CALIFORNIA DEPARTMENT OF FOOD AND AGRICULTURE
FERTILIZER RESEARCH AND EDUCATION PROGRAM (FREP)

Final Report, June-'06

Project Title: Ammonia Emission Related to Nitrogen Fertilizer Application Practices

Duration: January, 2001 through December, 2003 (extended through December, 2004)
Project Leader: Charles F. Krauter, Professor of Soil and Water, Center for Irrigation Technology, CSU Fresno
Cooperators: Christopher Potter, NASA Ames Research Center, Moffett Field, CA
Steven Klooster, CSU Monterey Bay and NASA Ames Research Center

Executive Summary

The scientists listed as PI and cooperators conducted a series of studies funded from May, 1999 to June, 2005 by the California Air Resources Board (ARB) and NASA-Ames with these objectives:

1. *Determine the major agricultural field sources of atmospheric ammonia emissions in the Central Valley of California.*
2. *Determine the seasonal flux rates of atmospheric ammonia emissions in the Central Valley of California.*
3. *Determine a regional budget of annual atmospheric ammonia emissions in the Central Valley of California.*

This project involved the adaptation of techniques currently used to measure trace gasses in the atmosphere of urban areas, to the monitoring of ammonia from agricultural applications of various N fertilizers. The data collected in the field was used with GIS databases for the valley to model the occurrence of atmospheric ammonia related to fertilizer application. Ammonia has significance to air quality both as a buffer against atmospheric acidity and as a precursor of $PM_{2.5}$ particles. The ARB funded project focused on monitoring fertilizer applications and the validation of the sampling method. The CDFA-FERP project used the methodology and equipment 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 atmospheric ammonia levels are found in a field, existing literature suggests those levels exist for only a short time. The final results of the research confirmed the fact that ammonia emissions were only significant for a short time (24-48 hours) following a fertilizer application. The emissions from the field were only significant during this short period following the application. No correlation was found between crop type or soil texture but emissions were found to be higher during the day and in the summer leading to the conclusion that emissions are strongly correlated with temperature. The methodology developed in this research was used to monitor differences in ammonia emissions from a variable rate N trial in 2004, also funded by CDFA-FREP. A summary of the various components of the project and related research was presented at the 2005 FREP conference. The paper from the proceedings is attached as Appendix A.

Objectives

The project has one primary and two secondary objectives. They are each related to the objectives of the ARB study as stated above in the summary. The objectives of the CDFA-FERP project are to further refine those models and conclusions to a level beyond the scope of the work funded by the ARB.

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 monitoring will be used in atmospheric models to add the seasonal data to the flux rates and regional budgets related to fertilizer applications as studied in the ARB project.

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

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

Workplan, Results, Discussion and Conclusions:
The primary objective will involve one task, repeated over at least ten different crop/soil/fertilizer combinations as monitored in the ARB study of fertilizer applications. The ten crop/soil/fertilizer combinations will be selected after the data has been analyzed from the initial year.

Task 1. Monitor atmospheric ammonia on a regular basis from the preliminary soil preparation to the post harvest cultural practices of a crop. The purpose of this task is to measure ammonia in the atmosphere from a crop during its entire season in order to compare the values with those that occur briefly as a result of the application of fertilizer.

Initiation – January, 2001 Completion: December, 2004

Subtask 1.1: Select at least ten crop/soil/fertilizer combinations of the sixteen that were chosen for the ARB study. The actual field sampled in the ARB study will be used if possible or a similar combination will be chosen if necessary.
Activity: The following crops were selected and locations determined for sampling in the first season: alfalfa, almonds (2), barley, citrus, corn, cotton, grapes (3), irrigated pasture (2), tomatoes (2), turf, and walnuts. In addition, natural vegetation sites were also selected to be sampled including: foothill range (4), Sierra Nevada conifer forest (2), and redwood forest. Sites for the crops were primarily located on the CSUF farm/laboratory and the Linden area. The range sites were at the San Joaquin Experimental Range-Oneals and Lawrence Livermore National Lab, the forest sites were selected in consultation with the US Forest Service and the redwood forest was selected in cooperation with UC Santa Cruz. Other crop and natural vegetation sampling sites will be selected later.

Subtask 1.2: Sample the atmospheric ammonia levels in the field in the same manner as detailed in the ARB study utilizing the sample traps and meteorological monitoring. A day and night sample for each crop will be taken every 15 to 30 days through the season.
Activity: All of the sampling sites identified in 1.1 have been sampled from the beginning of the crop through harvest where applicable. An additional two sampling systems have been constructed to bring the total to five. Data collection in the field will continue through the crop season.

Subtask 1.3: Include the seasonal ammonia values in the atmospheric flux and regional atmospheric budget models developed by Dr. Steve Klooster of CSU Monterey Bay and Dr. Chris Potter of NASA-Ames.
Subtask 1.4: Compile and submit an interim report to CDFA. Select further crops and soils to investigate in year 2 of the project.
Activity: The data collected to date is still being processed. Data sets for sites that have been completed were shared with the ARC-NASA scientists who will continue to update their model.

RESULTS from Task 1: Emissions of ammonia were very low and could not be correlated with crop/vegetation type. The emissions could be correlated with season and time of day. Ammonia emissions were significantly higher in the day time and in summer. It is apparent that ammonia emissions are primarily affected by soil and air temperature, not crop type or soil conditions. Detailed results from this portion of the project are included in the final report to the CSU Agricultural Research Initiative attached as Appendix B.

Task 2. Monitor atmospheric ammonia in a manner similar to that in Task 1 in crops with a range of soil textures and possibly other factors that are identified as affecting the emission of ammonia. The purpose of this task is to relate the emission of ammonia to differences in soil texture and other factors that will allow the application of precision agriculture practices to minimize the effect of those differences on fertilizer efficiency.

Initiation: January 2002 Completion: variable to December, 2004

Subtask 2.1: Select at least three crop/fertilizer combinations from the ARB matrix that are commonly found on a variety of soil textures. Locate at least three examples of each crop/fertilizer combination on soils with significantly different textures
Activity: Initial work on this task indicated little correlation with soil texture so emphasis was shifted to an investigation of other factors that influence ammonia emissions.

Subtask 2.2: Monitor ammonia emissions using the same methods developed for the ARB project for a period of 5-7 days around the application of N fertilizer to each soil texture of the three crop/fertilizer combinations.
Activity: Fertilizer ammonia emissions were shown to be correlated with weather conditions, soil pH and method of application rather than soil texture.

Subtask 2.3: Compare the emission of ammonia with the soil textures for the crop/fertilizer combinations. Prepare a report detailing the magnitude of the effect of soil texture and the potential for the utilization of precision agriculture techniques.
Activity: Initial work on this task indicated little correlation with soil texture so emphasis was shifted to an investigation of other factors that influence ammonia emissions. However, fertilizer ammonia emissions appear to be correlated with weather conditions, soil pH and method of application rather than soil texture.

Subtask 2.4: If the results of the project in year 2 warrant further work, prepare a plan to demonstrate the effectiveness of precision agriculture practices to minimize the effect of soil texture on ammonia loss.
Activity: Ammonia emissions monitoring was added to a study of variable rate planting and N applications affected by salinity and past yield on cotton in Kings County in 2003 and 2004. The project, directed by Bruce Roberts. It should be noted that participation in this project, also sponsored by FREP was one of the primary reasons for requesting the extension of this project.

RESULTS from Task 2: Though the expected correlation with soil texture did not occur, the monitoring techniques were able to detect small differences in ammonia emissions in the variable rate trial conducted by Dr. Roberts. The emissions monitoring portion of this project was conducted by a graduate student, Matthew Beene.

Task 3. Validate and disseminate methodology for monitoring atmospheric ammonia associated with crops and soils.

This task is to publicize the methods developed and validated in the ARB and CDFA-FERP projects for further research and routine monitoring of ammonia emissions from agricultural situations.

Initiation: January 2002 Completion: December, 2004

Task 3.1: Write a short document detailing the methodology of sampling and analysis used in the ARB project and Tasks 1 and 2 of the CDFA-FERP project. This document will be available to accompany any written report, oral presentation or inquiry regarding these projects by December, 2001.
Activity: Papers detailing the methodology and results from the initial project were prepared and presented at several professional meetings. See outreach summary

Task 3.2: Follow up and encourage and provide assistance to anyone attempting to use the methodology for monitoring ammonia emission in year 2 and 3 of this project.
Activity: The CSU Fresno research team was approached by the ARB, the San Joaquin Air Pollution Control District and the dairy industry and are currently applying the sampling methodology to monitor ammonia and other gasses related to dairy operations. The project began this work in the fall of last year and will continue through June ‘09. A part of these projects is to monitor land applications of dairy effluent to determine the emission patterns in a manner similar to those established for fertilizer applications in this project. The emissions data will be used to modify a bio-geochemical model, DNDC developed at U New Hampshire to predict ammonia and N_2O emissions from dairy operations.

Task 3.3: Write a document to be available through various agencies including but not limited to California Agricultural Technology Institute, CSUF Center for Irrigation Technology and CDFA-FERP regarding the method and relating experiences with it in these and other projects. This document would be available December, 2002.
Activity: This task has been satisfied by the presentation of several papers and posters at professional meeting that published the details of the method. The methodology is presented in detail in the CSU-ARI final report attached as Appendix B.

RESULTS from Task 3: The determination of ammonia emissions using ambient samples and dispersion modeling was generally successful in accomplishing the tasks of this and the related research projects. It is, however, difficult and expensive to a degree that prevents its use as a method for routine monitoring by technical rather than research personnel. New methodology has been adapted from air quality research programs to be used to monitor specific sites at dairy operations. The use of Tunable Diode Lasers and Flux Chambers provide more precision and better modeling data. Those field and laboratory methods will be presented in subsequent reports and presentations from those new studies.

Project Evaluation:

This project, though it did not achieve the expected results from Task 2, provided information that has already been used to refine the emissions inventory for California. The original estimate used by the CARB that 5% to 10% of applied N fertilizer is emitted as atmospheric NH_3 has been shown to be a significant overestimation. The actual average is less than 3% and the highest emission rate monitored, under the most extreme conditions of a surface application to a high pH soil was less than 7%. Further investigations, primarily from the FREP funding, indicated the NH_3 emissions from crop production during the rest of the season are insignificant compared to those that occur within a few days of a fertilizer application. The final evaluation of the work done with the CDFA-FREP funding would be that it played a significant role in the development of a considerable body of knowledge related to NH_3 emissions related to crop production and fertilizer applications. That body of knowledge is now the basis of the current CARB Emissions Inventory for agricultural emissions from crop fertilization. The methodology developed in these studies is currently being used to validate the effects of practices that can reduce ammonia emissions from fertilizer applications and dairy operations.

Outreach Summary:
A number of papers, presentations, posters and project reports were based on research funded by this project. In addition to the CSU-ARI final report (Appendix B) and the Masters Thesis, the following have been written or presented at various professional venues. In each case, the funding and other support from CDFA-FREP was gratefully acknowledged.

Publications:

Krauter, Charles, Dave Goorahoo, Steven Klooster, and Christopher Potter, Ammonia Emission Related to Nitrogen Fertilizer Application Practices, Proceedings of the California Department of Food and Agriculture Fertilizer Education Program Conference, Tulare, CA, November, 2001

Potter, Christopher, Charles Krauter and Steven Klooster. Statewide Inventory Estimates of Ammonia Emissions From Chemical Fertilizers in California. Project report to the California Air Resources Board. July, 2001

Fitz, D.F., J.T. Pisano, D. Goorahoo, C.F. Krauter and I.L. Malkina. 2003. A passive flux denuder for evaluating emissions of ammonia at a dairy farm. Submitted Agricultural Waste Management. *In Press.* (Peer Reviewed).

Beene M., C. Krauter and D. Goorahoo. 2002. Seasonal ammonia emissions from crops in the San Joaquin Valley, California. Proceedings of the Annual Crops, Soils and Agronomy Societies of America meeting held in Indianapolis, IN., in November 2002.

Krauter, C.F., C. Potter and S. Klooster. 2002. Ammonia Emission Related to Nitrogen, Proceedings of the California Department of Food and Agriculture Fertilizer Education Program Conference, Tulare, CA, November, 2002

Krauter C., D. Goorahoo, C. Potter and S. Klooster 2003. Ammonia Flux Profiles For Various Soil and Vegetation Communities in California. Proceedings of the EPA Emission Inventory Conference in San Diego California on April 30th 2003.

Krauter, C. F., D. Goorahoo and M. Beene. 2003. Atmospheric Ammonia Profiles Over Various Crops in the San Joaquin Valley. Proceedings of the California Plant and Soil Conference. American Society of Agronomy meeting in Modesto, CA in February, 2003.

Krauter, C. F. and S. Olsen. 2003. Air Sampling Indicates Dairy Emissions Lower Than Previously Believed. CATI Update, page 1, Spring 2003.

Krauter, C. M. Beene, D. Goorahoo. Ammonia Emissions From Fertilizer Applications. Proceedings of the CDFA-FREP Conference. November, 2005. Salinas, CA.

Presentations:

Krauter, Charles. Ammonia Emissions and Fertilizer Application Practices in California's Central Valley. Plant and Soil Conference. American Society of Agronomy California Chapter. Fresno, CA February 2001

Krauter, Charles and Dave Goorahoo. Ammonia Emissions from Nitrogen Fertilizer Applications - Field Sampling Methodology. Central California Research Symposium. Fresno, CA. April 2001

Krauter, Charles. Ammonia Emissions and Fertilizer Application Practices in California's Central Valley. Plant and Soil Conference. American Society of Agronomy California Chapter. Fresno, CA February 2001

Krauter, Charles; Christopher Potter and Steven Klooster. Emissions Inventories for Ammonia in Agricultural Systems of California. California Air Resources Board Workshop. Sacramento, CA October, 2000.

Krauter, Charles and Dave Goorahoo. Monitoring Volatile Ammonia As a Result of Nitrogen Fertilizer Applications. Natural Resources Conservation Service Workshop. Fresno, CA. August, 2000

Krauter, Charles and Dave Goorahoo. Ammonia Emissions from Nitrogen Fertilizer Applications - Field Sampling Methodology. College of Agricultural Sciences & Technology Faculty Seminar Series, March, 2002

Krauter, Charles, Dave Goorahoo, Steven Klooster, and Christopher Potter, Ammonia Emissions and Fertilizer Application Practices in California's Central Valley. Emissions Inventory Conference. Air Quality Planning and Standards Division, Environmental Protection Agency. Atlanta, GA, April, 2002

Krauter, Charles, Dave Goorahoo and Chris Potter Ammonia Emissions and Fertilizer Application Practices in California's Central Valley. Plant and Soil Conference. American Society of Agronomy California Chapter. Fresno, CA January 2002

Goorahoo, Dave, Charles Krauter, Chris Potter and Steve Klooster. Monitoring Volatile Ammonia As a Result of Nitrogen Fertilizer Applications. Soil Science Society, Annual Meeting -2001. Durham NC. October 2001

Krauter, Charles. Ammonia Emissions and Fertilizer Application Practices in California's Central Valley. Proceedings of the American Agronomy Society - California Chapter, pp.93-99. February 2001

Goorahoo D., M. Beene and C. Krauter. Air Quality-Agriculture Related Research at CSUF. Workshop conducted as part of the con-current sessions at the CA Chapter of the Soil and Water Conservation Society Conference in Fresno on May 2nd 2003.

Goorahoo D., and C. Krauter. Ammonia losses during fertilizer and irrigation practices. Seminar conducted for visiting scientists on April 29th 2003 as part of the Cochran fellowship hosted by CIT.

Krauter C, M. Beene, and D. Goorahoo. Measurement of Reactive Organic Gasses (ROG) at a Dairy Correlated with Ammonia Emissions. Presented at the EPA Emissions Inventory Conference in San Diego California on April 30th 2003.

Krauter C, D. Goorahoo, and M. Beene. Air Quality Research Related to Dairy Operations. Presented at the Air and Waste Annual Technical Conference in Bakersfield on March 25th 2003

Krauter C, D. Goorahoo, and M. Beene. Air Quality Research Related to Dairy Operations. Presented at the Central California Research Symposium at CSUF on April 17th 2003.

Goorahoo D., and C. Krauter. Compensating for ammonia losses during fertigation. Presented at the Vegetables West Expo in Salinas CA. on February 20, 2003.

Krauter, C., D. Goorahoo, and M. Beene. Ammonia Emissions and Fertilizer Application Practices in the Central Valley. World Ag Expo. Tulare, CA. February 2003

Krauter C, D. Goorahoo, and M. Beene. Air Quality Research Related to Crop Production and Dairy Operations. Presented to the Lawrence Berkeley Laboratory – California Water Institute Workshop for cooperative research. May 2, 2003

Krauter C, D. Goorahoo, and M. Beene. Air Quality Research Related to Dairy Operations. Invited testimony to the California State Senate Select Committee on Air Quality in the Central Valley. Shafter, CA on May 1, 2003

Krauter, C. M. Beene, D. Goorahoo. Public meeting held by Congressmen Costa and Nunes. Dairy Air Quality Research at CSU Fresno. August 29, 2005. Fresno, CA

Krauter, C. M. Beene, D. Goorahoo, B. Goodrich. California Department of Food and Agriculture – Air Quality Hearings. Air Quality Research Projects and Results at CSU Fresno. October 26, 2005. Sacramento, CA

Krauter, C. M. Beene, D. Goorahoo. Western Dairy Air Quality Symposium. Ammonia Emissions From Dairy Operations in California. March, 2006. Las Vegas, NV

Krauter, C. M. Beene, D. Goorahoo. California Department of Food and Agriculture – Fertilizer Research and Education Program Conference. Ammonia Emissions From Fertilizer Applications. November, 2005. Salinas, CA.

Krauter, C. M. Beene, D. Goorahoo. Ecological Society of America. Workshop on Agricultural Air Quality: The State of the Science. Ammonia Emissions From Dairy Operations in California. June, 2006. Annapolis, MD

Krauter, C. M. Beene, D. Goorahoo. Environmental Protection Agency's 18th Emissions Inventory Conference. Ammonia Emissions From Dairy Operations in California. May, 2006. New Orleans, LA

Appendix A

Ammonia Emissions and Fertilizer Applications in California's Central Valley.

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Ammonia Emissions Estimates for Various Fertilizer Applications

Ammonia is the dominant gaseous base in the atmosphere and a principal neutralizing agent for atmospheric acids. The NH_3 in the atmosphere, along with alkaline soil dust, may control the acidity of precipitation. Volatilized NH_3 may react to form ammonium nitrate or ammonium sulfate and thereby contribute to airborne particulate matter (PM). National standards in the United States for PM apply to the mass concentrations of particles with aerodynamic diameters less than 2.5 microns ($PM_{2.5}$) and less than 10 microns (PM_{10}). Estimated patterns of nitrogen deposition suggest that, for California locations close to photochemical smog source areas, concentrations of oxidized forms of N dominate, while in areas near agricultural activities the importance of reduced N forms may increase significantly according to Bytnerowicz and Fenn (1996)

NH_3 remains one of the most poorly characterized atmospheric trace compounds in terms of overall sources. This situation persists as a result of several factors such as; experimental difficulties associated with NH_3 measurements, rapid gas-to-particle conversion of NH_3 in the atmosphere, the capacity of soils, organic matter, vegetation to act as both sources and sinks for atmospheric NH_3, and variability in nitrogen fertilizer management and related NH_3 emissions (Langford et al., 1992). Consequently, there is a limited amount of published information from which to develop direct emissions estimates of NH_3 for the state of California in general, and the state's Central Valley in particular. Preliminary measurements of NH_3 background concentrations in the San Joaquin Valley by Fitz et al. (1997)estimated February levels of 3-16 $\mu g\ m^{-3}$ near alfalfa fields. The magnitude and distribution (both regionally and seasonally) of current NH_3 emissions from fertilizer and other agricultural sources is still largely undetermined for the state of California and many other large regions where agriculture is a major land use (Matthews, 1994).

The objectives of this study were to measure and characterize rates of ammonia emissions related to applications of N fertilizer followed by an investigation of the variability of atmospheric ammonia as it is affected by climate, time of day, crop type and other environmental factors. Finally, an attempt to measure the effects of variable rate N applications on ammonia emissions was added to the project in its final year.

The sampling device selected for the project was an active denuder. It represented an established method in air quality studies and it satisfied the inventory development requirement for continuous sampling of emissions over relatively long time periods and large plot areas. The denuder is a medium through which an air stream is passed in a manner similar to a filter for particulates. In the case of NH_3 it is a fibrous material, usually glass, treated with a substance (citric acid) that will react with NH_3 to form a solid. For this study, a 47 mm 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 with a flow regulator was used to pull air through the denuder disk at a rate of about four liters per minute. Air flow was monitored by a rotameter accurate to 0.1 liters/minute and the flow was recorded at the beginning and end of each sampling period. 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 CSU-Fresno, College of Agricultural Science and Technology for analysis. The NH_4-citrate was extracted from the denuder with distilled water and analyzed with a spectrophotometer. The amount of ammonia on the denuder disk was reported in $\mu g\ NH_3$. 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 (m^3) of air pumped through the denuder in the sampling period to derive the concentration in units of $\mu g\ N\ NH_3\ m^{-3}$ air at the sampling point.

The concentration of NH_3 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 air at the sampling point. The value necessary to characterize the sampling point was the flux in $\mu g\ N\text{-}\ NH_3\ m^{-2}\ s^{-1}$. The initial assumption during the planning of the project 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 co-located at 1, 2, 5, 10 and 18 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 would be found and could be used to determine the magnitude of the emission factor for the sampling period. Prior to the fertilizer 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. The stomata and internal structure of the leaf that functions to absorb CO_2 from the air should also effectively absorb NH_3 from the atmosphere near the foliage. Alternatively, the sampling at a site might well exhibit what appears to be a negative gradient, as NH_3 in air from nearby point sources (such as livestock or other fertilizer applications) moves over the field and is sampled. The actual results varied somewhat from the initial assumption in that the gradient of NH_3 was almost always from the ambient atmosphere to the soil/vegetation surface over the elevation range that was sampled. The magnitude of the NH_3 fluxes increased following the fertilizer application but the gradient almost always remained negative.

Field Sampling Results

Measurement results confirm that field sampling by the micrometeorological mass balance method can detect volatile NH_3 from an application of N fertilizer. In each of the applications for which data is available; an increased level of atmospheric NH_3 was measured compared to the levels sampled both before and after the application. The expected positive gradient of NH_3 fluxes from the surface toward the ambient atmosphere was apparent at only one of the sites, the pasture fertilized with effluent from a dairy shown in Figure 1. The traditional fertilizer applications at the other sites exhibited the increase in NH_3 flux that indicated a positive emission factor but the gradient of the fluxes remained lower at the soil/vegetation surface as shown in Figure 2. The line in Figures 1 and 2 labeled "Application" is the average of 2 to 5 sampling periods during which the N application was actually occurring. The lines labeled "Pre-application" and "Post-application" were the averages of 2 to 10 samples taken prior to and after the application. The "Application" values were greater than those before and after in each of the sites analyzed. This is the basis for the conclusion that the methodology can detect volatile NH_3 resulting from a fertilizer application.

Figure 1. Ammonia flux profiles for dairy lagoon effluent applied to irrigated, sheep pasture on the CSU Fresno farm- laboratory June, 2000 (site L).

