-0.237754926		<b>RMSE (ppm)</b>	<b>0.1112</b>
rsquare	0.991406882			



ppm N2O	5/7/12	predicted	error	error^2
0.321	37672	0.279	0.042	0.002
0.321	37117	0.271	0.050	0.002
0.321	37161	0.272	0.049	0.002
0.998	93612	1.070	-0.072	0.005
0.998	94377	1.081	-0.083	0.007
0.998	94162	1.078	-0.080	0.006
3.17	227016	2.957	0.213	0.045
3.17	237166	3.101	0.069	0.005
3.17	255326	3.358	-0.188	0.035
slope	1.41435E-05		Msq error	0.0123
intercept	-0.253706837		<b>RMSE (ppm)</b>	<b>0.111</b>
rsquare	0.991688559			

ppm N2O	9/28/12	predicted	error	error^2
0.998	71213	0.964	0.034	0.001
0.998	79779	1.108	-0.110	0.012
0.998	80517	1.120	-0.122	0.015
0.321	30656	0.286	0.035	0.001
0.321	31736	0.304	0.017	0.000
0.321	31285	0.296	0.025	0.001
3.17	220024	3.454	-0.284	0.081
3.17	196346	3.058	0.112	0.013
3.17	185538	2.877	0.293	0.086
slope	1.67324E-05		Msq error	0.0232
intercept	-0.227282071		<b>RMSE (ppm)</b>	<b>0.152</b>
rsquare	0.984259091			

<b>ppm N2O</b>	<b>10/2/12</b>	<b>predicted</b>	<b>error</b>	<b>error^2</b>
0.998	90595	1.168	-0.170	0.029
0.998	90564	1.168	-0.170	0.029
0.998	89990	1.158	-0.160	0.026
0.321	33761	0.234	0.087	0.008
0.321	33007	0.221	0.100	0.010
0.321	31308	0.194	0.127	0.016
3.17	206853	3.080	0.090	0.008
3.17	198625	2.945	0.225	0.051
3.17	220112	3.298	-0.128	0.016
slope	1.64443E-05		Msq error	0.0214
intercept	-0.321337277		<b>RMSE (ppm)</b>	<b>0.146</b>
rsquare	0.985509576			



**Figure 1A.** Vented chamber used for nitrous oxide flux measurements in the field and exetainers used to store the air samples.

## APPENDIX B:

### Flux Calculations:

The nitrous oxide flux was calculated as either the change in concentration divided by the chamber deployment time (linear regression), multiplied by V/A, Or

if  $(C_1 - C_0)/(C_2 - C_1) > 1$ ,

then  $f_0 = V(C_1 - C_0)^2 / [At_1 (2C_1 - C_2 - C_0)] \ln[(C_1 - C_0)/(C_2 - C_1)]$

where  $f_0$  is the instantaneous flux at time 0,  $C_0$ ,  $C_1$ , and  $C_2$  are the chamber headspace gas concentrations (ppm(v)) at time 0, 1, and 2, respectively,  $t_1$  is the time interval between gas sampling points,  $V$  is the chamber volume, and  $A$  is the area covered by the chamber (Hutchinson & Mosier, 1981).

The flux calculated from either linear regression or the non-linear (H&M) model was converted from volumetric units (e.g. mL N<sub>2</sub>O m<sup>-2</sup> h<sup>-1</sup>) to mass units, using ideal gas relations [e.g. (28 g N<sub>2</sub>O-N/24205 mL N<sub>2</sub>O)(295)/(273+T<sub>Chamber</sub>)], where T<sub>Chamber</sub> is the chamber temperature, and 295 is the laboratory temperature at which the standards were prepared, both in Kelvin units].