Ammonia Emission Related to Nitrogen Fertilizer Application Practices

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Introduction

This project involves the adaptation of techniques developed to measure trace gasses in the atmosphere of urban areas to the monitoring of ammonia from agricultural operations. Ammonia has significance to air quality both as a buffer against atmospheric acidity and as a precursor of $PM_{2.5}$ particles. The study began in the fall of 1999 as a California Air Resources Board (ARB) project to develop and validate a method for monitoring NH_3 volatile losses from fertilizer applications. This CDFA-FERP project continues the use of the methodology from the ARB project to extend the monitoring of atmospheric ammonia to the whole crop season of some of the crop/fertilizer/soil combinations. While the fertilizer application process is likely to be the point at which the highest ammonia losses occur in a field, literature suggests and project results confirm, those levels exist for only a short time. In order to accurately model the ammonia losses from cultivated crops, monitoring of the atmospheric levels during the rest of the crop season is also necessary. In the second year of the project 10 crops and 3 natural vegetation communities were monitored several times each to begin to establish the seasonal levels and variability of atmospheric ammonia.

Objectives

The project has one primary and two secondary objectives to further refine the models and conclusions to a level beyond the scope of the initial study.

Objective 1. Determine the ammonia levels in the atmosphere related to several crop/soil combinations in the San Joaquin Valley over the entire crop season by monitoring on a 15-30 day frequency from initial soil preparation through post harvest cultural practices. This data will be used in atmospheric models to add the seasonal emissions to the flux rates monitored for fertilizer applications.

Objective 2. Investigate the effect of soil texture and other factors on ammonia emissions with the goal of using precision agriculture techniques to adjust N fertilizer applications in fields where factors change significantly.

Objective 3. Document and disseminate the sampling method developed in the ARB project to the agriculture and fertilizer industry.

Description

The initial ARB project was to measure the magnitude of volatile NH_3 loss and its duration as a result of various N fertilizer applications. The volatile loss percentage for a specific N application is influenced by several factors that could be identified in the statewide database developed by the NASA-Ames cooperators. The first step in the project was to list those factors in a matrix and then select representative combinations from the matrix cells to monitor in the field. The first factor identified was crop type. The database utilized county-based crop maps from the California Department of Water Resources. The second factor was soil. Initially, the soil texture was considered to be the most likely soil characteristic to affect NH_3 volatilization. Four general soil texture classes were selected based on %clay. The most significant chemical soil characteristic was assumed to be pH. The intention was to select sites with different textures and pH values on which the specific crop types were common. The most subjective selections for the sampling matrix were the fertilizer forms and application methods. Six combinations of a material and application method were selected as common to many of the crops and soils for the completion of the sampling matrix. Prior to the sampling, ten crops, four soil textures and six fertilizers resulted in a matrix of 240 cells. Changes in the matrix during the sampling period produced a final matrix of 936 (nine crops X thirteen fertilizer/application methods X two pH categories X four soil texture) categories. Three sites were located on the CSUF farm/laboratory, the rest were in commercial fields. The sampling period for the ARB funded project was the calendar year, 2000. 19 individual applications were sampled and usable data was obtained from 14 of those. Table 1 is a list of the sites sampled in 2000. Table 2 is a listing of ammonia emissions by county. These were calculated by applying the appropriate emission factor from the field monitoring to the crops identified in the database developed from the DWR crop maps.

An active denuder was selected for the initial sampling season of this project because it represents an established method in air quality studies and it satisfied the requirement for continuous sampling. A 47mm disk of glass fiber filter paper was treated with citric acid (5% in 95% ethanol) and dried. A commercially available, 12 volt air sampling pump was used to pull air through the denuder disk at a rate of about four liters per minute. Previous work suggested differences in day and night levels of NH_3 in the air so the sampling was diurnal with the denuders changed at dawn and dusk. Samples were refrigerated and taken to the Graduate Laboratory of the CSUF College of Agricultural Science and Technology, to be analyzed by project personnel. The NH_4-Citrate was extracted from the denuder with distilled water and analyzed with Nessler's Reagent in a spectrophotometer. The amount of ammonia on the denuder disk was reported in □g NH_3. The concentration of NH_3 in the air at the sampling point could be determined by dividing the amount of ammonia on the disk by the volume (meter^3) of air through the denuder in the sampling period to get □gNH_3/meter^3 of air.

The measurement of NH_3 concentration at a particular sampling point is not sufficient to determine the emission factor for a particular field site. The amount of NH_3 in the atmosphere depends not only on the concentration but also the flow of the air mass (wind velocity) at the sampling point. The value necessary to characterize the sampling point was the flux in □gNH_3/meter^2/second. This ammonia flux is the amount of NH_3 passing through a 1meter^2 cross section per second at the sampling point. The measurement of the flux of a single sample is not enough to determine an emission factor. The plan was to monitor ammonia flux at several elevations above the field surface to characterize the gradient between the soil surface and the ambient atmosphere. Denuders and anemometers were located at 1, 2, 5, 10 and 20 meters above the soil surface. Initially it was assumed that a positive NH_3 flux gradient from the soil surface, decreasing as the elevation increased could be used to indicate the magnitude of the emission factor for the sampling period. Prior to the application, it was suspected that negative gradients, with higher flux rates in the atmosphere, decreasing at elevations closer to the soil surface might be found due to ammonia absorption by foliage and/or a moist soil surface.

This field data was analyzed further by the cooperating atmospheric scientists at NASA-Ames. They subtracted the background NH_3 from that present during the application, fit a curve to the resulting differences and integrated under the curve to determine the quantity of NH_3 in the atmosphere as a result of the fertilizer. That value divided into the fertilizer rate produced the percentage of NH_3 lost through volatilization. This percentage is termed the emission factor by the atmospheric scientists and the ARB.