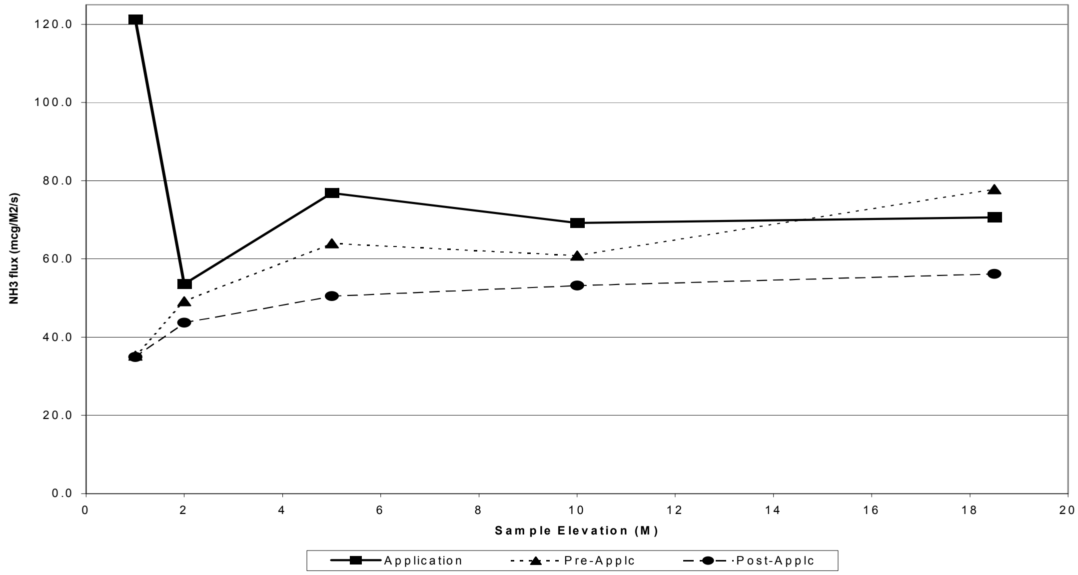
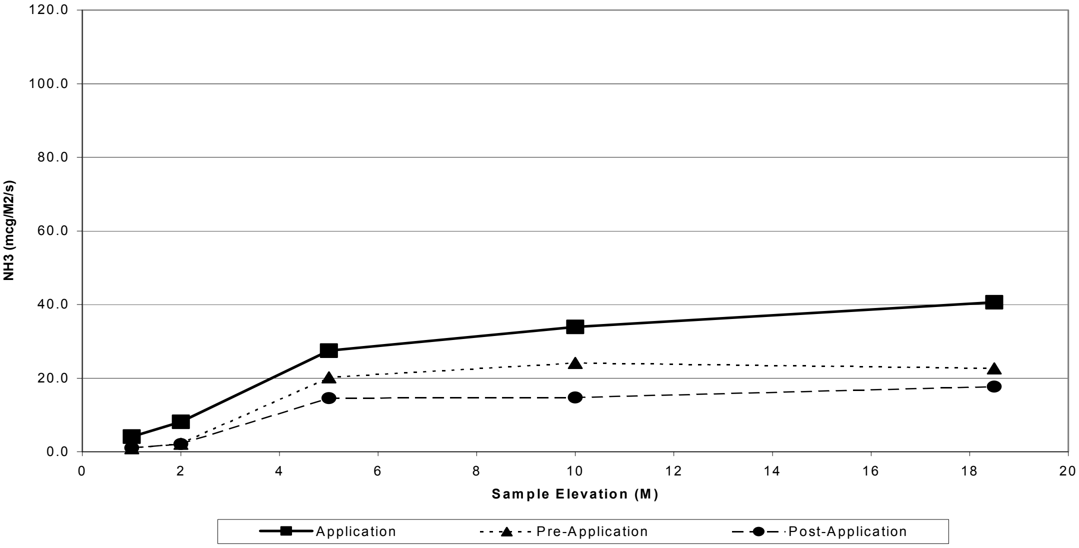


Figure 2. Ammonia flux profiles for NH_4NO_3 broadcast on the soil surface of an orange grove near Sanger, California, February, 2000 (Site D).



Standard mass balance micrometeorological techniques (Denmead, 1983) were used to estimate the integrated NH_3 flux by combining measurements of wind speed and NH_3 air sample concentrations from height-dependent sampling locations mounted on the portable mast.

The surface flux density of a gas can be calculated according to equation 1.

Equation (1) $F = {}_0\!\int^{z} U\ (\rho_g - \rho_b)\ \partial z$

where

F = the surface flux density of a gas
$U(z)$ = the horizontal wind speed at sampling height z
ρ_g = the atmospheric gas concentration at the height of the sampler
ρ_b = the background atmospheric gas concentration from upwind of the field plot

Previous field tests (Leuning et al. 1985) suggest that this equation tends to overestimate true fluxes due to turbulent diffusive flow in the opposite (upwind) direction. Therefore, following the recommendation from Denmead, emissions calculated from this equation were reduced by 15%.

To describe the NH_3 emission resulting from the fertilizer application, integration calculations were made using a fourth-order polynomial fit to the height-dependent horizontal flux points for each sampling period. Integration under the time series curves and adjustment for fetch distance were made to determine the total $N\text{-}NH_3$ emitted as vertical fluxes over the entire time period sampled, beginning at the time of the first fertilizer application. To compute the site emission factor, the total $N\text{-}NH_3$ emitted was divided into the total kg N applied m^{-2} area for that site sampling period.

Emission flux totals of NH_3 for all fertilized sites analyzed to date show a notable consistency of emission factor estimates among the different crop types and fertilizer amounts applied as shown in Table 1. While total NH_3 nitrogen losses ranged from 0.01 to 0.7 g $N\text{-}NH_3$ m^{-2}, the estimated emission factor values for the sites analyzed range from 0.05% to 6.6% with the average at about 3.2%. It appears the sites that produced lower emission factor estimates were primarily those sites where fertilizer was applied in a manner that placed the fertilizer material below the soil surface.

Table 1. Summary of field sampling sites with fertilizer, irrigation and emission factor estimates.

SITE	CROP	N lb/Ac	g N m^{-2}	Fertilizer Type	Irrigation Type	Soil pH	Emission g NH_3 m^{-2}	Emission Factor
B	Almonds	100	10.9	C	G	8.1	0.72	6.6%
D	Citrus	50	5.5	C	G	6.1	0.24	4.3%
E	Almonds	100	10.9	D	M	6.4	0.51	4.7%
F	Onion	40	4.4	D	S	8.4	0.28	6.5%
G	Tomato	100	10.9	D	G	7.9	0.10	0.9%
H	Garlic	50	5.5	D	G	7.9	0.32	5.8%
I	Cotton	100	10.9	A	G	8.5	0.62	5.6%
J	Cotton	100	10.9	A	G	7.8	0.43	3.9%
K	Almonds	9	1.0	A	M	6.4	0.00	0.0%
L	Pasture	100	10.9	F	G	6.6	0.32	2.9%
M	Broccoli	60	6.5	C	S	7.9	0.10	1.6%
Q	Lettuce	40	4.4	D	G	7.8	0.02	0.5%
R	Tomato	80	8.7	A	G	7.9	0.01	0.1%
S	Cotton	100	10.9	A	G	8.5	0.14	1.3%
							Ave. Emission Factor	3.2%

Fertilizer Type Codes
A = anhydrous NH_3 or Urea-Ammonium Nitrate below the soil surface at 10-20 cm depth
C = dry Ammonium Nitrate/Sulfate applied to soil followed by irrigation
D = Urea-Ammonium Nitrate (UAN) liquid mixed into irrigation water
F = dairy lagoon effluent mixed in irrigation water

Irrigation Type Codes
G = gravity, surface/flood
S = sprinkler
M = microsprayer/drip

Statewide Ammonia Emission Estimates From Fertilized Crops

The emission factors estimated from the field data, shown in Table 1 were used with correlating data from several sources to build a database for an atmospheric model used at the Ames Research Center - NASA. This database included crop acreage and locations by counties, soil information, and fertilizer application amounts and methods. The crop acreage data was obtained from the California Department of Water Resources. Fertilizer applications were not available from any public source so data was estimated by questioning farmers, fertilizer industry members, county farm advisors and other crop specialists. The practices varied across the state, as expected but could be correlated with the county based crop acreage data. The database was used to estimate the application of the various types of N fertilizer to the crops of the state. These estimates were checked by comparing them with the public records of fertilizer sales from the California Department of Food and Ag.,(1999).

The estimated fertilizer applications over the state were then matched with ammonia emission factors from the most similar site monitored during the field study. The soil pH and textural data from the Natural Resources Conservation Service were used along with the rest of the database in a rule-based atmospheric model at the Ames Research Center - NASA to estimate the distribution of ammonia emission across the state from fertilizer applications to agricultural land. The rule-based model was used to assign NH_3 emission factors, together with the county level fertilizer application rates to create the statewide inventory estimate for emissions of NH_3 directly from fertilizer applications shown in Table 2. The total of these emissions is estimated to be 11.7×10^6 kg N- NH_3 annually. The leading counties for annual emissions of NH_3 directly from fertilizer sources are Imperial, Fresno, Kern, Tulare, and Kings. Overall, the San Joaquin Valley area accounts for more than one-half of the state's total annual emissions of NH_3 directly from fertilizer sources. The Imperial Valley accounts for a higher proportion of the state's total annual emissions of NH_3 from fertilizer sources than would be predicted from crop area alone, primarily due to the high proportion of soils with pH above 8 and a major portion of the estimated fertilizer applications to the soil surface.

Table 6. 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%**

Emission flux totals of NH_3 for fertilized sites in California's Central Valley shows consistency of emissions factor estimates, regardless of the crop types and fertilizer amounts. Total measured NH_3 losses for the fertilizer applications ranged from less than 0.1 to 0.7 g N-NH_3 m^{-2} (equal to 0.9 to 6.2 lbs. N-NH_3 emitted per acre). The estimated NH_3 emission factor values for the field sites analyzed to date range from 0.05% to 6.6% of total applied N fertilizer with an average at about 3.2% of applied nitrogen.

Field flux measurements imply that the single most important factor affecting the NH_3 emission rates from cropped sources in the Central Valley is the amount of chemical fertilizer applied. Field flux measurements suggest that other significant limiting factors of NH_3 emission rates from fertilizers include soil pH and the method of N fertilizer application. When the fertilizer ammonia emission factors developed through this research are used to calculate statewide ammonia emissions for fertilizer application, the average fertilizer NH_3 emission factor for California is 2.4% of the total applied N fertilizer.

Statewide emissions of NH_3 directly from chemical fertilizer applications are estimated to total nearly 12×10^6 kg N- NH_3 annually. The San Joaquin Valley accounts for just over one-half of the state's total annual emissions of NH_3 directly from agricultural application of fertilizers. On the basis of DWR crop types, it appears that the generalized categories of field crops and truck crops each account for about one-third of the state's total annual emissions of NH_3 directly from chemical fertilizer sources. Grain, pasture grass, and rice crop categories also contribute large fractions of the state's total annual emissions of NH_3 directly from chemical fertilizer sources.

Ammonia Flux Profiles for Various Soil and Vegetation Communities in California

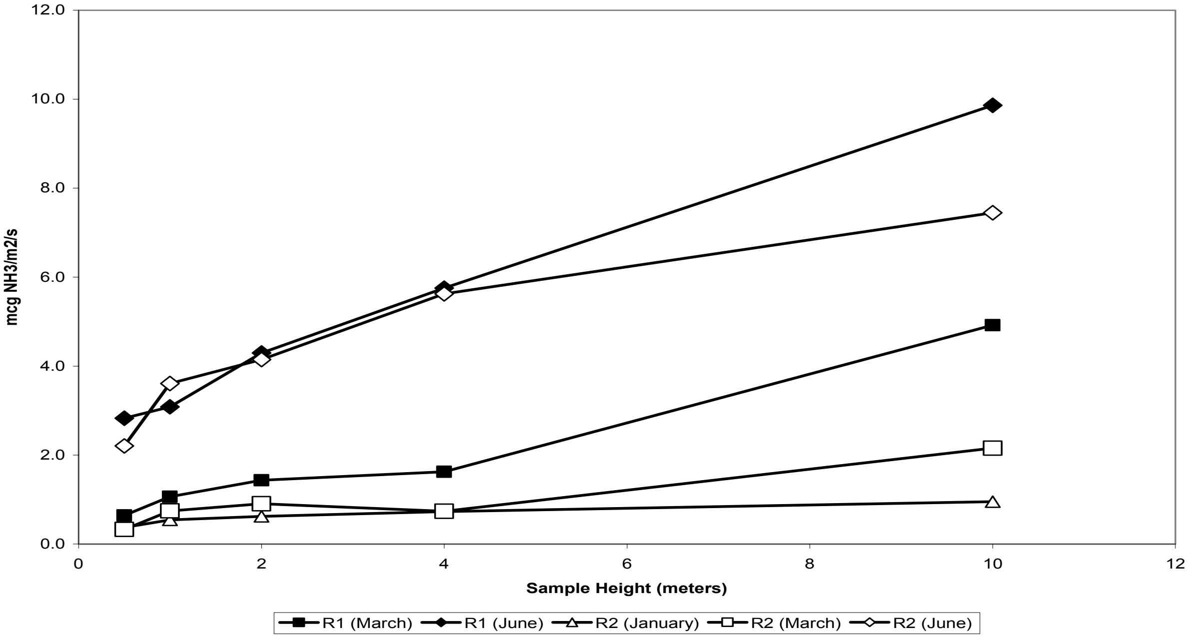
In the second phase of the project, atmospheric ammonia was sampled using the same active denuders co-located with wind instruments on a mast from near the soil surface to a height of 10m. NH_3 flux profiles were calculated from the data for a variety of soil/vegetation communities in central California. Profiles were calculated from samples taken several times during the season at the same location. Sites included rangeland in the Sierra Nevada foothills, various crops and a dairy operation in the San Joaquin Valley. The magnitude and characteristics of the NH_3 flux profiles were compared to similar data from other research outside California and correlations with air temperature and diurnal differences were similar to those found elsewhere. Some indication of NH_3 absorption by active vegetation was found under circumstances where ambient concentrations were high.

Ammonia is one of the end products of organic matter decomposition by soil fungi and bacteria. Some NH_3 will find its way to the atmosphere and, under certain soil conditions, there may be significant volatile losses. The fate of the NH_3 after it reaches the atmosphere is less well known. The formation of secondary particles, $PM_{2.5}$ described above, is certainly one possibility. However, the fate of NH_3 in the micro-climate near active vegetation appears to be complex. The interior structure of the typical plant leaf is adapted to absorb atmospheric CO_2 for photosynthesis. The diffusive characteristics of NH_3 in the atmosphere are likely to be similar to CO_2 suggesting the possibility of NH_3 absorption as well. Harper et al. (1983) found NH_3 losses to the atmosphere from tropical pastures in Australia after fertilization and at various other times through the season. NH_3 losses were correlated with high air temperatures and solar radiation levels. Absorption by vegetation was observed during the same study correlated with dawn and dusk periods. Harper et al. (1996), on a temperate grassland in Georgia, found emissions after fertilization but again measured NH_3 absorption by the vegetation. He estimated 6% of the N in the vegetation was absorbed as atmospheric NH_3 in the cooler part of the growing season and 11% in the summer. An earlier investigation by Harper and Sharpe,(1995) on irrigated corn in Nebraska used ^{15}N labeled fertilizer to show both emission and absorption of NH_3 by the crop at various times through the season. Some absorption of ^{15}N labeled NH_3 by crops that had not been fertilized was detected; indicating the possibility that emission of NH_3 from fertilized plots was absorbed by nearby vegetation. NH_3 absorption was correlated with air temperature, solar radiation, soil moisture, soil N levels but primarily with NH_3 concentration in the atmosphere. High atmospheric NH_3 resulted in absorption regardless of the other factors. Absorption of NH_3 has been reported in other research, notably Porter et al.(1972), where corn seedlings were placed in an atmosphere spiked with labeled $^{15}NH_3$. They found absorption of up to 30% of NH_3 in a 24 hour period.

The somewhat contradictory findings sited above illustrate the complexity of NH_3 transport in the soil-plant-atmosphere system. The data presented below are from a variety of soils and vegetation communities in California. The same sites were sampled at various times of the year. Sampling was continuous over several days and included separate diurnal samples. The results, to date, suggest both emission and absorption correlated with many of the same factors seen in the previous research.

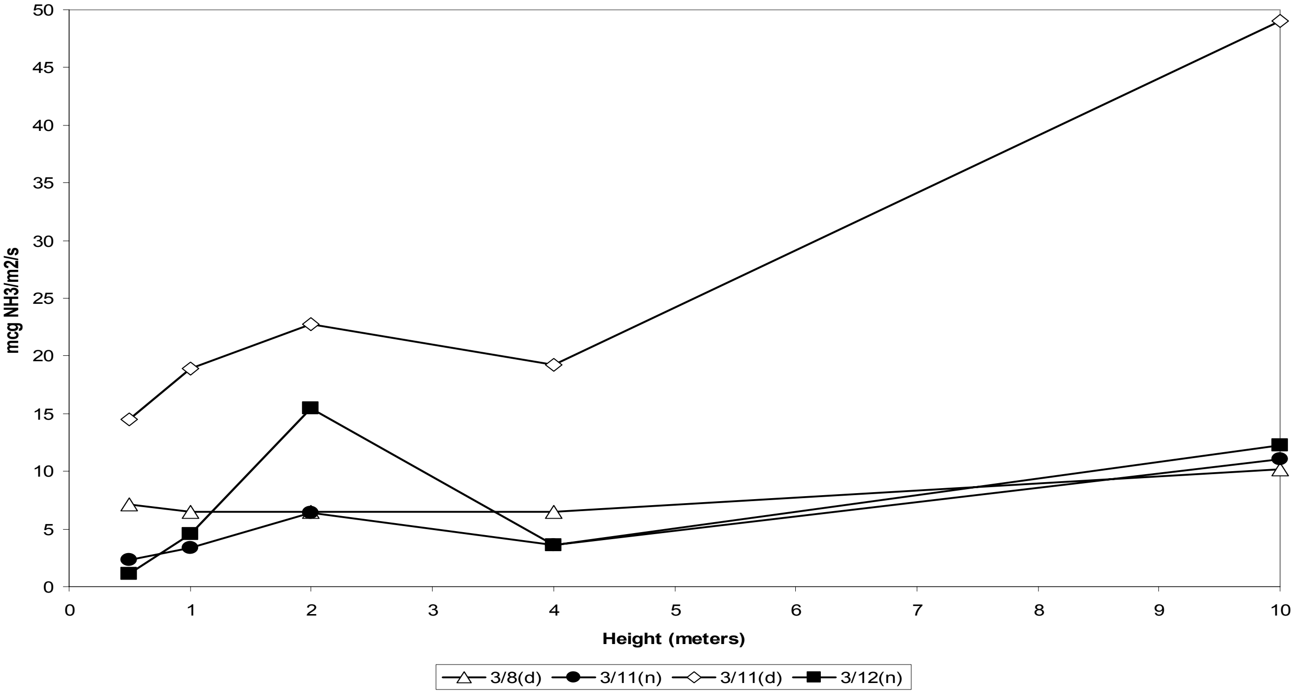
A correlation between air temperature and NH_3 levels was anticipated. One of the reasons for sampling the same site at various times through the year was to verify that relationship. The magnitude of the flux and the characteristics of the vertical profile did appear to correlate with the average air temperature. The San Joaquin Experimental Range is a 2000 Ha field site administered by CSU Fresno for the US Forest Service. Two sampling sites were designated and sampled every few months beginning in January of 2002. Some of the data is shown below in Figure 3. The average air temperature during the sampling in January was 8.6 C. In March the average was 14.6, and in June the temperature averaged 24.0 C. The lowest NH_3 values were in January, the highest in June. There were two sampling sites and both sets of flux profiles appear to be correlated with temperature. Site R1 was in an open meadow of annual grasses. Site R2 had brush and trees enclosing a small area of grasses. It is likely that the air temperature, particularly in the shade, near the soil surface was lower at R2. The NH_3 flux values were higher for the R1 site sampled at the same time as the R2 site, particularly at 10m. The difference may be due in part to temperature. The R1 site had no tall vegetation within 50m of the mast compared to the R2 site where there were 20m trees within 5m of the mast.

Figure 3. Ammonia flux profiles for two rangeland sites located 40 km north of Fresno at an elevation of 300m. Each line represents an average of 3 to 5 days of continuous sampling. The two sites were about 200m apart. R1 (closed graph symbols) was an open grassland with no trees or brush within 50m of the mast and R2 (open symbols) had a higher level of vegetation; a mix of grass, brush and trees.



A second relationship between an environmental factor and atmospheric NH_3 flux profiles is the distinct, diurnal difference. In each sampling episode to date, at least one day of collection was divided into a day and night sample. Nearly every one of those diurnal sample pairs showed considerably more NH_3 during the day compared to the night sample. Figure 2 is data from a field planted to barley. There were three periods of sampling from the seedling stage in November of 2001 to the harvest in March, 2002. The average of the flux profiles for each sampling period showed the same correlation with air temperature as the rangeland in Figure 3. Figure 4 shows the diurnal differences for the last sampling in early March.

Figure 4. Ammonia flux profiles over a barley crop just prior to cutting for silage. Plant height was about 1m. Day time samples are designated by (d) in the legend and an open symbol on the graph. Night data is shown as (n) and a closed symbol.

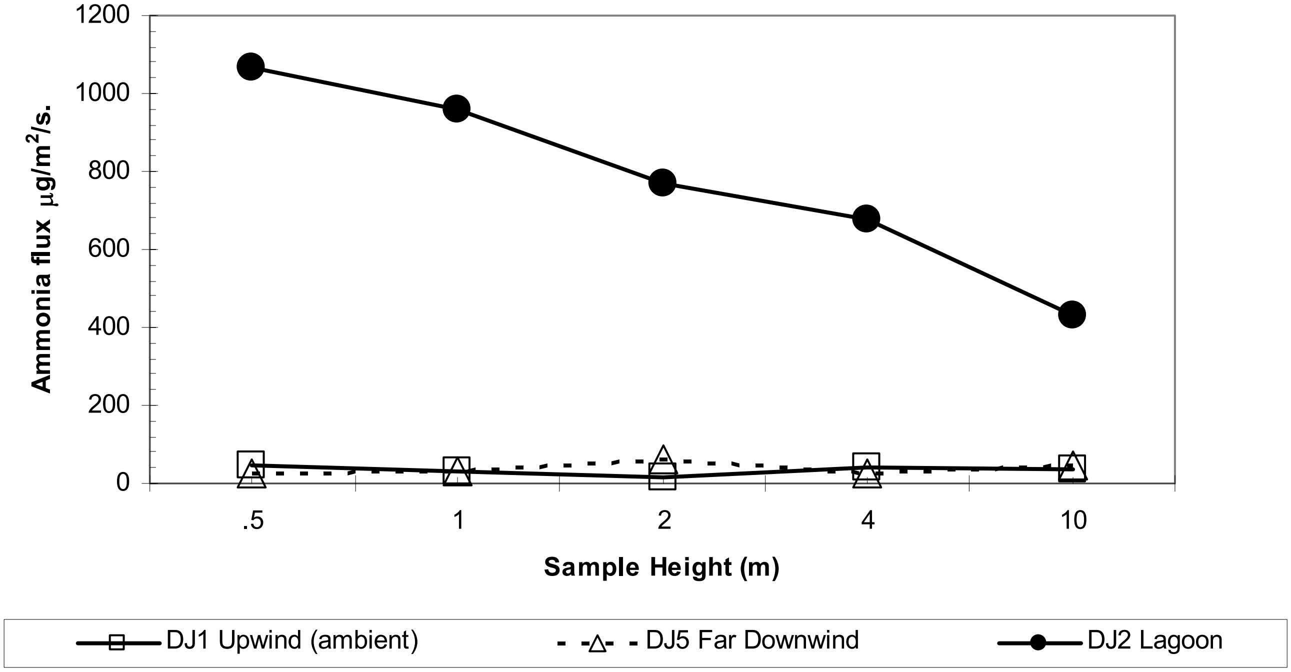


The two night samples are lower in magnitude and show less profile difference over the sampling heights. The day sample for March 11 is typical of day samples for most of the vegetation types in the study. The magnitude is considerably higher and there is a more pronounced gradient of flux values between the 10m sample and the 0.5m sample. The other day sample, March 8, appears to violate the postulated correlation. Its profile is more characteristic of a night sample. March 11 was a typical spring day in the San Joaquin Valley. The average temperature was 19.9 C, relative humidity was 41%, with a light wind. March 8 was a cool day (13.5 C) near the end of a storm event that dropped 12mm of rain. The air temperature during the storm was more characteristic of night time levels. It is also likely the moisture in the air reduced the NH_3 values. Increased atmospheric moisture, either elevated humidity or precipitation, has been linked to lowered NH_3 levels in previous work.

The NH_3 absorption by active vegetation that was suggested in Harper's research also appears to apply to the data collected for this study. Many of the flux profiles shown in the previous figures indicate a gradient of NH_3 from the atmosphere to the soil/vegetation surface. While the transport pathways in the microclimate from the surface up to 10m are likely to be complex and variable for different times of the day and season; it is possible to speculate that the vegetation is acting as a net absorber of NH_3 when the flux profile shows a steep gradient from the ambient atmosphere toward the surface. Both Harper and Porter's work concluded absorption of NH_3 by the plant from the air was related to the amount of atmospheric NH_3 surrounding the plants. Harper noted several factors that sometimes correlated with absorption but stated the concentration of NH_3 in the air was the most consistent factor affecting NH_3 absorption and found it would supersede the other factors. Atmospheric NH_3 concentrations found by Harper to result in measurable absorption were less than most of those monitored at10m in this study. The ability of a vegetation/soil community to both emit and absorb atmospheric NH_3 may be illustrated by data from another sampling location of this project. A dairy near Merced was chosen for a series of air quality samples and a variety of constituents including NH_3 were collected. Ammonia profiles were measured at three sampling locations at the dairy:

The NH_3 flux profile for the DJ1 (upwind location) resembles those found for similar crops in central California. The winter silage is not unlike the barley and corn crops shown in Figures 2 and 3; and the flux profiles are similar in both magnitude and shape. The Lagoon sampling location, DJ2, shows a significant increase in NH_3 magnitude, which is to be expected from the 3500 Holsteins located between the two sampling points. Most of the NH_3 is probably from catalysis of urea by urease in the soil of the free stall, open areas and lagoon system of the CAFO. The sampling site was located 5m from the downwind edge of the lagoon. Absorption of NH_3 from the air by a surface across which the air passes may also be indicated by the NH_3 flux profile at DJ5, the sampling site downwind from DJ2. The typical wind direction is directly from DJ2 to DJ5. The primary influences on the NH_3 profile between those two points would be various dispersion mechanisms in the atmosphere and emission/absorption of NH_3 by the surface. The fluxes downwind of the field have dropped to those monitored at the upwind site, DW1, which would be considered background. The surface over which the air passed from DJ2 to DJ5 was the winter silage crop. The high ambient NH_3 levels at DJ2 would, according to Harper, indicate the absorption of atmospheric NH_3 by the leaves of the vegetation. The reduction of the fluxes to background levels after crossing 500m of vegetation appears to be strong evidence that vegetative absorption of atmospheric NH_3 is taking place.

Figure 5. Ammonia flux profiles associated with a Central Valley Dairy. The upwind was 50m NW of the first dairy barn, the lagoon sample was along the southern edge of the lagoon and the Far Downwind sample was taken at the SE corner of the field downwind of the dairy, approximately 500m from the lagoon..



A number of the project's initial assumptions appear to be on the way to confirmation and the significance of some others may be greater than was originally assumed. It certainly appears that atmospheric NH_3 is higher during the day compared to night. The increase in NH_3 emissions with higher air temperatures suggested by Harper and others is also consistent with the data collected in this research. The characteristic shape of most flux profiles suggests a net absorption of NH_3 near the surface. Knowledge of the N cycle, particularly for cultivated, fertilized crops would suggest there is a significant amount of NH_3 produced by soil microbes. The fate of the NH_3 produced in the soil is complex and not well documented but emission of a portion of it to the atmosphere is almost a certainty, as modeled by CASA. The intriguing suggestion, originally from Harper and others is the fact that NH_3 absorption by vegetation is as viable a fate for atmospheric NH_3 as is the hydrolysis by rain and dew, dry deposition, and the combination with NO_x and SO_x to form secondary $PM_{2.5}$ particles; the reason this study was commissioned.

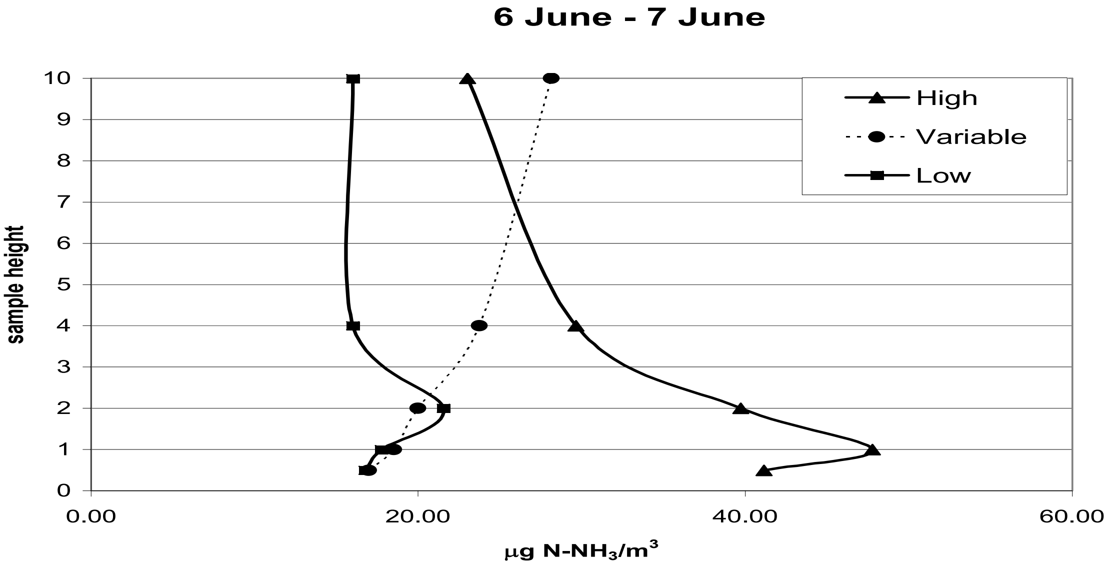
Ammonia Emissions From N Applied in a Site Specific Manner

Cotton ranks as one of the major crops in California in terms of total acreage and income. Most cotton production in the state of California takes place in the San Joaquin Valley. Fertilizer rate were shown in the previous phases of this project to be a factor in ammonia volatilization. The objective of this study was to evaluate the effect of fertilizer rate on ammonia emissions following a variable rate fertilizer application. If applying a reduced rate of nitrogen fertilizer reduced ammonia emissions than variable rate technology which only places fertilizer where it is needed, would reduce ammonia emissions as well as decrease inputs for cotton growers. This is significant in that not only are growers saving money on nitrogen fertilizers, but as less ammonia is emitted there is a reduced environmental impact.

A nitrogen fertilization trial was conducted on a cotton crop (Phytogen 72) in the years 2003 and 2004 near Lemoore, CA. by the University of California (FREP Contract #01-0507). The objective of the trial was to evaluate various rates of nitrogen fertilizer as well as a variable rate application on a cotton crop. The trial was a completely randomized design replicated four times. Four different rates were evaluated including a low, medium, high, and variable or prescribed rate. The fertilizer applied was anhydrous ammonia shanked into the soil at a depth of 10cm. The rates for the 2003 test were 56, 127, and 198 kg N ha. The next year rates evaluated were 31, 131 and 230 kg N ha for the low, medium, and high plots while the variable rate averaged out to be 189 kg N ha. Plots were eight rows across or 7.7m. and ran the length of the field approximately 500m. Ammonia sampling was conducted within some of the nitrogen trial plots before, during, and after the fertilizer application in order to detect the ammonia emissions from differing rates of applied anhydrous ammonia. In plots where ammonia sampling sites were placed plot sizes were increased to 32 rows or 31m in order to create a larger fetch for the samples. Ammonia samples were collected using the same methodology as in the previous studies at sunrise and sunset in order to capture diurnal ammonia variations.

Atmospheric ammonia concentrations increased appreciably over background concentrations the night after the application in all treatment plots (low variable, and high) in 2003 and 2004. Higher concentrations of ammonia were monitored in the high rate plot compared to the low and variable rate plots (Figure 6) the night after the application.
After 2 days, ammonia concentrations in all plots (low, variable, and high rates) were back close to background concentrations.

Figure 6. Ammonia concentration profiles the night after the nitrogen application.



Regression analysis were run on ammonia emissions concentrations in treatment plots verses rates of applied anhydrous ammonia fertilizer in order to evaluate the link between the two variables. Samples with a higher slope in the equation of the regression were considered to more closely link atmospheric ammonia concentration to applied nitrogen.

Slope values increased after application of nitrogen indicating that applied amount of nitrogen has an effect on ammonia emissions. Values of regression slopes decreased when ammonia emissions had ceased (Table. 3).

Table 3. Summarization of data collected at 0.5 m during 2003 trial
* Indicates the beginning of ammonia emissions due to the fertilizer application
** Indicates the ammonia emissions from fertilizer application has ceased

Sample Height - 0.5 m							
			Concentrations				
Date	Sample Period	Sample Description	High	Variable	Low	Regression Slope	Wind Speed
5 June	Day	Day before application	22.0	16.5	11.4	0.0746	1.8
5 June - 6 June	Night	Night before application	20.1	23.2	16.0	0.0289	0.9
6 June	Day	Day of application	7.6	17.6	14.4	-0.0479	1.9
6 June - 7 June	Night	Night after application	41.1	17.0	16.8	0.1711 *	1.2
7 June	Day	Day after application	18.4	18.3	7.3	0.0782	1.9
7 June - 8 June	Night	2 nights after application	15.9	20.7	21.8	0.0451	1.1
8 June	Day	2 days after application	17.0	21.9	17.4	-0.0028 **	1.5
8 June - 9 June	Night	3 nights after application	17.6	16.1	29.9	-0.0862	0.9
9 June	Day	3 days after application	17.9	16.5	18.2	-0.0022	1.5
9 June - 10 June	Night	4 nights after application	14.2	16.9	15.7	-0.01	1.6
10 June	Day	4 days after application	41.1	15.7	13.4	-0.1953	1.3
10 June - 11 June	Night	5 nights after application	18.5	23.5	14.4	-0.029	1.5

Atmospheric ammonia concentrations increased significantly over background concentrations the night after the application in all treatment plots (low variable, and high) in 2003 and 2004. The highest concentrations of ammonia detected both years occurred during the night after the application. After levels of ammonia peaked during the night after the application, they decreased close to background concentrations 2 days after the application

The method employed to detect differences in levels of ammonia emissions was successful in quantifying higher concentrations of ammonia in the plots with the highest nitrogen rates. Slopes of regression analysis identified an increase in atmospheric ammonia within plots fertilized with an increased amount of nitrogen fertilizer after a short post application lag period. This lag period between application and emissions indicates most emissions occur after the actual application and not during the act of application. This link between applied nitrogen fertilizer and atmospheric ammonia decreased with time after the application.

Variable rate fertilizer decreases the net loss of ammonia volatilized as less fertilizer is applied when compared to a blanket application of a high rate. Implementing variable rate applications will not only reduce input costs but will reduce the environmental impact of the possible over application of fertilizers. New applications of variable rate technology must be investigated for benefits such as those observed in this study.

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Appendix B

STATEWIDE INVENTORY ESTIMATES OF AMMONIA EMISSIONS FROM NATIVE SOILS AND CHEMICAL FERTILIZERS IN CALIFORNIA

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Report Prepared for the California State University
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Submission to CARB: December 31, 2003

Final to CSU-ARI: June 30, 2005

Matching Funding From:
California Air Resources Board
Contract Number ID 98-716 to CSU Fresno Foundation

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Disclaimer

The statements and conclusions in this Report are those of the contractor and not necessarily those of the California Air Resources Board and the California State University. 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.

Foreword and Acknowledgments

Particulate matter (PM) is a concern for air quality officials because of its adverse impacts on health and visibility. PM is any material (except uncombined water) that exists in the solid or liquid state in the atmosphere. The size of particulate matter can vary from coarse wind blown dust particles to fine particle combustion products. In July 1997, the United States Environmental Protection Agency (U.S. EPA) promulgated new National Ambient Air Quality Standards for PM. The national standards for PM apply to the mass concentrations of particles with aerodynamic diameters less than 2.5 microns ($PM_{2.5}$) and less than 10 microns (PM_{10}). Recent measurements of $PM_{2.5}$ in California have shown that on average, the highest 24-hour concentrations in 1999 occurred in January, November, and December, while the lowest concentrations occurred between March and August. Seasonality is found to be most pronounced in the San Joaquin Valley Air Basin, where the January-November-December concentrations were on the order of 4 to 5 times greater than those for March through August.

Ammonia (NH_3) gas can react in the atmosphere to produce PM constituents, such as ammonium nitrate or ammonium sulfate. The California Air Resources Board (ARB) has developed preliminary emissions inventories for NH_3 from most potential sources in the state (Gaffney and Shimp, 1999), all of which were reported with high initial uncertainties for source contributions. Most of the potentially significant sources of ammonia are dispersed, area-wide sources such as livestock, fertilizer applications, and soils. Until the ARB is able to gather consistent and locally applicable emissions and activity data for these types of sources, statewide NH_3 emission estimates will carry relatively low confidence levels.

The purpose of this report was to generate new emissions inventories of ammonia volatilization from surface applied fertilizers and from native soil (background) sources for the state of California using a combination of field measurements and computer modeling of major nitrogen transformations in the soil that can lead to NH_3 emission fluxes. To establish a new set of farm-based measurements of NH_3 emission rates from fertilized fields in the Central Valley of California, we carried out a year-round sampling campaign on a series of private farms undergoing actual fertilizer applications for commercial crop production. From this uniquely local set of new fertilizer source estimates of NH_3, we have developed a highly detailed daily fertilizer NH_3 emission inventory for the state. Emissions of NH_3 for a variety of fertilizer types and application methods have been mapped to the major crop types in California's four main agricultural valleys. These data can be used to further evaluate background agricultural soil NH_3 levels by comparing ammonia emission estimates prior to and several days following fertilizer application. Modeling of NH_3 emissions from native soils includes limiting factors of soil type (pH), climatic conditions, plant-soil nitrogen cycling, and other relevant environmental factors.

The authors of this report would like to acknowledge the contributions of the following individuals and institutions, whose support and cooperation made the work significantly more effective and timely. California State University Fresno Plant Science Department: Mahlon Hile, Phillip Jost, Earl Bowerman, and Gino Favagrossa; Center for Irrigation Technology: David Goorahoo and David Zoldoske; NASA Ames Research Center and California State University Monterey Bay: Vanessa Brooks-Genovese and Alicia Torregrosa, who supported all the spatial data analysis and quality control for statewide data sets; Dennis Fitz for support on the use of ammonia sampling equipment; Casey Walsh Cady for support of the California Dept. Food and Agriculture; University of California Cooperative Extension: Blake Sanden in Bakersfield (for Kern County), and Bruce Roberts in Hanford (for Kings County); Steve Spangler of Unocal, Roger Isom of the California Cotton Ginners and Growers Associations, Mike Hemman of Dow AgroScience, Rene Shoemaker of Helena Chemical, Jack King, Eric Athorp of J. G. Boswell, Randy Jacobsen of Jacobsen Consulting, Lee Simpson and Deborah Agajanian of Simpson Vineyards, and Phillip Washburn of Washburn Farming Co. Michael Benjamin and Patrick Gaffney of the California Air Resources Board provided consistent and timely guidance on air quality research issues related to ammonia emission inventory developments in California and nationwide.

We gratefully acknowledge support for this research by the California Air Resources Board. This report was submitted in fulfillment of ARB Contract No. 98-716 to California State University Fresno and to California State University Monterey Bay, “Development of Emissions Inventories for Ammonia in Agricultural Systems of California”. The field and modeling work for this report was completed as of December 31, 2000.

STATEWIDE INVENTORY ESTIMATES OF AMMONIA EMISSIONS FROM NATIVE SOILS AND CHEMICAL FERTILIZERS IN CALIFORNIA

ARB Contract Number ID 98-716

CSU-ARI Contract Number 00-1-013-33

EXECUTIVE SUMMARY

This report provides new emission inventories of ammonia volatilization from surface applied fertilizers and from native soil (background) sources for the state of California. We have used a combination of field measurements of NH_3 emissions together with computer modeling of major nitrogen transformations in the soil that can lead to NH_3 emission fluxes. To establish a new set of farm-based measurements of NH_3 emission rates from fertilized fields in the Central Valley of California, we carried out a year-round sampling campaign on a series of private farms undergoing actual fertilizer applications for commercial crop production. From this uniquely local set of fertilizer source estimates of NH_3, we have developed a detailed fertilizer NH_3 emission inventory for the state. Emissions of NH_3 for a variety of fertilizer types and application methods have been mapped to the major crop types in California's four main agricultural valleys using the most recent Department of Water Resources (DWR) crop maps available. Modeling of NH_3 emissions from native soils includes limiting factors of soil type (surface pH), climatic conditions, plant-soil nitrogen cycling, and other relevant environmental factors.

An active denuder methodology was selected for the emission measurement component of this project, because it represented an established method in air quality studies and it satisfied the requirement for continuous sampling. In most of the sampling applications for which complete data are available, an increase in atmospheric NH_3 was measured compared to the levels sampled both before and immediately after the target application. Based on more than 15 sampling site data sets analyzed to date, it was found that total N losses from fertilizer applications ranged from less than 0.1 to 0.7 g N-NH_3 m^{-2} (equal to approximately 1 to 6 lbs. N-NH_3 emitted per acre). The estimated emission factor values for the sites analyzed to date range from 0.05% to 6% (percent of total applied N fertilizer) with the average at about 3.6%. It appears that the two sites that produced lower emission factor estimates of between 0.05% and 1% loss of total fertilizer N applied were the main sites where fertilizer was applied in a manner that effectively buried the material several tens of cm below the soil surface, either by buried drip method or side-dressing method. Soil pH stands out as another primary regulator of NH_3 emission factors in the overall measurement data set for surface fertilizer application.

In a new statewide inventory estimate, emissions of NH_3 directly from chemical fertilizer applications in California total nearly 12×10^6 kg N-NH_3 annually (1 kilogram = 2.2 pounds). As in the case of overall fertilizer use rates, the leading counties for annual emissions of NH_3 directly from chemical fertilizer sources are shown to be Imperial, Fresno, Kern, Tulare, and Kings. The San Joaquin Valley area accounts for more than one-half of the state's total annual emissions of NH_3 directly from chemical fertilizer sources. The Imperial Valley accounts for a higher proportion of the state's total annual emissions of NH_3 directly from chemical fertilizer sources than would be predicted from crop area alone, mainly because of the high proportion (> 65%) of soils with pH above

8 and a major portion of the total fertilizer applied by surface methods to grain crops and pasture grasses. When analyzed on the basis of DWR crop types, it appears that the generalized categories of field crops and truck crops each account for about one-third of the state's total annual emissions of NH_3 directly from chemical fertilizer sources. Grain, pasture grass, and rice crop categories also contribute notable fractions of the state's total annual emissions of NH_3 directly from chemical fertilizer sources.

Lacking a comprehensive measurement data set for NH_3 from native soil sources in California, a computer modeling approach was used to estimate statewide annual emission rates of N-NH_3 from native soils and indirectly from residual fertilizer N sources in cultivated soils. The use of remote sensing drivers in our model has clear advantages for scaling up to regional predictions of vegetation production that can drive natural trace gas emission estimates. Our modeling system is based on regional data sets (8-km resolution) from a geographic information system (GIS) developed specifically for this ARB-sponsored research on N-NH_3 emissions. The general conditions favoring soil NH3 emissions from soils (high pH, low moisture) are included in the 'NASA-CASA' model formulation. Based on our model inventory estimate, statewide emissions of NH_3 from native soil N sources total between 12 to 57 x 10^6 kg N-NH_3 annually. The most important land cover type in terms of contributions to the statewide emission inventory is cropland and semi-agricultural lands, which make up nearly one-third to one-half of the total native soil N sources for NH_3 emissions annually. Other native areas that contribute substantially to the statewide emission inventory for emissions of NH_3 are soils of the evergreen needleleaf forests, woodland, and wooded grassland ecosystems, mainly on the basis of their large area coverage of the state's natural areas. The model predicts that October is the peak month overall for NH_3 emissions from native soils in California. When totaled for the entire region, native soil sources of NH_3 predicted for Central Valley counties are consistently high from July through January. This seasonal pattern in predicted soil NH_3 emission is fairly consistent with observed seasonality in $PM_{2.5}$ levels for the San Joaquin Valley Air Basin. The combination of productive vegetation communities growing on (even slightly) alkaline soils results in the largest annual emissions of NH_3 from native soil N sources.

The results of this project provide important information necessary for evaluating how ammonia emissions may affect air quality. For example, the design of this new ammonia emission inventory uses California-specific measured emission factors, rather than values from literature sources derived from other states or countries. The method estimates NH_3 emissions based on the actual fertilizer and application methods used by California farmers, not just a few generalized protocols. The method computes emissions within the framework of a geographic information system (GIS) based model, which provides the ARB with location-specific estimates that can be used for local or statewide analysis. Emissions results are displayed graphically and in gridded formats on maps, not just as tables. Soil type data underlies this GIS approach at all locations in the state.

This project provides valuable tools that are needed now to help understand the complete influence of the many sources of ammonia on air quality and particulate matter formation. This work will ultimately assist the state in evaluating the important, but sometimes conflicting needs of maintaining both good air quality and a vital California agricultural industry. To provide even more complete information in the future, additional work is ongoing to more accurately estimate the ammonia emissions from both fertilizer applications and native soil emissions. This work will provide refined spatial and temporal ammonia emissions data, adding important information from local field measurements for upcoming particulate matter implementation plans for the state.

CHAPTER 1.