Results and Discussion

Table 1 shows the emission factors for each of the sampled sites. Comparison of the emission factors with the crop/soil/fertilizer combinations used to develop the original sampling matrix shows correlation with some characteristics but not others. The primary correlations appear to be with the application method and soil pH. All of the sites with emission factors higher than 1.3% involved fertilizers applied at the surface; banded, broadcast or in irrigation water. Most of the high % loss sites also had a soil pH near or above 8. Subsurface applications to both high and neutral pH soils had relatively low emission factors so it appears that placing the material well below the surface is efficient even at an unfavorable soil pH. There did not appear to be any correlation with crop type, fertilizer type or soil texture in the data from 2000.

Evolution of the study from data collection and a database of NH_3 emission factors for the ARB (Table 2) to an investigation of seasonal, volatile losses is the primary characteristic of the current FREP project. The existing sampling system proved to be effective in monitoring NH_3 emissions during fertilizer applications but the large, trailer-mounted tower was difficult to place properly in the field and difficult to relocate. It was also found, during the analysis of the data, that the measurement at 20 meters was not necessary. Consequently a smaller system on a tripod-mounted mast was developed that would sample up to a 10 meter elevation. This system is much more portable which makes it easier to place properly in a field. One of the smaller systems was built and used at several sites beginning in March, 2001. After several modifications, the design was adopted and six more portable sampling systems have been built. Two primary sampling units were constructed with five wind speed sensors. Four secondary units were built with simpler weather stations that monitor wind speed at only two heights. Each set of the tripod-supported masts can be used separately at three different sampling sites or together to monitor horizontal as well as vertical NH_3 gradients when monitoring point sources. The lowest sampling height during the ARB study was 1 meter. Some experimentation in the spring of 2001 indicated the need to sample closer to the surface, particularly when the crop was absent or very short. The sampling elevations on the tripod/mast units can be easily changed to allow samples at any height from the soil surface to 10 meters. A need to sample air immediately above the soil surface has also been addressed with several chamber and shield systems evaluated. A shield constructed of 6mm Lexan in a 1m circle that can be adjusted from 5cm to 20cm above the soil/vegetation surface has been adopted. A denuder is located at the center of the shield so that air must pass between the surface and the shield for 0.5m before it enters the denuder. The data from these devices is still being analyzed and will be reported next year.

The FREP sponsored project, at this point, has completed the development of the field sampling systems and has sampled at several sites on a regular basis through the current crop season. Some crop/soil sites have yet to be selected but each will be in place for at least one complete season prior to the end of the project in 2003. The field sampling with the denuder systems will be supplemented by a tunable diode laser to monitor ammonia through open-path spectroscopy. This will allow real time monitoring of ammonia over much shorter intervals than the denuders. Much of this work will be done in connection with monitoring dairy operations but several crop systems will also be included. The completion of the crop monitoring and correlation with the TDL project will be reported next year.

Table 1. Summary of Field Sampling Site Emission Estimates

SITE	CROP	N #/Ac	N g/m^2	Soil pH	Irrigation	NH_3 Emission g N m^{-2}	NH_3 Emission Factor
B	Almonds	100	10.9	8.1	Surface	0.72	6.6%
D	Citrus	50	5.5	6.1	Surface	0.24	4.3%
E	Almonds	100	10.9	6.4	Buried Drip	0.05	0.5%
F	Onion	40	4.4	8.5	Sprinkler	0.28	6.5%
G	Tomato	100	10.9	7.9	Furrow	0.10	0.9%
H	Garlic	50	5.5	7.9	Furrow	0.32	5.8%
I	Cotton	100	10.9	8.5	Furrow	0.62	5.6%
J	Cotton	100	10.9	7.8	Furrow	0.43	3.9%
K	Almonds	10	1.0	6.4	Microspray	0.00	0.0%
L	Pasture	100	10.9	6.6	Surface	0.32	2.9%
M	Broccoli	60	6.5	7.9	Buried Drip	0.10	1.6%
Q	Lettuce	40	4.4	7.8	Furrow	0.02	0.5%
R	Tomato	80	8.7	7.9	Fallow	0.01	0.1%
S	Cotton	100	10.9	8.5	Fallow	0.14	1.3%

Table 2. Estimated NH_3-N emission directly from chemical fertilizer application in counties of California.

	DWR area total (ha)	NH_3-N Emission 10^6 kg	Ave. NH_3 Emission Factor
San Joaquin Valley			
San Joaquin	232,531	0.66	2.41%
Stanislaus	158,549	0.40	2.38%
Madera	145,660	0.27	2.30%
Merced	226,158	0.65	2.64%
Fresno	538,163	1.46	2.47%
Kern	398,140	1.14	2.71%
Kings	236,465	0.74	3.06%
Tulare	307,772	0.78	2.35%
TOTAL	**2,243,437**	**6.11**	**2.54%**
Sacramento Valley			
Butte	106,658	0.41	2.26%
Colusa	130,851	0.61	2.58%
Glenn	111,747	0.42	2.30%
Sacramento	80,029	0.22	2.34%
Solano	83,183	0.26	2.40%
Sutter	119,301	0.55	2.74%
Yolo	147,605	0.49	2.43%
TOTAL	**779,373**	**2.96**	**2.43%**
Central Coast			
Monterey	107,251	0.28	1.57%
San Luis Obispo and Santa Barbara	125,976	0.34	1.45%
TOTAL	**233,227**	**0.61**	**1.51%**
Imperial Valley			
Riverside and San Bernadino	54,482	0.31	2.33%
Imperial	211,559	1.70	2.53%
TOTAL	**266,041**	**2.01**	**2.43%**
STATE TOTAL	**3,522,079**	**11.7**	**2.38%**