REVIEW OF AVAILABLE LITERATURE ON AMMONIA EMISSIONS FROM SOIL AND FERTILIZER SOURCES

Primary Investigators: Charles Krauter (CSUF), Christopher Potter (NASA Ames)

Introduction and Justification

Ammonia is the dominant gaseous base in the atmosphere and a principal neutralizing agent for atmospheric acids. The supply of alkaline soil dust and gaseous NH_3 available in the atmosphere may control the acidity of precipitation. Volatilized NH_3 may react to form ammonium nitrate or ammonium sulfate and thereby contribute to airborne particulate matter (PM). Nevertheless, NH_3 remains one of the most poorly characterized atmospheric trace compounds. This situation persists as a result of several factors: experimental difficulties associated with NH_3 measurements, rapid gas-to-particle conversion of NH_3 in the atmosphere, capacity of soils, organic matter, and vegetation to act as both sources and sinks for atmospheric NH_3, and variability in nitrogen fertilizer management and related NH_3 emissions (Langford, 1992).

There is a limited amount of published information from which to develop direct emissions estimates of NH_3 for the state of California in general, and the state's Central Valley in particular. Estimated patterns of nitrogen deposition suggest that, for California locations close to photochemical smog source areas, concentrations of oxidized forms of N (NO_2, HNO_3, PAN) dominate, while in areas near agricultural activities the importance of reduced N forms (NH_3 and NH_4^+) may increase significantly (Bytnerowicz and Fenn, 1996). Wintertime concentrations of PM in the San Joaquin Valley have been associated with high levels of ammonium nitrate (Chow et al., 1992). Preliminary measurements of NH_3 background concentrations in the San Joaquin Valley by Fitz et al. (1997) estimated February levels of 3-16 $\mu g\ m^{-3}$ around open alfalfa fields. However, the magnitude and distribution (both regionally and seasonally) of current NH_3 emissions from fertilizer and other agricultural sources is still largely undetermined for the state of California and many other large regions where agriculture is a major land use (Matthews, 1994).

Review of Fertilizer Emission Controllers

The general conditions favoring soil NH_3 emissions from chemical fertilizers have been documented to a limited degree. As a first approximation, high NH_3 volatilization is strongly associated with high soil pH (7-9) levels, although volatilization losses can occur from acid as well as from alkaline soils, due to elevated pH and NH_4^+ concentrations at wet "microsites" where surface-applied urea ($CO[NH_2]_2$) fertilizer particles dissolve and hydrolyze (Fenn and Richards, 1986). Microsite formation of ammonium carbonate (NH_4^+ HCO_3^-) by the soil microbial enzyme urease can promote high NH_3 volatilization losses, well after urea is incorporated into the soil organic matter.

Moisture

Soil wetting patterns can strongly influence NH_3 losses. Generally, moist soils emit less NH_3 than drier soils, owing to lower gas diffusivity in wetter soils. However, under certain application conditions, moist soils can emit more of applied fertilizer NH_3 than drier soils (Denmead et al., 1978; McInnes et al., 1986; Burch and Fox, 1989; Al-Kanani, 1991). As already mentioned, hydrolysis of urea is promoted under conditions of elevated soil moisture, which can then enhance evaporation losses as NH_3 and CO_2. Volatilization rates are typically diminished when, for example, urea can be transported rapidly to deeper soil layers following heavy irrigation (Fenn and Miyamoto, 1981). Field studies suggest that merely delaying urea application for a few hours after irrigation to avoid accumulation at wet soil surfaces may be a practical way to reduce NH_3 volatilization in humid areas (Priebe and Blackmer, 1989). High temperatures and strong winds may interact with humidity and soil moisture to promote higher volatilization losses. However, in the winter, natural snow cover and cold temperatures can decrease airborne soil dust and possibly the evolution of NH_3 from soils (Munger, 1982).

Application Method

Methods of fertilizer application and tillage also have notable impacts on soil gas losses. As a general trend, the potential for NH_3 volatilization loss is highest where surface application of fertilizers is practiced (Fox and Piekielek, 1987), particularly when combined with no-till management. High rates of band-applied anhydrous ammonia in alkaline soils may retard nitrification for many days, promoting high NH_3 volatilization rates. Nitrogen oxidizing reactions may increase as heavy moisture input or mass particle movement subsequently dilutes the fertilizer-soil microsite reaction zone.

Timing of Application

Understanding the timing of NH_3 volatilization loss from chemical fertilizers is crucial to accurate field emission measurements. Emission rates measured by Denmead et al. (1982a) suggest that with anhydrous ammonia injection into a moist clay soil, peak concentrations occurred about 2 hrs after application and remained elevated at about 25% of peak concentrations 24 hrs later. In other cases, maximum volatilization rates have been reported to occur between two to six days after fertilizer application (Purakayastha et al., 1997). Typical gas densities measured for NH_3 in fertilized agricultural systems are on the order of 10-600 $\mu g\ m^{-3}$ Denmead (1983).

Crop Type

To a limited degree, crop attributes have been shown to influence NH_3 volatilization loss rates. For example, Denmead et al. (1982b) reported that tall (2 m) crops (of corn, in this case) has lower losses of N during application of anhydrous NH_3 than a shorter (1 m) crop, the difference attributed to attenuation of wind by the taller crop. Volatilization loss rates of NH_3 from flooded rice fields can be higher than generally measured in unflooded soils (DeDatta et al., 1991; Bouldin et al., 1991).

Organic Fertilizers

In addition to chemical fertilizer sources, NH_3 volatilization losses from organic fertilizers can be substantial. Use of liquid manure may result in loss of up to >90% of ammonium nitrogen from the organic mixture, depending on the intensity of sunlight during field application (Braschkat et al., 1997). Acidification of slurry can reduce NH_3 emission rates (Bussink et al., 1994). If organic waste is applied to fields in non-liquid form, irrigation immediately after spreading may significantly reduce NH_3 emissions from the manured plots (Rodhe et al., 1996). Composting at relatively high temperatures may also reduce NH_3 fluxes from liquid manure (Brinson et al., 1994).

Loss of NH_3 from stored organic manures and compost has been studied using micro-meteorological mass balance and small wind tunnel experiments, mainly for the purposes of odor control and animal health. It appears that ammonia can be produced from manure via both biological and chemical pathways. Reports indicate that up to about 25% of the total manure nitrogen could be volatilized as NH_3 over a several week period during manure storage, and that changes in pH (>7.5) had the most significant effect on ammonia emissions (Dewes, 1996). Ammonia volatilization from mulches could be negatively correlated with leaf lignin content, whereas green manures seem to emit little NH_3, on either unlimed and limed soils (Glasener and Palm, 1995).

Literature Research Results

This report on documented NH_3 emission estimates from soils and fertilizers is intended to support subsequent crop field measurements (Krauter et al., this report) and computer modeling (Potter and Klooster, 1998 and this report; Davidson et al., 1998) for improved accuracy in the extrapolation of NH_3 emissions from agricultural systems in California's Central Valley and from native (mainly uncultivated) soils statewide. For this report, we did not attempt to replicate the recent world-wide 'emission factor' reports prepared for the Environmental Protection Agency (EPA), including those by Battye et al. (1994) and MRI (1998). Instead, we report here mainly on the potential range of NH_3 emission estimates for various crop types, fertilizer application methods, and natural vegetation types that are most common to California.

Because the vast majority of NH_3 emission factors reported in the literature have not been measured in California, these data cannot be used directly for accurate extrapolation to a statewide emission budget for soils and crop fertilizers. Moreover, measured trace gas emission rates from soils are highly variable in space and time, which makes average emission estimates less meaningful and underscores the critical need to characterize local emission conditions for accurate extrapolations in any region. Consequently, the data summarized in this report are intended mainly to furnish guidance for new measurements and regional model development on the potential scope of NH_3 emission rates expected in environments similar to those found in California. In this manner, new measurements of NH_3 emissions from fertilizer and soil sources in California can be better placed into the larger context of pollution emissions nationwide.

An initial computerized search of the literature uncovered over 80 potential publications and reports from which NH_3 fertilizer emissions might be summarized, compared, and compiled into a useful reference data base for emission ranges. We located approximately 25 citations in the on-line computer listings matching key words for NH_3 emissions and chemical fertilizer management, and more than 60 citations matching key words for NH_3 emissions and organic fertilizer/compost management. In addition, we located several unpublished reports of NH_3 volatilization flux estimates that are accessible on the World-Wide Web (www) sites of numerous agricultural research organizations.

Reported NH_3 emission rates were extracted from these literature and www sources and entered into a spreadsheet data base for a systematic comparison and synthesis of standardized flux ranges, grouped according to natural vegetation types of California (Mayer and Laudenslayer, 1988), predominant crop types in the Central Valley (DWR, 1993-1998), fertilizer application types, and domestic animals common to California. Crop types follow the land use legend from the California Department of Water Resources system of definitions (DWR, 1993). To additionally support regional computer modeling for soil NH_3 fluxes (see, for example, Davidson et al., 1998), these crop types have been cross-referenced in a geographic information system (GIS) to STATSGO soil types and seasonal land-cover regions of the United States derived from multi-temporal analysis of satellite images by the U.S. Geological Survey (Loveland et al., 1995).

The comparison of emission estimates for native soils (Table 1.1) reveals many missing data values for major natural vegetation types common to California. Only shrub lands and rangelands are represented with more than a few published emission measurements. Percentage loss rates may be over 20% of mineralized soil nitrogen, although there is little knowledge of the potential timing and extent of such high NH_3 emissions from natural rangelands. No emission information for soil NH_3 is currently available for oak woodland and chaparral ecosystems, which cover a substantial portion of California's wild lands. Information on net NH_3 fluxes in conifer forests of the Sierra Nevada mountain regions is also lacking in the available literature.

It should be noted that, on the basis of the several available measurements reported for natural vegetation types, these maximum flux rates for uncultivated soils are generally 1000 times lower than NH_3 flux rates measured for various crop fertilizer application methods common in California (Table 1.2). Judging from these data, NH_3 emission rates as a fraction of applied fertilizer N in the forms of urea and organic fertilizer sources appear to be the highest measured so far in agricultural systems, with maximum reported loss rates more than 50% of applied fertilizer N. Maximum loss rates for all other fertilizer types are reported at less than 10% of applied fertilizer N.

Emission factors were categorized also by crop type (Table 1.3), which again shows the paucity of information available for crop types common in California. Highest percent loss rates have been measured from rice fields, although potential NH_3 emissions may be high in pastures also. No measurement reports for NH_3 emissions were located for common crop types of fruit trees and vineyards in California. Hence, it is anticipated that the field flux measurements for NH_3 emissions reported in the following chapters of this document for California's Central Valley (Krauter et al., Chapter 2 of this report) will be the first of their kind made for crop types of grains, truck crops, and fruit trees.

Tables 1.1

Table 1. Ammonia Emission Factors for Natural Vegetation Types of California

Code	Vegetation Type	Flux (ug N m-2 hr-1)		Percent Loss		References
		Minimum	Maximum	Minimum	Maximum	
	Tree dominated					
T1f	Needleleaf (mixed)	4.0				Langford & Feshenfeld (1992)
				0.3		Camire and Bernier (1981)
T2a	Broadleaf (oak)					
T2b	Broadleaf (mixed)					
T3	Oak woodland					
T4	Oak savanna					
	Shrub dominated					
S1	Chapparal					
S2	Tall shrubland					
S3	Mixed shrubland					
S4	Low shrubland		5.7			Woodmansee (1978)
S5	Desert shrubland	0.6	114.0			Schlesinger & Peterjohn (1991); West & Skujins (1977
S6	Mixed rangeland	1.3				Schimel et al. (1986)
	Herb dominated					
H1	Shortgrass rangeland	11.4	200.0			Woodmansee (1978); Denmead et al. (1976)
				1.6	23.0	Van der Weerden & Jarvis (1997)
H2	Wet meadow					

Notes:
Single enteries were placed in the minimum column

Tables 1.2 and 1.3

Table 2. Ammonia Emission Factors for Fertilizer Types Comnon in California

Code	Fertilizer Type	Flux (ug N m-2 hr-1)		Percent Loss		References
		Minimum	Maximum	Minimum	Maximum	
A	Anhydrous NH3 injected					
				0.9	4.0	Denmead et al. (1977); Bouwman et al (1997)
B	Urea dry					
				4.0	46.0	McInnes et al. (1986); Hargrove et al. (1987)
C	NH4+ compounds dry					
				1.3	3.7	Harding et al. (1963); Kelly & Mengel (1986)
D	UAN liquid					
				2.5		Bouwman et al (1997)
E	Anhydrous NH3 liquid	2760	81000			Denmead et al. (1982b)
				4.0	7.0	Bouwman et al (1997); Denmead et al. (1982b)
F	Organic waste liquid	1980	18000			Vandre and Kaupenjohann (1998)
				14.0	99.0	Braschkat et al. (1997)

Notes:

Code A is mainly by injection into soil behind a shank or knife to 10-20 cm depth
Code B is mainly incorporated into soil furrow
Code C is mainly ammonium nitrate, incorporated into soil furrow
Code D is urea ammonium nitrate, mainly dripped into irrigation water run
Code E is mainly dripped into irrigation water run
Code F is mainly in slurry form added into irrigation water run

Table 3. Ammonia Emission Factors for Crop Types Comnon in California

Code	Crops	Flux (ug N m-2 hr-1)		Percent Loss		References
		Minimum	Maximum	Minimum	Maximum	
G	Grain & Hay					
F	Field & Row	2760	81000	1	7	Denmead et al. (1978); Denmead et al. (1982b)
P	Pasture					
				2.2	43	Kissel et al. (1977); Reynolds & Wolf (1988)
T	Truck & Nursery					
D	Deciduous Tree					
C	Citrus Tree					
V	Vineyard					
R	Rice					
				4	54	Bouldin et al. (1991); DeDatta et al. (1991)

Notes:

G is a mixture of barley, wheat, and oats
F is mainly cotton with some corn
P is mainly alfalfa
T is mainly tomatoes and melons
D is mainly almonds and peaches
C is mainly oranges

CHAPTER 2.

FIELD MEASUREMENTS OF FERTILIZER AMMONIA EMISSIONS FROM CROPPED SOILS

Primary Investigators: Charles Krauter (CSUF), David Goorahoo (CSUF), Christopher Potter (NASA Ames)

Summary of Field Measurement Results for NH_3 Emissions

The main objective of this study component was to determine rates of atmospheric ammonia emissions related to applications of chemical N fertilizer for agricultural field sources in the Central Valley of California. Identification of chemical fertilizer sources depends on estimation of NH_3 emissions in terms of the amount of the applied fertilizer nitrogen lost from the soil as NH_3 to the ambient atmosphere. This value, termed the 'emission factor' by the atmospheric modelers, would be more familiar to agronomists as "percentage of volatile losses".

An active denuder NH_3 sampling methodology was selected for the field component of this project because it represented an established method in air quality studies and it satisfied the requirement for continuous sampling. Denuders and anemometers were co-located at 1, 2, 5, 10 and 18.5 meters above the soil surface on a single, portable tower (Photo 2.1). In each of the sampling applications for which data are available, an increase in atmospheric NH_3 was measured compared to the levels sampled both before and after the application. Based on more than 15 sampling site data sets analyzed to date, it was found that while total N losses from fertilizer applications ranged from less than 0.1 to 0.7 g N- NH_3 m^{-2} (equal to 0.9 to 6.2 lbs. N-NH_3 emitted per acre), the estimated emission factor values for the sites analyzed to date range from 0.05% to 6% with the average at about 3.6% of applied N. It appears that fields produced lower emission factor estimates of between 0.05% and 1% loss of total fertilizer N where fertilizer was applied in a manner that effectively buried the fertilizer material several cm below the soil surface, either by buried drip irrigation, injection in the anhydrous form or side-dressing of ammonia compounds.

For comparison, emission factors used by the Air Resources Board prior to this project were generally higher than those measured in the Central Valley fertilizer applications sampled for this report. These earlier values, ranging from 5% to 10%, were based on limited information from work done primarily in climates and on soils outside of California.

Field Sampling Methodology

The field sampling phase of the project was designed to measure the magnitude of volatile NH_3 loss and its duration as a result of an actual commercial fertilizer application. The percentage loss for a specific N application would be influenced by several factors that could be identified in a statewide database. 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 (Table 2.1). The first factor identified was crop type. The statewide database for this study utilized county-based crop maps from the California Department of Water Resources (DWR, 1993-1998). The second factor was soil. A simple separation of the state soils into four categories based on

%clay (A= <5%, B=5%-10%, C=10%-20%, D=>20%) was used for the initial database development. 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. The ten crops, four soils and six fertilizers resulted in a matrix of 240 cells. The sampling period for this ARB funded study was the calendar year 2000. It was planned to sample 15 - 20 individual applications during that time period.

The actual sites sampled did not always match exactly with the initial plan, but each site corresponded to a cell of the original matrix (Table 2.1). Sites were chosen based on matching the matrix, accessibility, and available personnel and resources, in that order of priority. The actual sites sampled from December, 1999 to December, 2000 are shown in Table 2.2, including geographic locations (Table 2.2a), fertilizer application amounts and types (Table 2.2b), and soil conditions at the point of fertilizer application (Table 2.2c).

Once the sampling matrix had been determined, the next step was to select a field sampling procedure that would characterize the emission factor for each site in a manner suitable for the needs of the statewide database. The magnitude and duration of the volatile losses must be measured to establish an emission factor. Duration could be characterized easily as long as a continuous sampling method was used. The initial plan was to sample for two days prior to an application to determine background levels. Sampling would proceed through the application of the fertilizer and continue for five days afterward to monitor the expected spike of atmospheric NH_3 from the application. This sampling schedule was used through the year and proved to be adequate to establish the duration of the NH_3 emission.

Sampling Procedures

Monitoring of volatile NH_3 in commercial agricultural settings has not been a common practice in agronomic research. Therefore, a short trial period was necessary to develop a reliable sampling procedure to measure the magnitude of the NH_3 emissions before, during, and after fertilizer application. Closed chambers in the lab or greenhouse have been used but were not considered suitable for this project in which field monitoring was mandated. Field measurement of NH_3 has been done in air quality studies, primarily in urban settings. Two basic methods have been employed; denuders and open-path spectroscopy. The denuder is a medium through which an air stream is passed in the same manner as a filter for particulates. In the case of NH_3 it is a fibrous material, usually glass, treated with a substance (citric acid) that will react with NH_3 to form a solid. The denuder is usually an active sampler utilizing a pump to pull a known flow of air through a disk of the treated material in a filter holder located at the point of measurement. This requires a pump, power system and air flow measurement for each sampling point. Denuders can also be passive, depending on wind to move the air through the denuder medium.

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 satisfies the inventory development requirement for continuous sampling of soil gas emissions over relatively long time periods (hours-days-weeks) and over plot areas on the order of square kilometers. A 47 mm 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. Filter 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 μg 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 (m^3) of air pumped through the denuder in the sampling period to derive concentrations in units of μg N-NH_3 m^{-3} air at the sampling point.

The denuder method for measuring NH_3 concentration proved to be appropriate for the needs of the project at the present stage. The second method of NH_3 monitoring in a field setting, open-path spectroscopy, was also considered. The method has a number of advantages for such a study. Similar to laboratory spectroscopy, an electromagnetic signal is generated and detected at specific wavelengths (λ). NH_3 absorbs very strongly at a specific near infra-red λ. The IR λ is propagated along a path in the air to a detector. The absorption at the specific λ can be used to determine the amount of NH_3 in the air along the path, just as it can in a cuvette in the laboratory. Two methods of open-path monitoring are Fourier Transform Infra-Red (FTIR) and Tunable Diode Laser (TDL) spectroscopy. Each can provide rapid, real-time data over paths of 1000 m or more. These methods are also very costly and require a high level of operator expertise for reliable measurements. The spectroscopy methods offered no practical advantage over the active denuder for the long-term, continuous sampling required during the past year. However, open path spectroscopy may be needed by this research in the next phase for shorter term monitoring of NH_3 from dairy operations.

The measurement of NH_3 concentration at a particular sampling point (elevation) 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 air at the sampling point. The value necessary to characterize the sampling point was the flux in μg N-NH_3 m^{-2} s^{-1}. Our initial assumption during the planning of the project 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 to be located at 1, 2, 5, 10 and 18 meters above the soil surface (Photo 2.1). The ammonia flux is the amount of NH_3 passing through a 1 m^2 cross section of air per second.

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. The stomata and internal structure of the leaf that functions to absorb CO_2 from the air might be effective as absorbers of NH_3 as well, although there is no convincing empirical evidence to support that conclusion at this time. Alternatively, if there is a negligible source of NH_3 from fertilizer application at the soil surface, the sampling at a site might well exhibit what appears to be a negative gradient, as NH_3 in air from nearby point (sources such as livestock) moves over the field and is sampled for a short period of time.

Portable Tower Instrumentation

The requirement to sample and measure wind speed at five elevations for 7 to 10 days in different locations remote from electrical power sources made a self-contained, portable sampling system necessary. An instrument tower 15 m in height that would telescope down to 5 m was borrowed from a completed UC Davis (investigator Ken Tanji) project for the duration of our study. The mast tower was mounted on a trailer constructed by the Farm Machinery Center at CSU Fresno. The trailer served as a base for the tower when erected and allowed the mast tower to collapse and pivot to a horizontal travelling position. Storage and instrument compartments mounted on the trailer held the air pumps, flow measurement devices, power monitors, controls, the data logger for the meteorological instruments and the four golf cart batteries used for powering the sampling system. By the end of the first sampling season, the tower/trailer unit had been developed to the point where one person could tow the trailer to a sampling site, erect the tower, and begin sampling in two hours.

Conditions from the first three sampling sites (A to C) were monitored during the developmental phase of the sampling system. The final configuration of the tower/trailer was complete for Site D though some changes in the air pump system were made prior to Site L. A single anemometer was used for wind speed at both 1 m and 2 m until Site K. Data analysis suggested the wind speed was in fact significantly different at those two sampling elevations, so the anemometer at 10 m was shifted to the 2 m height and the unit that had been at 1.5 m was lowered to 1 m. Subsequent data analysis indicated the wind speed at 1 m is generally only 30% to 70% of the wind speed at 2 m. The wind speed at 10 m was assumed to be near the average of the measured values at 5 m and 20 m. Analysis of the field data confirmed this assumption.

Ammonia Emission Calculations

Standard mass balance micrometeorological techniques (Denmead, 1983 and 1995) were used to estimate the integrated NH_3 flux by combining measurements of wind speed and NH_3 air sample concentrations from height-dependent sampling locations mounted on the portable mast tower. The surface flux density (F) of a gas can be calculated according to the equation:

$$F = \int_0^z U \ (\rho_g - \rho_b) \, \partial z$$

where U (z) is the horizontal wind speed at sampling height z, ρ_g is the atmospheric gas concentration at the site of the plot tower sampler, and ρ_b is the background atmospheric gas concentration from upwind of the field plot. Previous field tests (Leuning et al., 1995) suggest that this equation tends to overestimate true fluxes due to turbulent diffusive flow in the opposite (upwind) direction. Therefore, following the recommendation from Denmead (1995),we adjusted calculations based on this equation downward by 15%.

To describe the NH_3 emission resulting from the fertilizer application, integration calculations were made using a fourth-order polynomial fit to the height-dependent horizontal flux points for each sampling period. Final integration under the time series curves and adjustment for fetch distance (in meters) were made to determine the total N-NH_3 emitted as vertical fluxes over the entire time period sampled, beginning at the first fertilizer application time. To compute the site 'emission factor', we compared the total N- NH_3 emitted to the total kg N applied m^{-2} area for that site sampling period.

One assumption worth noting for the calculations of NH_3 vertical fluxes is that, for sampling from the middle of a typical commercial field plot, any samples collected from >10 m probably do not provide any reliable information on soil surface emission of gases. It is generally assumed that there are too many other possible sources of contamination at such heights. Therefore, we adopted the general guideline that the ‘effective fetch’ is equal to about ten times the highest sample mast height (Denmead, 1983), an assumption which establishes the effective fetch for these vertical flux calculations (1 m - 10 m samples) at a consistent value of 100 m.

Field Sampling Results

Laboratory and data analysis were completed for sites A through S. Measurement results confirm that field sampling by the micrometeorological mass balance method can detect volatile NH_3 from an application of N fertilizer. In each of the applications for which data is available, an increase in atmospheric NH_3 was measured compared to the levels sampled both before and after the application. Figures 2.1 and 2.2 (Sites D and J) shown below are typical of the results analyzed. The line labeled "Application" is the average of 2 to 5 sampling periods during which the N application was actually occurring. The lines labeled "Pre-application" and "Post-application" were the averages of 2 to 10 samples taken prior to and after the application. The "Application" values were greater that those before and after in each of the sites analyzed. This is the basis for the conclusion that the methodology can detect volatile NH_3 resulting from a fertilizer application.

A typical horizontal flux profile (for Site J) is shown in Figure 2.3. The highest flux values are generally computed at between 5 m and 10 m height. However, during other sampling periods the highest flux values may be observed at between 2 m and 5 m height, which could be a function of variable wind speed and related turbulent flux conditions. Nevertheless, the vast majority of horizontal flux profiles generated for all site sampling periods show high statistical significance (> 90% confidence) when using the fourth-order polynomial equation, such as the one shown for Figure 2.3.

The vertical flux time series for all measured sites are shown in Figure 2.4. Site J (Cotton, June 2000) is used here as an example for discussion. Prior to the first fertilizer application, background fluxes from the cultivated soil at this site were determined to be on the order of 1000-3000 $\mu g\ N\text{-}NH_3\ m^{-2}\ h^{-1}$. Following the first fertilizer application in proximity to the portable sampling mast, vertical fluxes were estimated to increase nearly five-fold to 10,000 $\mu g\ N\text{-}NH_3\ m^{-2}\ h^{-1}$. Sampling during post-application periods over the subsequent 72 hours suggest a rapid decline in NH_3 emission fluxes, returning to near background flux levels commonly within 24 hours and always by the end of the site measurement time series of about 144 total hours. These measured flux rates at Site J are within the range of those reported by Denmead et al. (1982b) for ammonia emission from fertilized corn fields, estimated at between 3000 and 80,000 $\mu g\ N\text{-}NH_3\ m^{-2}\ h^{-1}$.

Emission flux totals of NH_3 for all fertilized sites analyzed to date show a notable consistency of emissions factor estimates among the different crop types and fertilizer amounts applied (Table 2.3). While total NH_3 nitrogen losses ranged from 0.01 to 0.7 $g\ N\text{-}\ NH_3\ m^{-2}$, the estimated emission factor values for the sites analyzed range from 0.05% to 6% with the average at about 3.6% (not including Sites E, G, K, and L). It appears that the sites that produced lower emission factor estimates of below 1% loss of total fertilizer N applied were primarily those sites where fertilizer was applied in a manner that effectively buried the fertilizer material below the soil surface, either by buried drip irrigation (site E), side dressing of urea (site G) or injection of anhydrous ammonia (site R). Site K was unusual as the only measured example of a micro-sprinkler application of fertilizer, which appeared to have a significant damping effect on soil NH_3 emissions for several days. Site L was not included in the average emission factor computed above, because it is the one site where an organic material, dairy effluent, (instead of chemical N fertilizer) was applied to a pasture in liquid form added to irrigation water run. Data collected from sites A and C proved to be incomplete or preliminary in quality, and therefore are not included in Table 2.3.

Although few comparable measurements exist for crop emission sources of NH_3 flux at locations outside of California, we find that the range of total NH_3 losses listed in Table 2.3 are on the same order of total NH_3 losses (0.32 $g\ N\ m^{-2}$) reported by Ryden and McNeill (1984) for a period of several days in grazed ryegrass sward at the Grassland Research Institute, Hurley, UK. For example, our Site L pasture measurements also generated a total NH_3 loss estimate of 0.32 g N m^{-2} associated with organic fertilizer application. Both studies used the micrometeorological mass balance method for determination of ammonia loss to arrive a nearly identical emission estimates.

Emission Factor Analysis

To better understand the factors that influence fertilizer ammonia emissions and to later extrapolate measured emission values to a statewide level, a rule-based model was developed for assignment of NH_3 emission factors, computed as the NH_3 emission total divided by the total N application rate. On the basis of all the site data collected for Table 2.3, the best rule-based model for assignment of NH_3 emission factors was based on two primary factors influencing N-NH_3 emissions among the sites -- method of fertilizer application (FA) and soil pH. Consequently, the following set of rules were assigned:

NH_3 emission factor (percent N applied)	Rules	Field Sites (Table 2.2)
6.5	FA=1 and pH=a	B, F
5.5	FA=1 and pH=b	H
4.0	FA=1 and pH=c	D, L
1.0	FA=2	G, J, R, S
0.5	Special case - buried drip	E
0.0	Special case – micro-drip	K

where FA type is categorized as 1=surface, 2=subsurface (injected/side-dressed), and soil pH at the point of fertilizer application is categorized as a=above pH 8, b=between pH 7-8, c=below pH 7.

Our collection of measured emission factors suggest that when N fertilizer is applied at the soil surface using broadcast, surface band, or water run methods, the soil pH at the point of application influences the fraction emitted as NH_3 at the level of about plus or minus 1.5 percent. When fertilizer is applied below the surface, using either NH_3 injection or side-dressed, the emission factor is reduced substantially, presumably because upward diffusion of NH_3 gas back to the soil surface is inhibited by absorption reactions within the soil matrix. This overall pattern of emission factors is consistent with results from previous studies on NH_3 loss from fertilizer sources (Fox and Piekielek, 1987).

Among the field sites sampled, there did not appear to be a consistent effect of soil clay content to include as a rule for assignment of N-NH_3 emission factors (Table 2.3). Likewise, extremes of soil moisture (flooding) due to irrigation may have had a secondary effect on N-NH_3 emissions among the sites, but this effect remains somewhat ambiguous in the measurement data set. Hence, the exceptions to the rules for N-NH_3 emission factors developed above remain Sites I and Q, which seem to fall into a category of being influenced by soil moisture management in a fashion not fully documented to date. Further emissions sampling with experimental adjustments on the primary factors (method of fertilizer application and soil pH) at additional field sites will be required to determine the importance of soil texture and moisture management on NH_3 emission factors.

Table 2.1. Proposed sampling matrix for measurements of ammonia emission fluxes from fertilized fields in the Central Valley of California.

Crop	DWR	Urea	UAN	NH_4X	NH_3	NH_3	Dairy
	category	dry	liquid	dry	injected	water run	Effluent
Cotton	Field Crop	D				B	
Corn	Field Crop				C		C
Melons	Truck Crop			B		C	
Tomato	Truck Crop		B			C	
Lettuce	Truck Crop		C	B			
Citrus	Citrus			B			
Small Grain	Grain	C			B		
Vineyard	Vineyard		B	A			
Decid. Trees	Decid. Fruit	B		A			
Rice	Rice					D	

Notes: Key to soil texture categories, based on clay content: A= <5%, B=5%-10%, C=10%-20%, D=>20%.

Table 2.2a. Field sampling site locations for the ammonia emissions from fertilizer applications.

Site	Crop	Latitude N degrees	Latitude minutes	Latitude W degrees	Latitude minutes	General Location
A	Almond	36	55.594	120	13.955	15 m West of Madera
B	Almond	36	56.693	120	15.697	16 m West of Madera
C	Almond	36	49.341	119	44.078	CSUF Farm
D	Citrus	36	46.708	119	33.217	5 m North of Sanger
E	Almond	36	47.039	119	33.656	7 m North of Sanger
F	Onions	36	23.820	120	7.320	3 m South of Five Points
G	Tomato	36	23.818	120	6.255	3 m SW of Five Points
H	Garlic	36	23.169	120	6.506	4 m SW of Five Points
I	Cotton	36	24.471	120	7.437	2 m SW of Five Points
J	Cotton	36	26.416	120	7.284	4 m West of Five Points
K	Almond	36	49.263	119	43.528	CSUF Farm
L	Pasture	36	48.874	119	44.241	CSUF Farm
M	Broccoli	36	40.971	120	29.491	8 m SW of Mendota
N	Cotton	36	13.599	119	56.942	5 m South of Lemoore NAS
O	Lagoon					CSUF Farm
P	Broccoli	36	40.971	120	29.491	8 m SW of Mendota
Q	Lettuce	36	22.301	120	7.791	3 m SW of Five Points
R	Cotton	36	22.712	120	9.378	4 m SW of Five Points
S	Tomato	36	24.073	120	7.216	2 m South of Five Points

Table 2.2b. Fertilizer applications at field sampling sites for the ammonia emissions.

Site	Crop	Fertilizer	N lb/A	Application Method	Application Point Depth (cm)
A	Almond	UAN-32	100	surface band, watered in	Surface
B	Almond	$(NH_4)_2SO_4$	100	surface band, watered in	Surface
C	Almond	Urea liquid	15	foliar with bloom spray	Foliar
D	Citrus	NH_4NO_3	50	Broadcast - rained in	Surface
E	Almond	UAN-32	100	Water Run-buried drip	50
F	Onions	UAN-32	40	Water Run-sprinkler	Water-run
G	Tomato	UAN-32	100	Side dressed	10
H	Garlic	UAN-32	50	Water Run-furrow	Water-run
I	Cotton	NH_3	100	Injected, 15cm shank	15
J	Cotton	NH_3	100	Injected, 15cm shank	15
K	Almond	21-21-21 (lq)	9	Water Run-microspray	Water-run
L	Pasture	effluent	200	Flood	Water-run
M	Broccoli	NH_4NO_3	60*	Surface spray for weed control	Foliar
N	Cotton	defoliant	0	Aerial Spray	Surface
O	Lagoon	effluent	NA	Ponded	Water-run
P	Broccoli	UAN-32	75*	Water Run-buried drip	15
Q	Lettuce	UAN-32	60	Water Run-furrow	Water-run
R	Cotton	NH_3	80	Injected, 15cm shank	15
S	Tomato	NH_3	100	Injected, 10cm shank	10

Notes: Depth at application point refers to the placement of the fertilizer by the application method. Surface indicates fertilizer applied to soil surface, Water-run indicates fertilizer applied in irrigation water. Foliar indicates direct application to vegetation

Table 2.2c. Soil conditions at field sampling sites for the ammonia emissions.

Site	Crop	Soil Name	Application Point Soil pH	Application Point Clay Content.	Application Point Moisture Content
A	Almond	Grangeville f sandy loam	6.7	9%	high
B	Almond	Fresno/ElPeco loam (sl alk)	8.1	9%	high
C	Almond	Hanford sandy loam	6.4	9%	high
D	Citrus	Atwater sandy loam	6.1	4%	low
E	Almond	San Joaquin loam (shallow)	6.4	15%	high
F	Onions	Panoche clay loam (sl alk)	8.5	23%	high
G	Tomato	Panoche clay loam	7.9	23%	medium
H	Garlic	Panoche clay loam	7.9	23%	high
I	Cotton	Oxalis silty clay (sl alk)	8.5	30%	medium
J	Cotton	Lethent silty clay (mod alk)	7.8	30%	medium
K	Almond	Delhi loamy sand	6.4	4%	high
L	Pasture	Hanford sandy loam	6.6	9%	high
M	Broccoli	Panoche loam	7.9	18%	low
N	Cotton	Panoche clay loam (sal alk)	8.5	23%	NA
O	Lagoon	Greenfield sandy loam	6.6	9%	high
P	Broccoli	Panoche loam	7.9	18%	high
Q	Lettuce	Oxalis silty clay (sl alk)	7.8	30%	high
R	Cotton	Panoche clay loam	7.9	23%	medium
S	Tomato	Panoche silty clay (mod alk)	8.5	32%	medium

Notes: Soil pH at application point refers to the soil pH at the depth of fertilizer placement. Soil pH may be different at other depths. Percent of soil particles smaller than 0.005 mm is used to classify the clay fraction of soil texture. Moisture at the application point is a relative evaluation of the soil moisture content at the point and time of fertilizer application: ‘High’ is approximately Field Capacity, ‘Low’ would be near or below the irrigation point.

Table 2.3. Summary of ammonia emission estimates from field sampling sites.

		Application rate					
Site	Crop	N kg ha^{-1}	N g m^{-2}	Fert. Type	Irr. Type	NH_3 Emis. Tot	NH_3 Emis. Factor
						g N m^{-2}	(percent)
A	Almonds	109	10.9	b	G		

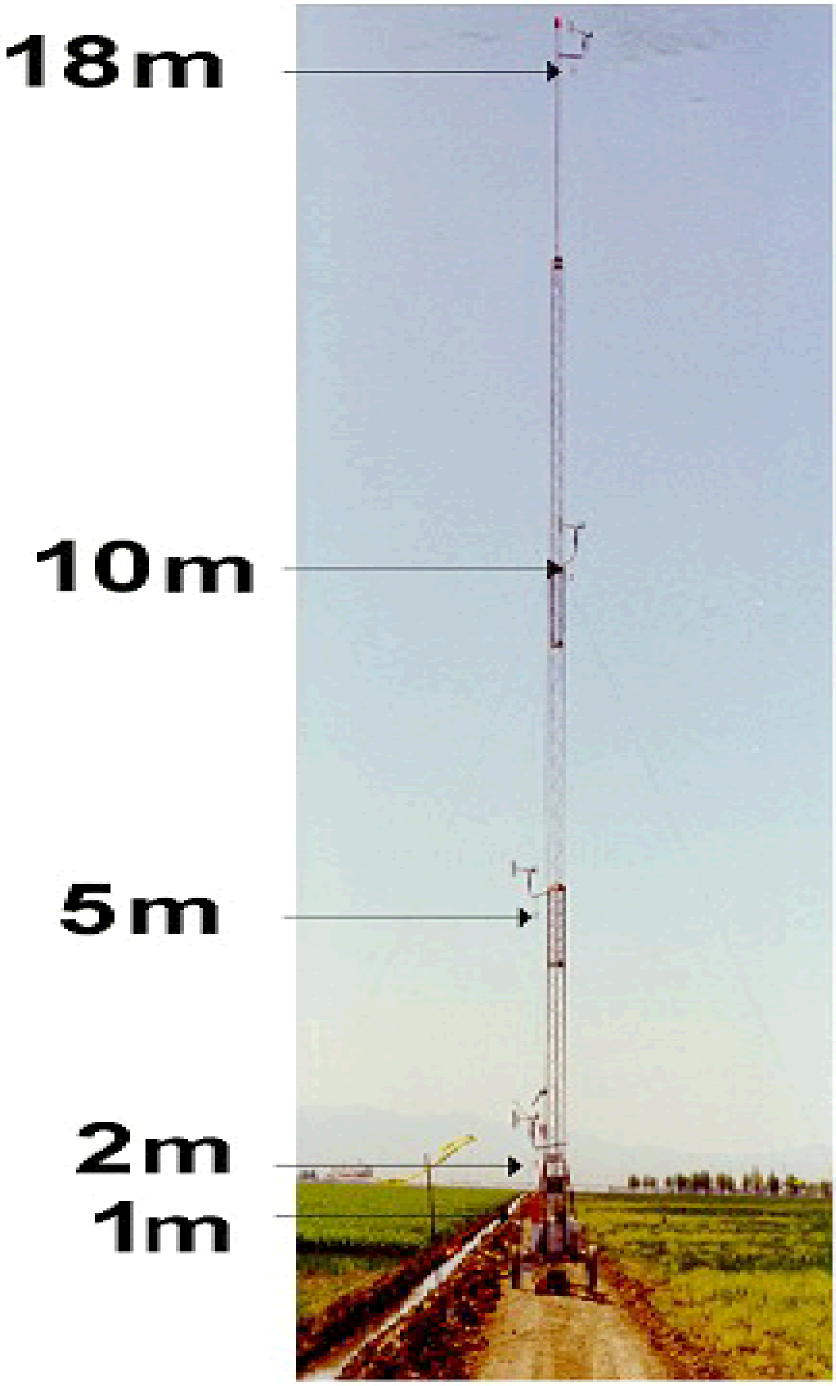
B	Almonds	109	10.9	c	G	0.72	6.6
C	Almonds	16	1.6	g	G		
D	Citrus	55	5.5	c	G	0.24	4.3
E	Almonds	109	10.9	d	M	0.05	0.5
F	Onion	44	4.4	d	S	0.28	6.5
G	Tomato	109	10.9	d	G	0.10	0.9
H	Garlic	55	5.5	d	G	0.32	5.8
I	Cotton	109	10.9	a	G	0.62	5.6
J	Cotton	109	10.9	a	G	0.43	3.9
K	Almonds	10	1.0	a	M	0.00	0.0
L	Pasture	109	10.9	f	G	0.32	2.9
M	Broccoli	65	6.5	c	S	0.10	1.6
Q	Lettuce	44	4.4	d	G	0.02	0.5
R	Tomato	87	8.7	a	G	0.01	0.1
S	Cotton	109	10.9	a	G	0.14	1.3

Notes: NH_3 emission factors are computed as the NH_3 emission total divided by the total N application rate. Data collected from sites A and C proved to be incomplete or preliminary in quality, and therefore was not reported. The conversion factor to English units is 1 kilogram per hectare = 0.892 pounds per acre.

Fertilizer Type Codes
Code a is anhydrous NH_3 injection into soil behind a shank or knife to 10-20 cm depth
Code b is dry urea applied to soil furrows followed by irrigation
Code c is dry ammonium nitrate/sulfate applied to soil furrows followed by irrigation
Code d is urea ammonium nitrate (UAN) liquid dripped into irrigation water run
Code e is anhydrous NH_3 liquid dripped into irrigation water run
Code f is organic waste in slurry form added to irrigation water run
Code g is urea ammonium nitrate (UAN) liquid foliar application with fungicide at bloom

Irrigation Type Codes
G is gravity surface/flood
S is sprinkler
M is microsprayer/drip

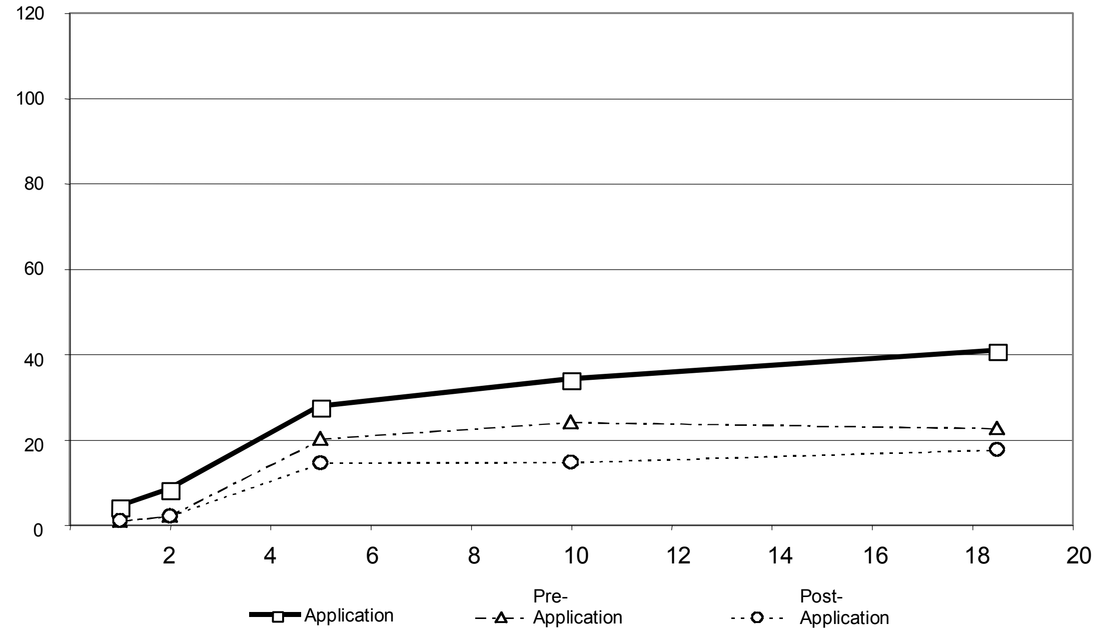
Photo 2.1. Typical sampling installation in the field at Site F.



Tower Deployment in Field

Figures 2.1 and 2.2. Flux curves for estimating fertilizer application emissions of ammonia.

Ammonium nitrate on Citrus (Site D)



Cotton soil injection (Site J)

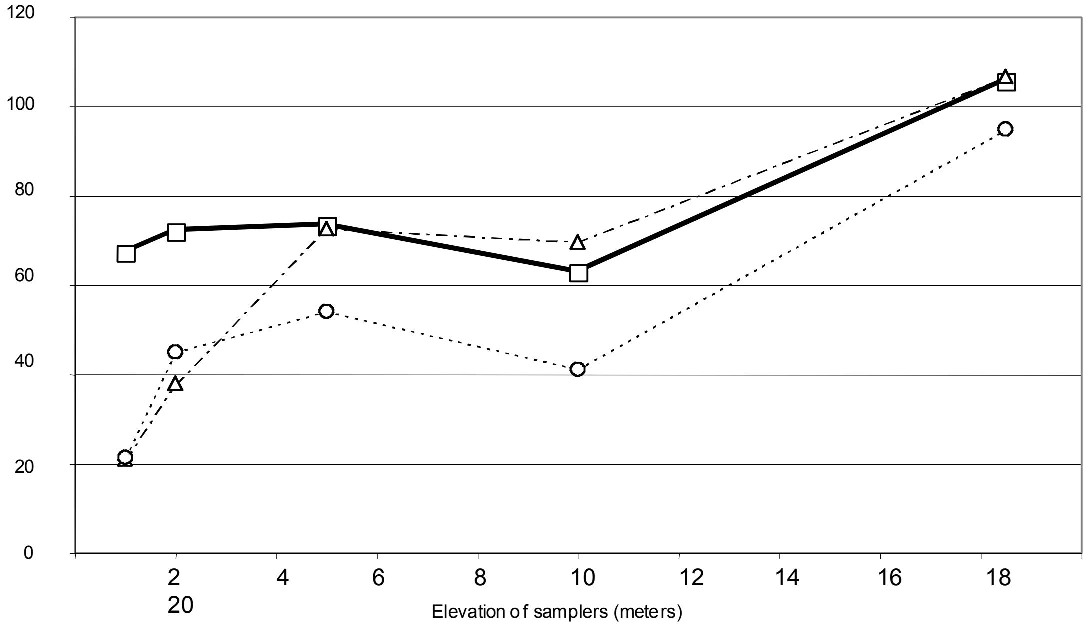


Figure 2.3. Ammonia flux integration from Site J for the sampling period covering approximately 76 h elapsed since the initiation of sampling. Flux units are μg N-NH_3 m^{-2} s^{-1}.

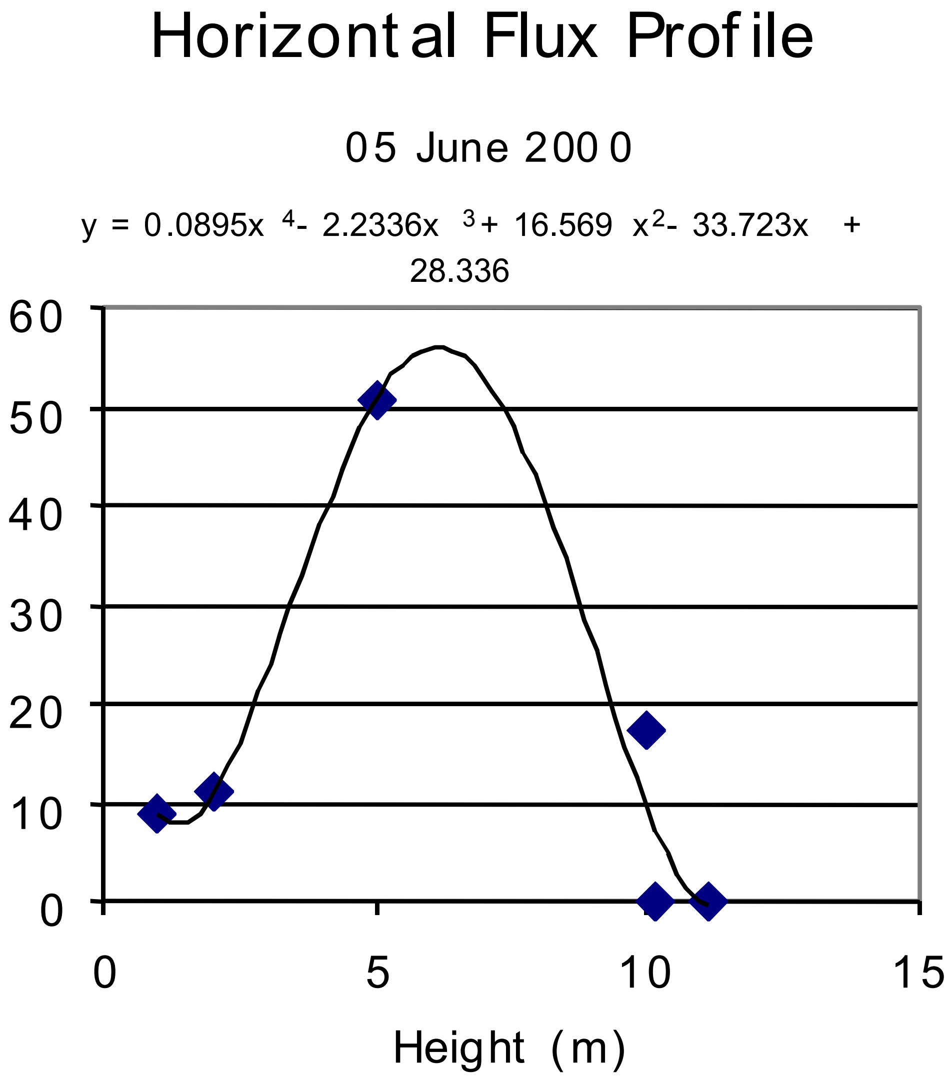
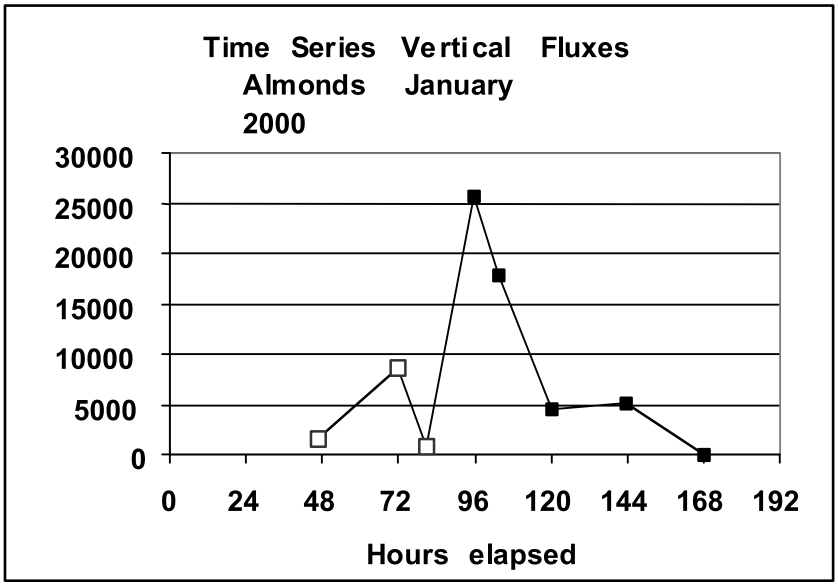
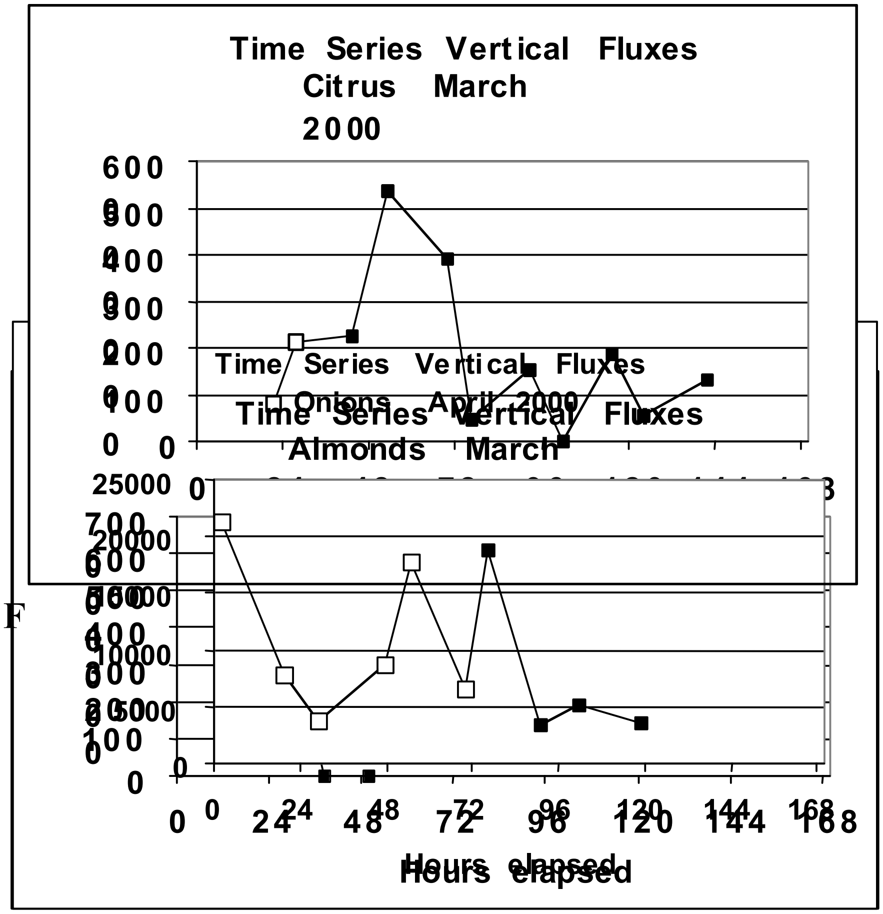


Figure 2.4. Ammonia flux time series for sites listed in Table 2.3. Vertical flux units are in µg N-NH_3 m^{-2} h^{-1}. Closed box symbols indicate measured emission fluxes during primary period of fertilizer application(s) in proximity to the NH_3 sampling mast location. Open box symbols indicate background flux rates prior to or following the primary period of fertilizer application. Secondary periods of fertilizer application at the site are included in the time series plots also as open box symbols. Time axis shows hours elapsed since the initiation of gas sampling. (Note: The entire data set of spreadsheet files have been provided to ARB on CD-ROM as complete documentation of the measurement data values collected, in addition to the subsequent NH_3 flux calculations).

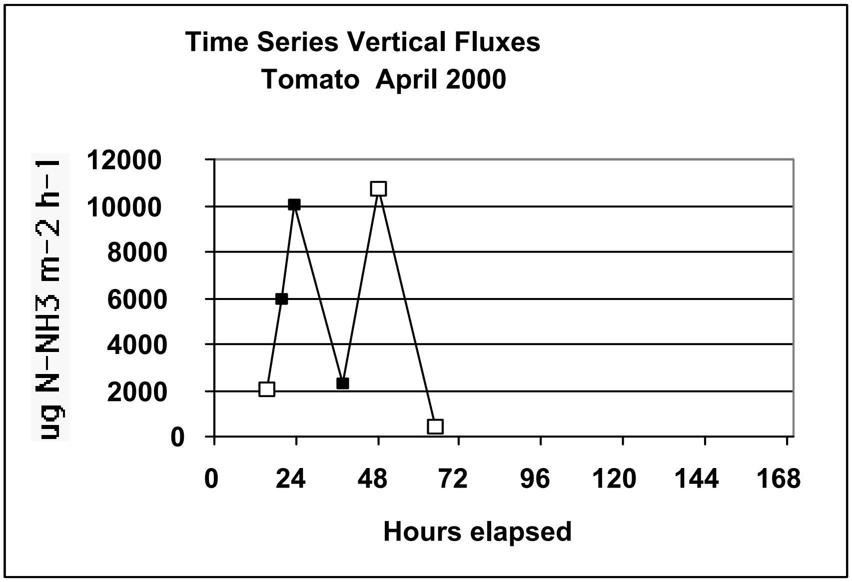
Sites B and D



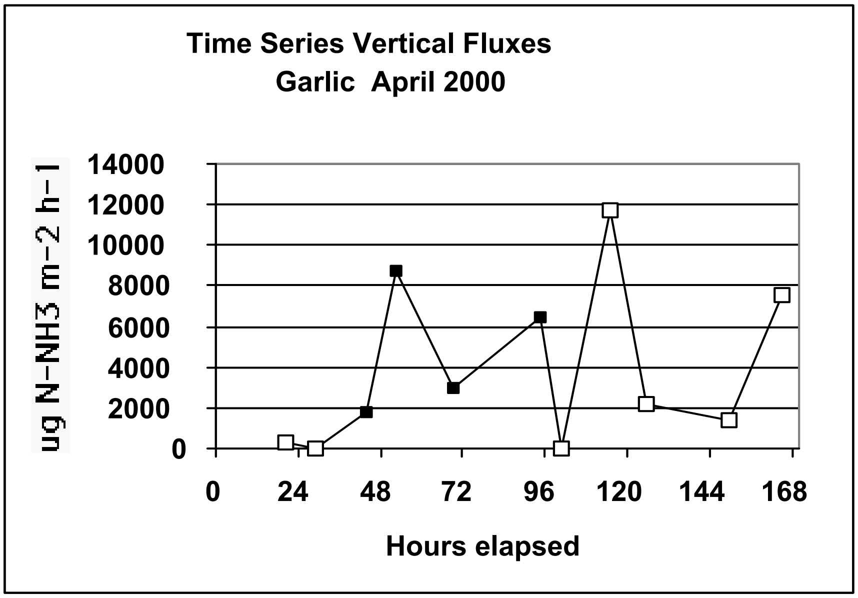


Sites E and F

Sites G and H

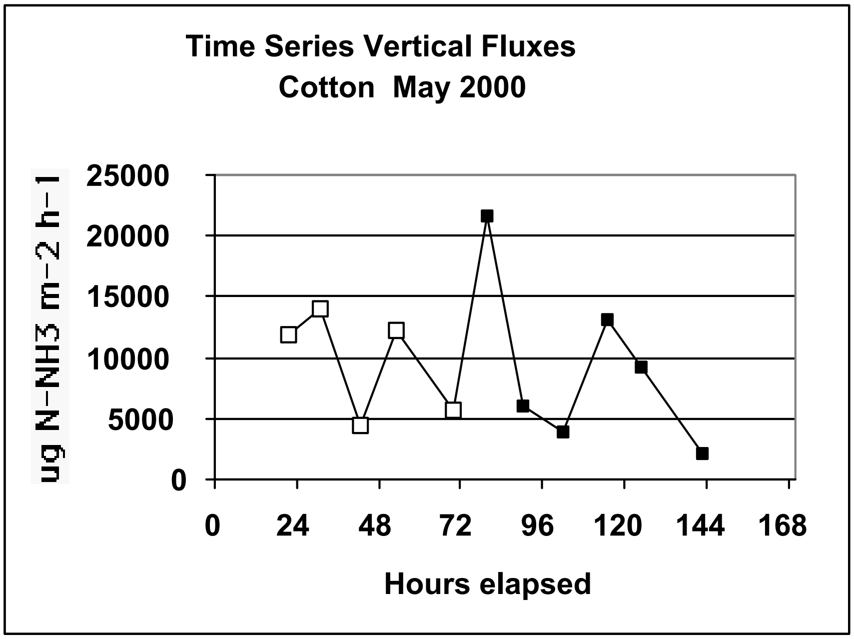


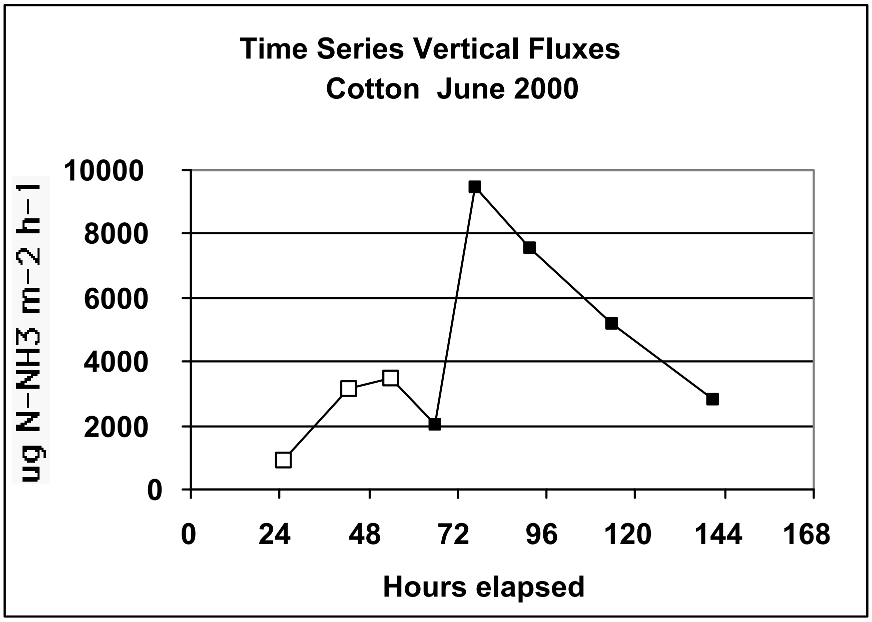
Time Series Vertical Fluxes
Tomato April 2000
ug N-NH3 m-2 h-1
12000
10000
8000
6000
4000
2000
0
0
24
48
72
96
120
144
168
Hours elapsed



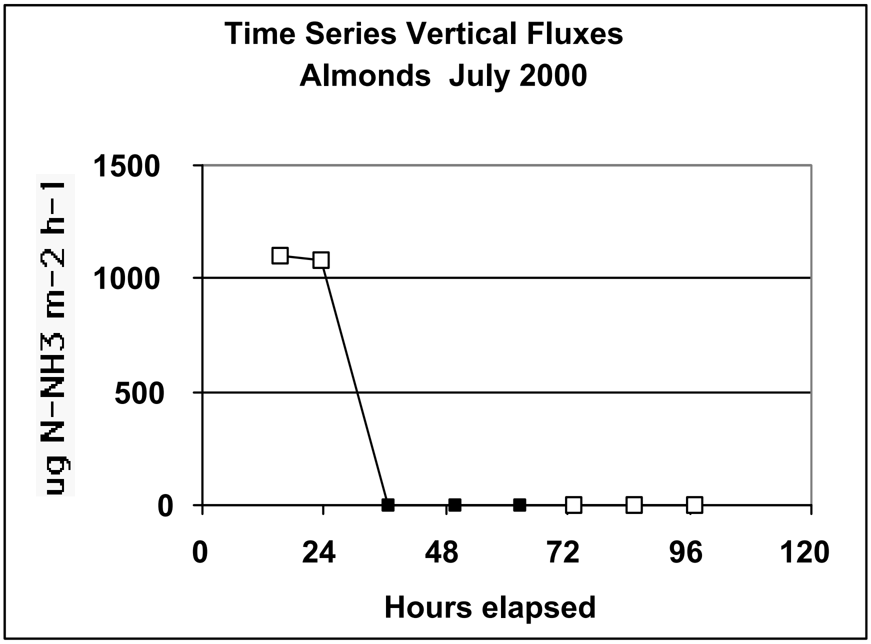
Time Series Vertical Fluxes
Garlic April 2000
ug N-NH3 m-2 h-1
14000
12000
10000
8000
6000
4000
2000
0
0
24
48
72
96
120
144
168
Hours elapsed

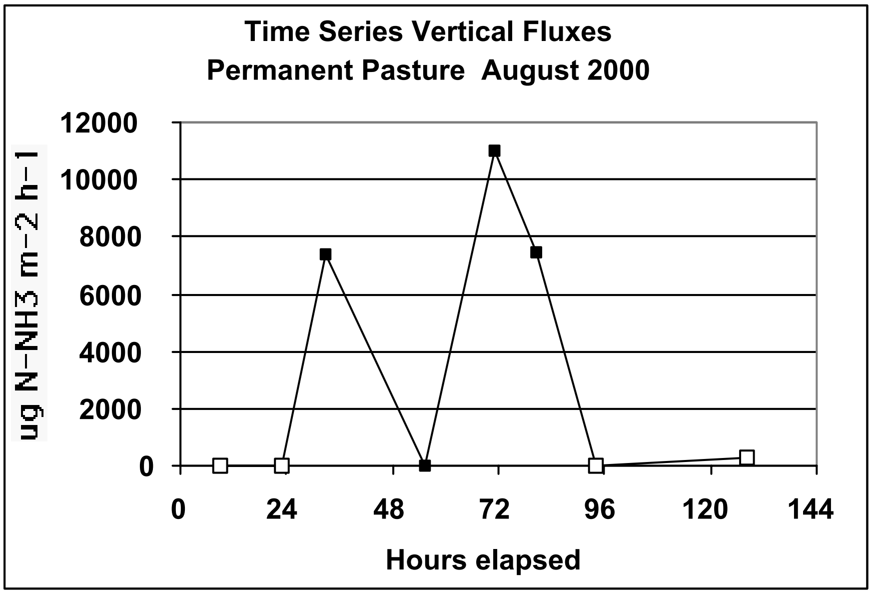
Sites I and J


Time Series Vertical Fluxes
Cotton May 2000
ug N-NH3 m-2 h-1
25000
20000
15000
10000
5000
0
0
24
48
72
96
120
144
168
Hours elapsed

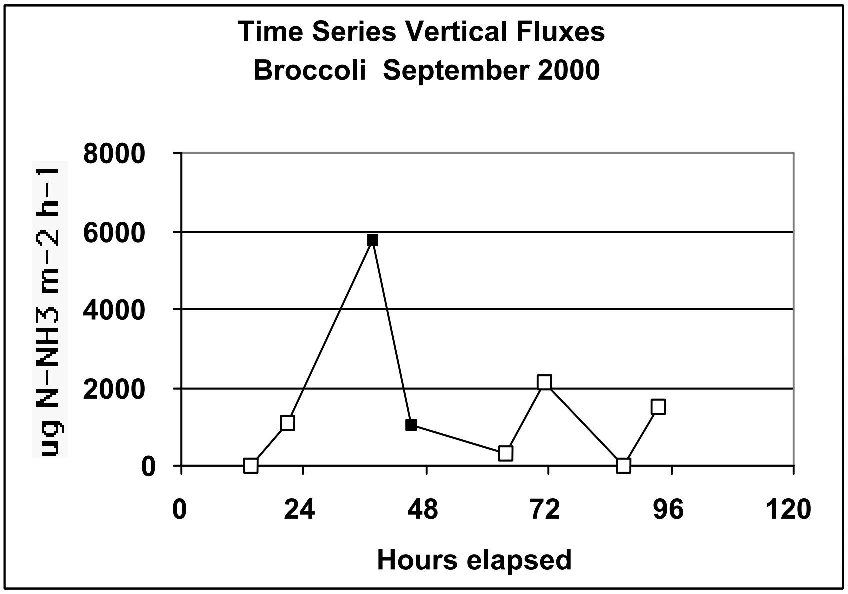

Time Series Vertical Fluxes
Cotton June 2000
ug N-NH3 m-2 h-1
10000
8000
6000
4000
2000
0
0
24
48
72
96
120
144
168
Hours elapsed

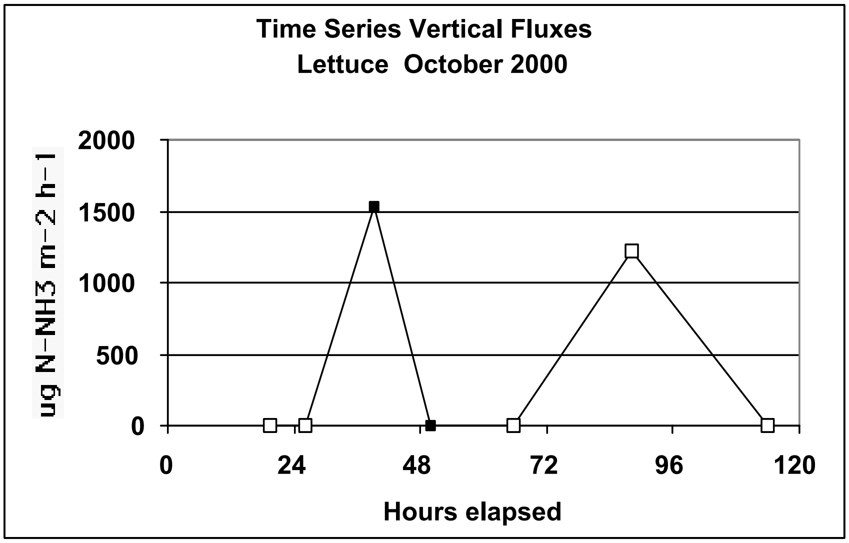
Sites K and L


Time Series Vertical Fluxes
Almonds July 2000
ug N-NH3 m-2 h-1
1500
1000
500
0
0
24
48
72
96
120
Hours elapsed

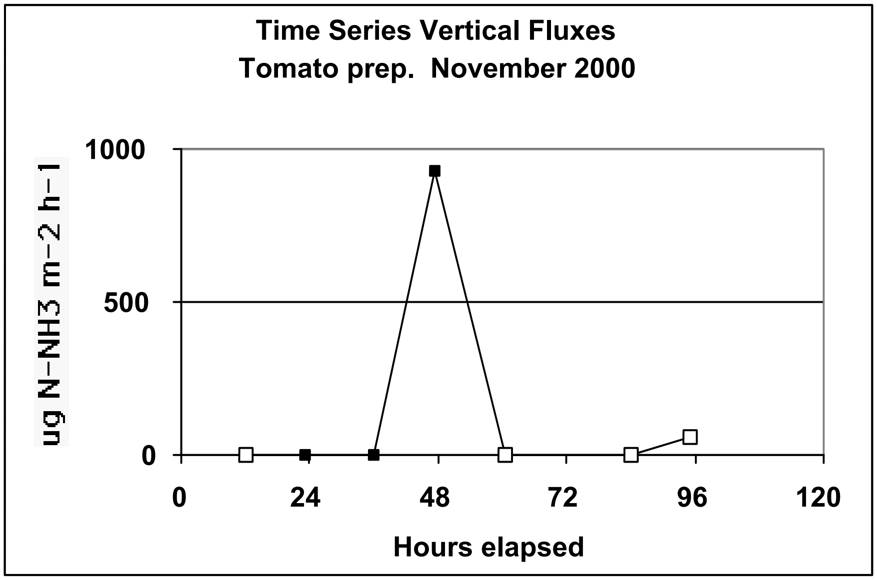

Time Series Vertical Fluxes
Permanent Pasture August 2000
ug N-NH3 m-2 h-1
12000
10000
8000
6000
4000
2000
0
0
24
48
72
96
120
144
Hours elapsed

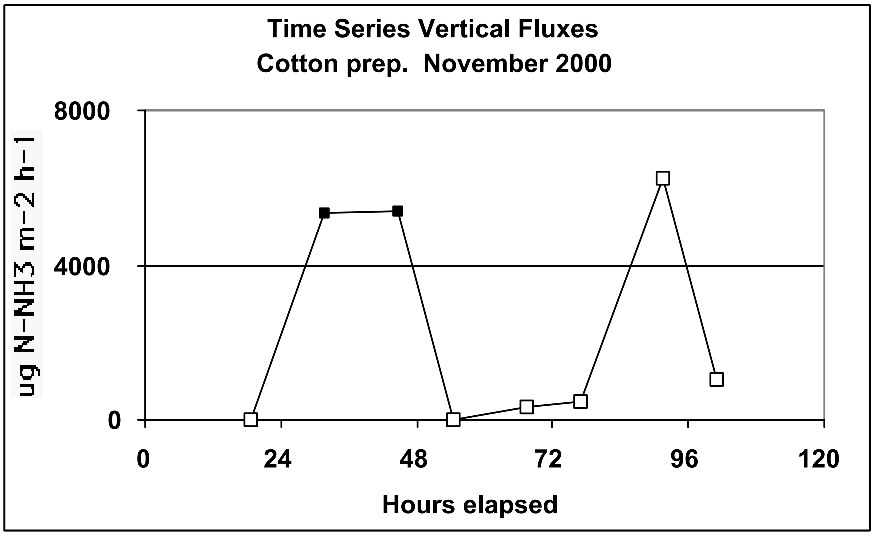
Sites M and Q


Time Series Vertical Fluxes
Broccoli September 2000
ug N-NH3 m-2 h-1
8000
6000
4000
2000
0
0
24
48
72
96
120
Hours elapsed


Time Series Vertical Fluxes
Lettuce October 2000
ug N-NH3 m-2 h-1
2000
1500
1000
500
0
0
24
48
72
96
120
Hours elapsed

Sites R and S


Time Series Vertical Fluxes
Tomato prep. November 2000
ug N-NH3 m-2 h-1
1000
500
0
0
24
48
72
96
120
Hours elapsed


Time Series Vertical Fluxes
Cotton prep. November 2000
ug N-NH3 m-2 h-1
8000
4000
0
0
24
48
72
96
120
Hours elapsed

CHAPTER 3.

STATEWIDE AMMONIA EMISSION INVENTORY FOR CHEMICAL FERTILIZER SOURCES

Primary Investigators: Christopher Potter (NASA Ames), Charles Krauter (CSUF)

Summary of the Inventory Results for Chemical Fertilizer Sources

As a new inventory estimate, statewide emissions of NH_3 directly from chemical fertilizer applications total nearly 12×10^6 kg N- NH_3 annually. As in the case of overall fertilizer use rates, the leading counties for annual emissions of NH_3 directly from chemical fertilizer sources are shown to be Imperial, Fresno, Kern, Tulare, and Kings. The San Joaquin Valley area accounts for more than one-half of the state's total annual emissions of NH_3 directly from chemical fertilizer sources. The Imperial Valley accounts for a higher proportion of the state's total annual emissions of NH_3 directly from chemical fertilizer sources than would be predicted from crop area alone, mainly because of the high proportion (> 65%) of soils with pH above 8 and a major portion of the total fertilizer applied by surface methods to grain crops and pasture grasses.

When analyzed on the basis of DWR crop types, it appears that the generalized categories of field crops and truck crops each account for about one-third of the state's total annual emissions of NH_3 directly from chemical fertilizer sources. Grain, pasture grass, and rice crop categories also contribute notable fractions of the state's total annual emissions of NH_3 directly from chemical fertilizer sources. As improved information becomes available for timing and amounts of fertilizer application rates in DWR crop types and the geographic distribution of fertilizer application methods, a refined model for daily NH_3 emissions directly from chemical fertilizer applications can be generated.

California Crop Type Classification

To improve statewide estimates of fertilizer NH_3 emission sources, crop types and area coverages were defined in our analysis according to the classification system of the California Department of Water Resources (DWR, 1993-1998). Since 1993, DWR has applied geographic information systems (GIS) technology to all new land use surveys. Recent aerial imagery of the survey area is obtained for the early to mid-growing season, usually late June or early July. Color plots of the imagery are then taken into the field and land uses and field boundaries are identified and delineated directly onto the plots. The identified field boundaries are then hand drawn onto U.S. Geological Survey 7.5 minute quadrangles and digitized, or the imagery is viewed directly on the computer monitor and the boundaries are digitized using the imagery for more accurate delineation. The DWR land use and crop type codes are added to each digitized parcel as attributes. The completed digitized maps are processed and data tabulated using GIS software, which includes checking digital line work and land use attributes for quality assurance and completeness.

Eight generalized crop types are included in the DWR system, G-grain and hay crops (6 types), R-rice, F-field crops (12 types), P-pasture (7 types), T-truck crops (25 types), D-deciduous fruits and nut crops (14 types), C-citrus fruits crops (10 types), and V-vineyards (3 types). We selected the most recently available DWR crop maps for the 22 primary agricultural counties of the state (in order of highest to lowest county DWR crop area coverage): Fresno, Kern, Tulare, Kings, San Joaquin, Merced, Imperial, Stanislaus, Madera, Yolo, Colusa, Santa Barbara, San Luis Obispo, Sutter, Glenn, Monterey, Butte, Solano, Riverside, San Bernadino, Sacramento, each of which represent at least 1.5% of the total DWR crop area for the state, and which together include nearly 95% of the total DWR crop area estimates for California. Each of these digital coverages was quality checked at NASA Ames, corrected for technical errors, and added to our statewide GIS for ammonia emission estimates (Figure 3.1).

Crop Fertilizer Application Rates

A database was developed for annual nitrogen fertilizer application rates in the eight general DWR crop types, broken down additionally by the four major valley growing areas of the state: San Joaquin Valley (SJV), Sacramento Valley (Sac), Central Coast Valleys (CCst), and Imperial Valleys (Imp). Table 3.1 lists the annual nitrogen fertilizer application rates assigned in our analysis, according to DWR crop type and valley growing areas. These fertilizer application rates (and associated application dates) were determined the result of consultation with several expert sources. California State University Fresno Plant Science Department faculty and staff included Mahlon Hile, Phillip Jost, Earl Bowerman, and Gino Favagrossa. University of California Cooperative Extension personnel from several counties in the San Joaquin Valley provided information, particularly Blake Sanden in Bakersfield (for Kern County), and Bruce Roberts in Hanford (for Kings County). The fertilizer and agricultural consulting industry provided considerable information of application rates as well. In particular, Steve Spangler of Unocal, Roger Isom of the California Cotton Ginners and Growers Associations, Mike Hemman of Dow AgroScience, Rene Shoemaker of Helena Chemical, Jack King, Eric Athorp of J. G. Boswell, Randy Jacobsen of Jacobsen Consulting, Lee Simpson and Deborah Agajanian of Simpson Vineyards, and Phillip Washburn of Washburn Farming Co.

In addition to the eight general crop types, several special land use categories exist in the DWR legend that require definition in terms of fertilizer application practices. The following adjustments were made in our statewide GIS calculations: "Multicrop" areas are counted as more than one crop fertilizer application specified for DWR crop types per polygon, "Intercrop" areas are counted as fertilizer application for F crops (presumably planted under a young D crop), "Doublecrop " areas are counted as fertilizer application for two crop types (usually G and F) as specified per polygon. Two other crop types, almonds and (non N-fixing) pasture grasses, were treated separately due to the predominant difference in fertilizer application rates.

Annual nitrogen fertilizer application rates (Table 3.1) were multiplied by the area coverage of each major DWR crop type in each county of the state to generate a totals for annual fertilizer use (Table 3.2). We note that these a county totals for annual fertilizer use are based on different years during which the most recent DWR crop type surveys were reported. Therefore, these totals for annual fertilizer use may not represent any single year's application total for a major valley growing areas of the state, but are instead are based on a combination of several recent years of annual fertilizer application practices and may include statewide changes in crop coverages. This 'bottom-up' method of determining N chemical fertilizer use results in a estimate of slightly more than 422,500 metric tons N fertilizer applied statewide (Table 3.2). The leading counties in terms of N fertilizer application were shown to be Fresno, Imperial, Kern, and Tulare (Figure 3.2).

To check the overall accuracy of the combined N application rates and DWR crop areas coverages derived in Table 3.2 for annual fertilizer application totals by county, we compared these 'bottom-up' estimates to country N fertilizer sales totals reported by the California Department of Food and Agriculture (CDFA, 1999). It was found that, for the entire state, our 'bottom-up' estimates of fertilizer application rates matched the country N fertilizer sales total with a low overall error of 9%. The match between our 'bottom-up' estimates of fertilizer application rates and country N fertilizer sales total was even better (5%) for the SJV area as a whole, which comprises almost two-thirds of the statewide DWR crop coverage. County-by-county comparisons of the 'bottom-up' fertilizer application rates with fertilizer sales totals are not as meaningful in terms of accuracy evaluations because of cross-county transportation of fertilizer chemicals and the geographic distribution of points of fertilizer imports to the state.

Statewide Ammonia Emission Estimates from Fertilized Crops

On the basis of our field measurement data reported in Chapter 2 of this report, a rule-based model was developed to extrapolate NH_3 emission factors to the statewide level. Gas emission factors are computed as the NH_3 emission total divided by the total N fertilizer application rate. The two primary factors influencing N-NH_3 emissions among the sites were method of fertilizer application (FA) and soil pH. Consequently, the following set of rules have been assigned:

NH_3 emission factor (percent N applied)	Rules	Field Sites
6.5	FA=1 and pH=a	B, F
5.5	FA=1 and pH=b	H
4.0	FA=1 and pH=c	D, L
1.0	FA=2	G, J, R, S
0.5	Special case - buried drip	E
0.0	Special case – micro-drip	K

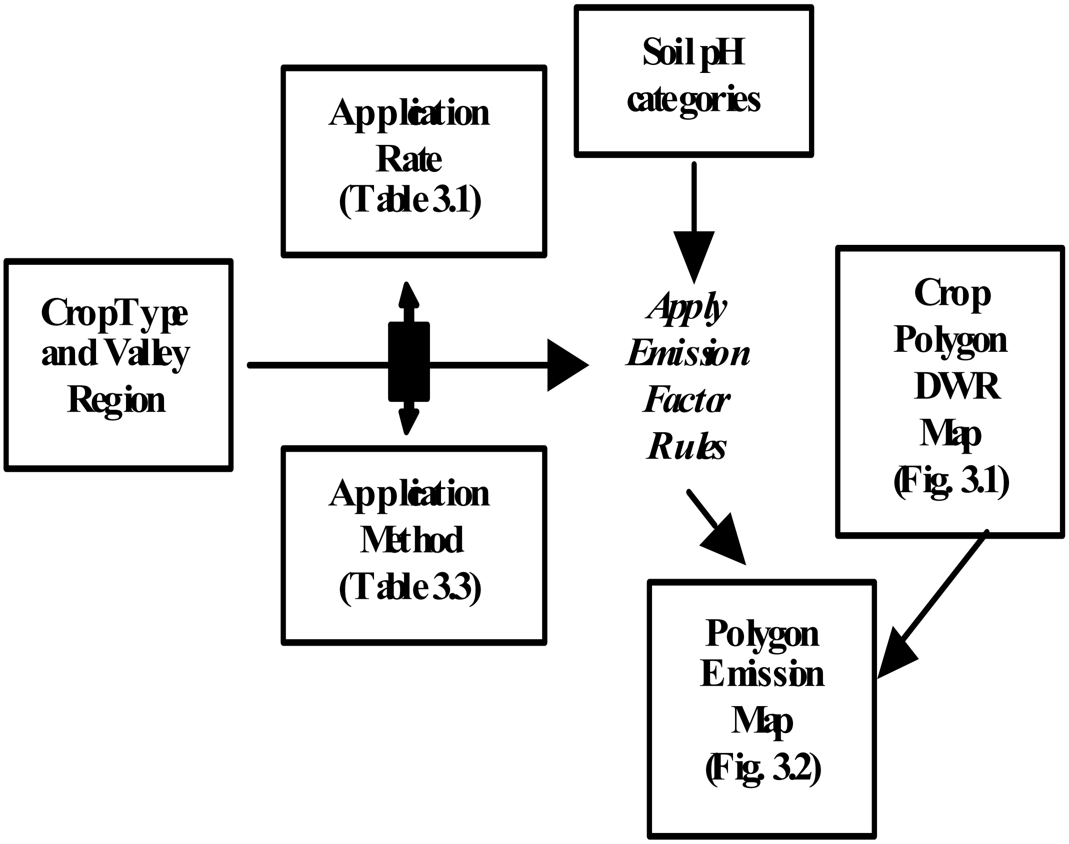
where FA type is categorized as 1=surface, 2=subsurface (injected/side-dressed), and soil pH at the point of fertilizer application is categorized as a=above pH 8, b=between pH 7-8, c=below pH 7.

The collection of measured emission factors for Central Valley crop sites suggest that in cases when N fertilizer is applied at the soil surface (using broadcast, surface band, or water run methods), plus soil pH at the point of application, influences the fraction emitted as NH_3 at the level of about plus or minus 1.5 percent. When fertilizer is applied below the surface, using either NH_3 injection or side-dressed, the emission factor is reduced substantially, presumably because upward diffusion of NH_3 gas back to the soil surface is inhibited by absorption reactions within the soil matrix. Among the field sites sampled, there did not appear to be a consistent effect of soil clay content to include as a rule for assignment of N-NH_3 emission factors. Likewise, extremes of air temperature or soil moisture (flooding) due to irrigation may have a secondary effect on N-NH_3 emissions among the sites, but these effects remain ambiguous in the measurement data set.

To apply the rule-based model, we assigned FA method according to common practices in the four major valley growing areas of the state (Table 3.3). Percentages of each FA method are based on the fraction of the crop fertilized with a particular method within a valley region. Where a crop is fertilized more than once during the season and FA methods are different, the percentages estimated in Table 3.3 reflect the fraction of fertilizer applications in each method category. In regions where there is a significant amount of drip application that is buried, the fractions have been adjusted reflect the percentage of these buried drip systems.

A flowchart of our methodology for generating statewide NH_3 emissions from the data sets produced from this work is shown below. Fertilizer application rates and application methods are assigned according to DWR crop types and valley regions

(Tables 3.1 and 3.3). Soil pH category distributions are added on a county-by-county basis to make the necessary emission factor assignment for each DWR crop polygon (Figure 3.1).



To estimate soil pH coverage, the STATSGO soils polygon map for the state of California was obtained from the National Resources Conservation Service. Soil pH content of the surface horizon was calculated for each map unit from the weighted average of all soil series indicated within the map unit, on the basis of methods described in detail by Davidson and Lefebvre (1993). Using county boundaries, we computed the surface soil pH (at the point of fertilizer application) in categories a=above pH 8, b=between pH 7-8, and c=below pH 7. On a statewide basis, the STATSGO data set indicates that about 1% of all soils are above pH 8, 21% are between pH 7-8, and 78% are below pH 7.

Computed using the rule-based model specified above, the average NH_3 emission factor for the DWR crops in state of California is 2.4% of the total applied N fertilizer (Table 3.4). An emission factor estimate of 1.5% of applied fertilizer for the Central Coast counties of Monterey, San Luis Obispo, and Santa Barbara is notably lower than the statewide average, mainly because of the higher proportion of crops fertilized using the micro-drip method in these areas. Emission factor estimates of higher than 2.5% of applied fertilizer were estimated for the counties of Imperial, Merced, Kern, Kings, and Sutter, chiefly because of the low proportion (< 30%) of soils with pH below 7. When computed by DWR crop type (Table 3.5), NH_3 emission factor estimates are highest for pasture grasses (3.9%) owing to the common practice of surface fertilizer application, and lowest for field crops (2.0%) owing to the increasingly common practice of sub-surface (injected) fertilizer application (Table 3.2).

Using the rule-based model specified above to assign NH_3 emission factors, together with county level fertilizer application rates for DWR crop types (Table 3.2), the statewide inventory estimate for emissions of NH_3 directly from chemical fertilizer applications is estimated to be 11.7×10^6 kg N- NH_3 annually (Table 3.4). As in the case of overall fertilizer application rates, the leading counties for annual emissions of NH_3 directly from chemical fertilizer sources are Imperial, Fresno, Kern, Tulare, and Kings. Overall, the San Joaquin Valley area accounts for more than one-half of the state's total annual emissions of NH_3 directly from chemical fertilizer sources. The Imperial Valley accounts for a higher proportion of the state's total annual emissions of NH_3 directly from chemical fertilizer sources than would be predicted from crop area alone, mainly because of the high proportion (> 65%) of soils with pH above 8 and a major portion of the total fertilizer applied by surface methods to grain crops and pasture grasses.

When analyzed on the basis of DWR crop types, it appears that the broad categories of field crops and truck crops each account for about one-third of the state's total annual emissions of NH_3 directly from chemical fertilizer sources (Table 3.5). Grain, pasture grass, and rice crop categories also contribute major fractions of the state's total annual emissions of NH_3 directly from chemical fertilizer sources.

As a follow-on to this report, fertilizer application schedules can be added to this inventory analysis to generate daily NH_3 emissions directly from chemical fertilizer applications, with timing throughout the year on a county-by-county, crop-by-crop scheduling basis. We anticipate from initial analyses that the highest NH_3 emission rates directly from fertilizer applications would be predicted during periods between February and September. However, as improved information becomes available for timing and amounts of fertilizer application rates in DWR crop types and the geographic distribution of fertilizer application methods, a refined model for daily NH_3 emissions directly from chemical fertilizer applications can be generated.

Table 3.1. Estimated N fertilizer application rates for cropland types in California.

DWR Crop	Description	Fertilizer N Application Rate			
		kg N ha^{-1}			
Class		SJV	Sac	CCst	Imp
C	Citrus & Subtropical Fruit	150	140	140	125
D	Deciduous Fruit & Nut (Non-Almond)	140	110	110	140
D12	Almond	100	80	80	100
F	Field	140	140	140	140
G	Grain &Hay	100	100	100	100
I	Idle	0	0	0	0
P(3,6,7)	Pasture Grass (non N-fixing)	100	100	100	100
P(1,2,3,4)	Pasture (Alafafa & Clover)	0	0	0	0
R	Rice	100	100	100	100
T	Truck, Nursery & Berry	250	210	300	300
V	Vineyard	70	60	60	75

Notes: Valley regions are abbreviated as San Joaquin Valley (SJV), Sacramento Valley (Sac), Central Coast Valleys (CCst), and Imperial Valleys (Imp). See Table 3.2 for list of counties included in each valley region. The conversion factor to English units is 1 kilogram per hectare = 0.892 pounds per acre.

Table 3.2. Estimated fertilizer N used in counties of California.

	Yr	DWR area total (hectares)	Metric Tons Nitrogen		Percent Difference
San Joaquin Valley			County Sales (CDFA, 1999)	DWR Crop Maps	
San Joaquin	96	232,531	77,701	25,360	67
Stanislaus	96	158,549	16,169	15,233	6
Madera	95	145,660	4,540	10,835	-139
Merced	95	226,158	17,008	22,782	-34
Fresno	94	538,163	47,546	60,625	-28
Kern	98	398,140	41,296	41,108	0
Kings	96	236,465	22,983	26,420	-15
Tulare	93	307,772	20,144	31,877	-58
TOTAL		**2,243,437**	**247,386**	**234,240**	**5**
Sacramento Valley					
Butte	94	106,658	19,496	15,942	18
Colusa	93	130,851	21,577	21,482	0
Glenn	93	111,747	12,420	15,636	-26
Sacramento	93	80,029	24,078	8,422	65
Solano	94	83,183	7,764	9,118	-17
Sutter	98	119,301	23,580	18,436	22
Yolo	97	147,605	14,126	18,515	-31
TOTAL		**779,373**	**123,039**	**107,551**	**13**
Central Coast					
Monterey	97	107,251	13,171	13,468	-2
San Luis Obispo and Santa Barbara	95	125,976	13,270	14,125	-6
TOTAL		**233,227**	**26,440**	**27,592**	**-4**
Imperial Valley					
Riverside and San Bernadino	93	54,482	14,516	9,086	37
Imperial	97	211,559	51,220	44,088	14
TOTAL		**266,041**	**65,735**	**53,173**	**19**
STATE TOTAL		**3,522,079**	**462,601**	**422,556**	**9**

Notes: Yr is the year of the most recent DWR county survey of crop type coverages.

Table 3.3a. Assignment of regional fertilizer application practices.

San Joaquin Valley

	Surface	Injected	Micro-irrigation	Buried Drip
DWR Crop	FA = 1	FA = 2		
C (Citrus)	50%		50%	
D (Decid. non-Almond)	60%		35%	5%
D12 (Almond)	50%		45%	5%
F (Field)	30%	60%	10%	
G (Grains)	60%	40%		
Pa(1,2,4,5)				
Pb(3,6,7)	75%	25%		
R (Rice)	50%	50%		
T (Truck)	40%	40%	15%	5%
V (Vines)	60%		35%	5%

Sacramento Valley

	Surface	Injected	Micro-irrigation	Buried Drip
DWR Crop	FA = 1	FA = 2		
C (Citrus)	50%		50%	
D (Decid. non-Almond)	60%		40%	
D12 (Almond)	50%		50%	
F (Field)	30%	60%	10%	
G (Grains)	70%	30%		
Pa(1,2,4,5)				
Pb(3,6,7)	80%	20%		
R (Rice)	50%	50%		
T (Truck)	40%	55%	5%	
V (Vines)	60%		40%	

Table 3.3b. Assignment of regional fertilizer application practices.

Salinas Valley, Central Coast

	Surface	Injected	Micro-irrigation	Buried Drip
DWR Crop	FA = 1	FA = 2		
C (Citrus)	25%		75%	
D (Decid. non-Almond)	35%		65%	
D12 (Almond)	10%		90%	
F (Field)	35%	35%	25%	5%
G (Grains)	70%	30%		
Pa(1,2,4,5)				
Pb(3,6,7)	80%	20%		
R (Rice)				
T (Truck)	30%	50%	15%	5%
V (Vines)	30%		70%	

Imperial Valley

	Surface	Injected	Micro-irrigation	Buried Drip
DWR Crop	FA = 1	FA = 2		
C (Citrus)	30%		70%	
D (Decid. non-Almond)	30%		70%	
D12 (Almond)	40%		60%	
F (Field)	35%	35%	25%	5%
G (Grains)	70%	30%		
Pa(1,2,4,5)				
Pb(3,6,7)	80%	20%		
R (Rice)	50%	50%		
T (Truck)	30%	50%	15%	5%
V (Vines)	30%		70%	

Notes:

FA = 1, Surface application methods include broadcast, surface band, water run.

FA = 2, Subsurface application methods include side-dressed, and NH_3 injection.

Micro-irrigation methods include conventional drip emitters and micro-spray/sprinklers used to apply fertilizer at low concentrations.

Buried drip method is a drip emitter system buried at least 5 cm below the surface applying low concentrations of fertilizer

Table 3.4. Estimated NH_3-N emission directly from chemical fertilizer application in counties of California.

		NH_3-N Emission	Average NH_3 Emission Factor
	DWR area total (ha)	10^6 kg	
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%**

Table 3.5. Estimated emission of N-NH_3 directly from chemical fertilizer application in crop types of California.

DWR Crop	Description	NH_3-N Emission	Average NH_3 Emission Factor
Class		10^6 kg	
C	Citrus & Subtropical Fruit	0.4	2.2%
D	Deciduous Fruit & Nut (Non-Almond)	0.5	2.6%
D12	Almond	0.3	2.2%
F	Field	2.3	2.0%
G	Grain &Hay	1.9	3.5%
I	Idle	0.0	0.0%
P(3,6,7)	Pasture Grass (non N-fixing)	2.5	3.9%
P(1,2,3,4)	Pasture (Alafafa & Clover)	0.0	0.0%
R	Rice	1.5	2.6%
T	Truck, Nursery & Berry	2.0	2.3%
V	Vineyard	0.3	2.6%
	GrandTotal	**11.7**	**2.4%**

Figure 3.1. Statewide distribution of DWR crop types. (Note: Original data from California DWR county crop maps, consolidated and quality checked at NASA Ames Research Center).

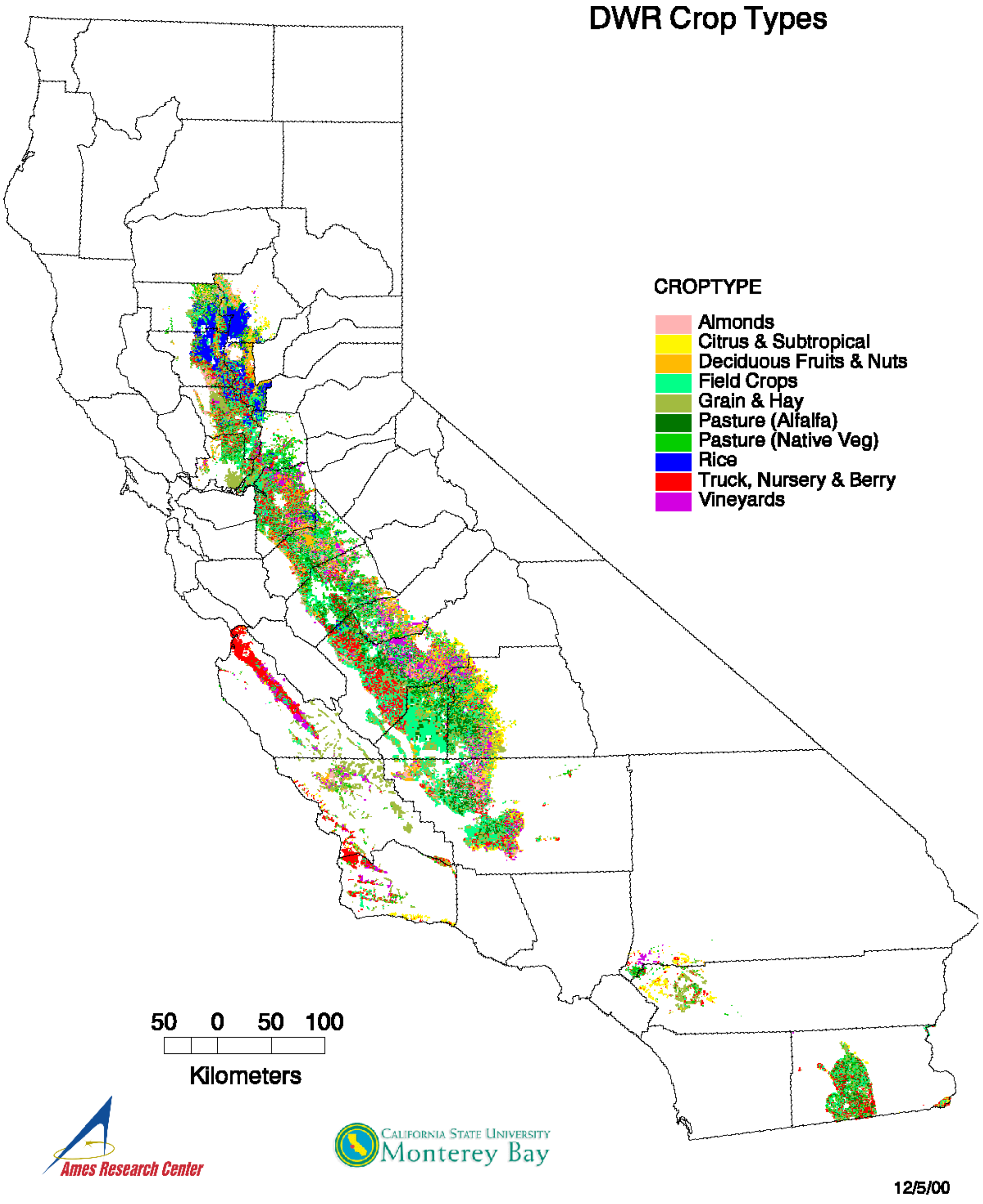
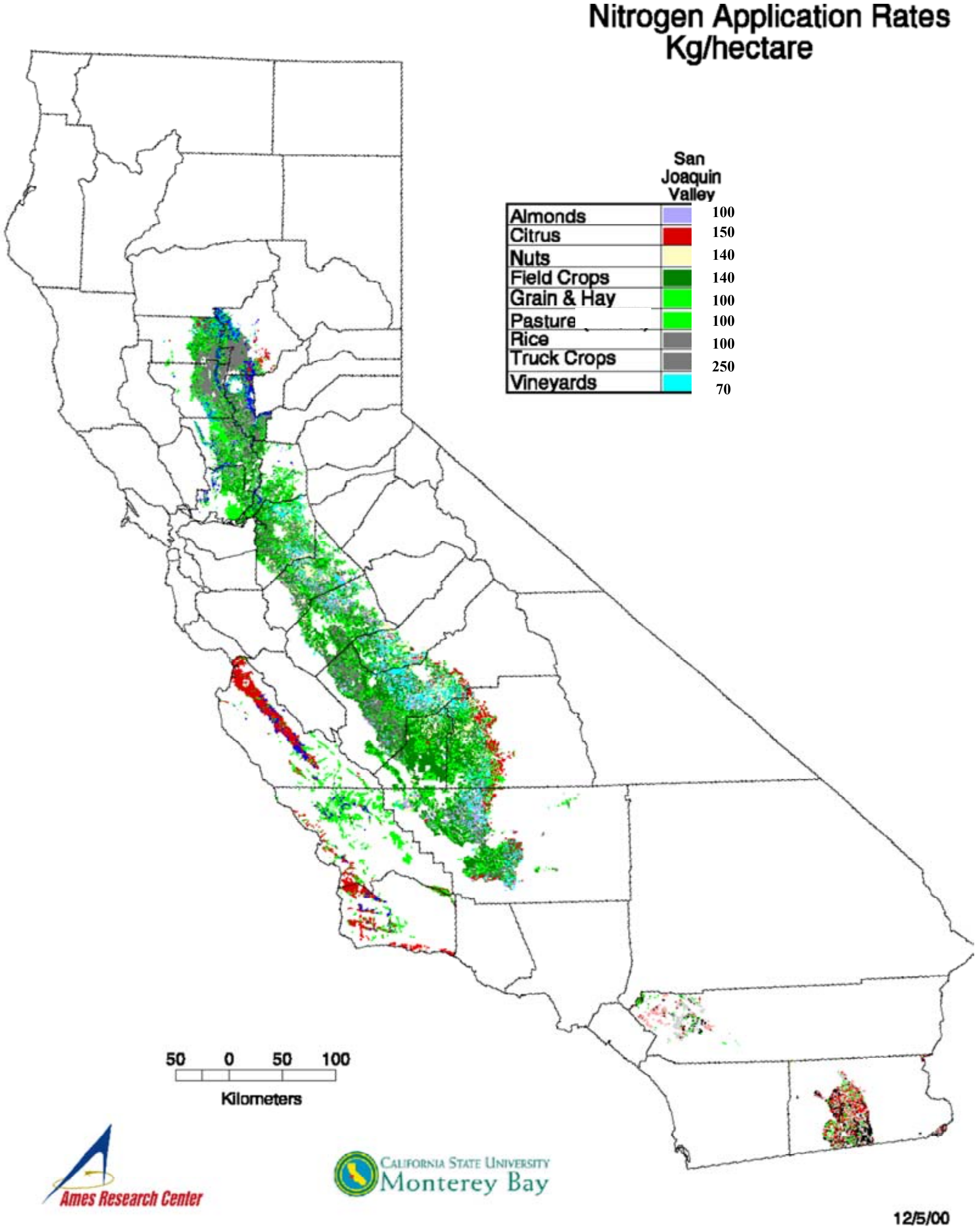


Figure 3.2. Statewide annual application rates for chemical N fertilizers. See Table 3.1 for annual application rates in all valley growing regions.



CHAPTER 4.

STATEWIDE AMMONIA EMISSION INVENTORY FOR NATIVE SOIL SOURCES

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Summary of the Inventory Results for Native Soil Sources

A comprehensive measurement data set is currently lacking upon which to build a reliable emissions inventory for NH_3 from native soil sources in California. Therefore, a computer modeling approach was used to develop an environmentally based estimate of statewide annual emission rates of N-NH_3 from native soils and indirectly from residual fertilizer N sources in cultivated soils. The NASA-Ames version of the CASA (Carnegie-Ames-Stanford Approach) ecosystem model for soil nitrogen gas emissions estimates seasonal patterns in carbon fixation, nutrient allocation, litterfall, and soil nitrogen mineralization, and soil ammonia emission.

The use of remote sensing drivers in CASA has clear advantages for scaling up to regional predictions of vegetation production that can drive natural trace gas emission estimates. This CASA modeling system for California is based on regional data sets (8-km resolution) from a geographic information system (GIS) developed specifically for this ARB-sponsored research on N-NH_3 emissions. The general conditions that potentially favor soil NH_3 emissions from soils (high pH, low moisture) are integrated in the NASA-CASA formulation.

Based on our CASA inventory estimate, statewide emissions of NH_3 from native soil N sources could range from 12-57 x 10^6 kg N- NH_3 annually, depending on the importance of soil pH on emission rates. The most important land cover type in terms of contributions to this statewide emission inventory is cropland and semi-agricultural lands, which make up one-third to one-half of the total native soil N sources for NH_3 emissions annually. Other native areas that contribute substantially to the statewide emission inventory for emissions of NH_3 are soils of evergreen needleleaf forests, woodland, and wooded grassland ecosystems, mainly on the basis of their large area coverage of the state's natural areas. The model predicts that October is the peak month overall for NH_3 emissions from native soils in California. When totaled for the entire region, native soil sources of NH_3 predicted for Central Valley counties are highest from July through January. This seasonal pattern in predicted soil NH_3 emission is fairly consistent with observed seasonality in $PM_{2.5}$ levels the San Joaquin Valley Air Basin. The combination of productive vegetation communities growing on (even slightly) alkaline soils results in the largest annual emissions of NH_3 from native soil N sources.

Statewide Geographic Information System Development

For this regional model application to the state of California, we used essentially the same NASA-CASA ecosystem model algorithms as for our previous global simulations (Potter, 1999; Potter and Klooster, 1998). However, in the place of global

1^{o} inputs, regional data sets (8-km resolution) from a statewide GIS were used as model drivers and land surface parameter files. Following the same general approach used by Davidson et al. (1998) for a regional application of NASA-CASA soil nitrogen model component in the southeastern U.S., we assembled a complete set of GIS raster coverages to serve as model-compatible inputs, including monthly rainfall and surface air temperature, surface solar radiation, soil texture, land cover type, and satellite vegetation index for the state of California and, in many cases, for the larger western U.S. region.

All raster maps were gridded at 8-km spatial resolution in an equal area projection. In terms of single grid cell size (64 km^2), this produces an improvement in spatial resolution of more than 150 times, compared to the global 1^{o} (ca. 10^4 km^2 cell size) data drivers for the model. The coastal boundary line file used as a base to geo-reference the 8-km map set was taken from the Digital Chart of the World (DCW, 1993).

Satellite Vegetation Index

In order to estimate ammonia emissions from native sources, it is necessary to identify the seasonal patterns of vegetation types throughout California. To do this, we obtained the monthly composites for the years 1982-1994 of Normalized Difference Vegetation Index (NDVI) from the Advanced Very High Resolution Radiometer (AVHRR), which is available from the NOAA/NASA Pathfinder AVHRR Land (PAL) program at NASA Goddard Space Flight Center's (GSFC) Distributed Active Archive Center (DAAC). Complete AVHRR data sets are produced from NOAA Global Area Coverage (GAC) Level 1B data, and consist of reflectances and brightness temperatures derived from the five-channel cross-track scanning AVHRR aboard the NOAA Polar Orbiter 'afternoon' satellites (NOAA-7, -9, and -11). DAAC references by Agbu and James (1994) and Kidwell (1991) provide more information on the derivation and potential use of these NDVI products.

Monthly composite data sets are designed to remove much of the contamination due to cloud cover present in the daily AVHRR data sets (Holben, 1986). To generate a composite data set, eight to eleven consecutive days of data are combined, taking the observation for each 8-km bin from the date with the highest NDVI value. Only data within 42 degree of nadir are used in the composite to minimize spatial distortion and bi-directional effect biases at the edge of a scan. A Rayleigh correction is calculated and applied using a standard radiative transfer equation and methodology, which follows the work of Gordon et al. (1988).

Having obtained original PAL files for NDVI, we ran a low-pass filter over the data to remove several narrow lines of anomalous high values which are presumably a result of compositing. The filter routine computes the mean of six nearby grid cell values (located two rows and three columns above each cell location), and compares this average to the actual cell value. If the difference between the original cell value and the average of the values above that cell was greater than 200 units, then the value of that cell is replaced by the average of the nearby cell values. Typically, less than 25% of the NDVI values over the entire regional land area required modification with this filtering step.

Although PAL composite data set are produced expressly for studies of temporal and interannual behavior of surface vegetation, subsequent processing is recommended if a more complete cloud-free signal is required. Consequently, we applied solar angle corrections (S) and Fourier smoothing algorithms (FA) developed by Los et al. (1994) for AVHRR data sets to further remove anomalous NDVI signals, due presumably to remaining cloud cover interference. Settings for this FA correction include three temporal harmonics and a weighted Fourier transform, i.e. values which fall above the Fourier curve are given more weight than values below the curve. This assumes that higher NDVI values are more likely to be correct than low NDVI values which could occur during periods of cloud or smoke formation. The FA algorithm modified mean annual NDVI values by more than +10% of their original values in approximately four out of every ten grid cells in the region.

From these 8-km monthly FAS-NDVI data sets, we applied empirical algorithms described by Potter et al. (1993) to compute second-level model drivers for the fraction of intercepted photosynthetically active radiation (FPAR) and leaf area index (LAI). For crop cover areas, we also computed the pattern of leaf cover development per month based on average 1-km FAS-NDVI values beginning 1 April, 1992. The source of this original 1-km NDVI comes from Eidenshink (1992) at the U.S. Geological Survey, EROS Data Center.

Land Cover Type

The land area within the state of California covers approximately 400,00 km^2. For land cover characterization at the 8-km resolution, we used the classification scheme of DeFries et al. (1995), which was generated from analysis of 1-km AVHRR - NDVI patterns over the year. Ten general classes are represented in this global land cover map at 8-km grid cell resolution (Figure 4.1). In California, evergreen needleleaf forest is the most common (31% of the total area), followed by open shrub land and deserts (24%), cropland and semi-agricultural lands (21%), woodlands (17%), and then all other cover types combined, including wetlands, river ways, and bare ground (8%). The combination of semi-agricultural lands, such as residential lawns, golf courses, parks, and marginal/fallow lands, together with the actively cultivated farming areas generally covered by the DWR crop coverage for each county of the state, makes the cropped land cover category about twice the size of the DWR crop coverage maps used for estimating emissions from active fertilizer application (see Chapter 3).

With respect to this application of the model algorithm coefficients, we did not attempt to distinguish between primary, secondary, or recently cleared forest types. In summary, we applied the same algorithm coefficients developed from the global version of the NASA-CASA model (Potter, 1999) for relatively undisturbed forests or grasslands and to their respective disturbed or converted cover categories. This means that any differences in model results reported for different forest cover types would not be attributable to internal model settings in the general land cover groups defined above, but instead to patterns in NDVI, climate, or soils inputs to the model.

Model parameters that are assigned according to the ten general (DeFries et al., 1995) land cover types include leaf litter nitrogen (Table 4.1) and lignin content (Potter, 1999), decomposition rates of soil carbon in cultivated soils, and plant rooting depth. For the forest classes, rooting depth is set uniformly to 2-m, whereas in the other land cover classes, it is set uniformly to 1-m.

Soil Attributes

STATSGO soils data for the state of California were obtained from the National Resources Conservation Service. Soil pH (Figure 4.2) and average clay content of the surface horizon was calculated for each map unit from the weighted average of all soil series indicated within the map unit, using methods described in detail by Davidson and Lefebvre (1993).

Soil map units were assigned to the four aggregated texture classes (FAO, 1971), according to their clay content (0-5% clay, 5-15% clay, 15-30% clay, > 30% clay). The most common texture class in the state is the coarse-medium 5-15% clay, which covers 30% of the area. Coarse (0-5% clay) and medium (15-30% clay) texture classes each make up about 22% of the state's soils. This spatial information on soil texture is used in the NASA-CASA model to define regional patterns of soil moisture holding capacity and rates of soil organic matter storage.

STATSGO data at the level of Soil Order in the U.S. classification system were used also to define three general soil fertility classes - low, medium, and high (Birkeland, 1974). On low fertility soils, an adjustment (+10%) is favored that allocates increasing root biomass for the acquisition of soil nutrients (Potter, 1999). On medium-to-high fertility soils, a similar adjustment is favored that allocates increasing stem and leaf biomass for light harvesting functions in the canopy.

Monthly Rainfall and Surface Air Temperature

Monthly mean climate maps for California were obtained from ZedX, Inc. (Boalsburg, PA, USA). We regridded the original files from 1-km spatial resolution to our nominal 8-km cell resolution. These average climate data sets are generated based on long-term (1961-90) records from weather stations in California, which are part of the Global Historical Climatology Network (GHCN) at the Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory (Vose et al., 1992). The spatial interpolation is done by three-dimensional linear regression. Accuracy of the resulting climate maps are checked by percent absolute difference analysis with comparison to original station values.

Monthly Solar Surface Radiation

Surface solar radiation flux (Srad) gridded for the state of California was not in the same format as other monthly mean climate maps. Therefore, we estimated Srad in monthly average units of W m^{-2}, based on dirunal temperature range (DTR) data reported in GHCN minimum and maximum temperature record. Our estimation technique for Srad is founded on the atmospheric transmittance theory from Bristow and Campbell (1984), who reported that the difference between maximum and minimum daily temperatures is closely correlated with the amount of solar radiation received. At times when the net flux of solar radiation at the Earth's surface is low (e.g., during overcast sky conditions), the difference in surface temperature extremes is also generally low. The opposite is true for clear sky conditions. Thus, measurements of daily temperature extremes should be related to the atmospheric transmittance for solar radiation flux using relatively simple least squares regression functions. This method to estimate regional patterns in Srad has been demonstrated for the continental United States as part of the VEMAP ecosystem simulation experiment (Kittel et al., 1995).

For our modeling purposes, a set global regression functions was developed for prediction of monthly mean Srad from DTR measurements. Calibration data sets for DTR were obtained as monthly mean values from the Climatic Research Unit

(CRU), University of East Anglia, gridded originally to 0.5° resolution (New et al., 2000). Multi-year DTR data (1983-91) from the CRU data set were used to develop third-order polynomial equations, which predict monthly mean Srad within four global latitude zones: > 50° N, 50° -10° N, 10° N - 20° S and > 20° S. The measured Srad data for these regressions were obtained from the SeaWiFS (Sea-viewing Wide Field-of-view Sensor) radiation flux estimates from Bishop and Rossow (1991), which are derived as a product of the International Satellite Cloud Climatology Project (ISCCP) and gridded originally at a spatial resolution of 2.5° for the period July 1983 to June 1991. Starting from weather station locations listed in the GHCN (Vose et al., 1992), we sub-sampled from the CRU globally distributed DTR coverage across each latitude zone on the basis of those locations producing the highest R^2 regression coefficients with Srad as the dependent variable. This subset of regression curves was selected to represent the four latitude zones. In cases of extreme DTR values beyond the applicable range of the regression curves (either lower or higher than the independent variable bounds), we set minimum and maximum Srad values predicted at the extremes of the calibration DTR values. The resulting Srad regression equation for California has an R^2 of 0.54 ($p<0.05$), applicable over the DTR of 3-16° C.

Emission Model Description and Implementation

Rather than simply apply generic fixed emission factors for soil types, as has been done in the past, the emission rates for this study were computed using an ecosystem model that takes into account water balance, snow melt, soil pH, and soil moisture. Our model, the NASA-Ames version of the CASA model for soil nitrogen gas emissions, has been documented in Frolking et al. (1998) and Potter and Klooster (1998). The model simulates seasonal patterns in carbon fixation, nutrient allocation, litterfall, and soil nitrogen mineralization, and soil ammonia emission (Figure 4.3). Several other soil trace gas fluxes (i.e., N_2O, NO, CH_4 and CO uptake) are simulated in NASA (Potter and Klooster, 1998). The use of remote sensing drivers in CASA (including NDVI) has clear advantages for scaling up to regional estimates of vegetation production that can drive trace gas fluxes. In NASA-CASA's spatial mode, the net fixation of CO_2 by vegetation, also called net primary production (NPP), and the plant uptake of soil N is constrained by satellite NDVI (Potter, 1999). Calculation of NPP in CASA is as a product of the fraction of intercepted photosynthetically active radiation (FPAR, from NDVI), surface solar irradiance, and an optimal light utilization efficiency term ($e_{\max}$), modified by surface temperature and soil moisture estimates.

The soil component of the NASA-CASA model simulates carbon-nitrogen cycling and associated flux of trace gases using a set of soil organic matter pools with a structure comparable to the CENTURY ecosystem model (Parton et al., 1992). First-order equations simulate exchanges of decomposing plant residue (metabolic and structural fractions) at the soil surface, together with surface soil organic matter (SOM) fractions that presumably vary in age and chemical composition. Active (microbial biomass and labile substrates), slow (chemically protected), and passive (physically protected) fractions of the SOM are represented. The model computes the fraction of water-filled soil pore space (WFPS) in the various layers in order to estimate scalars that represent the effect of soil moisture on organic matter turnover and CO_2 emissions rates, which couple to N mineralization fluxes and N trace gas emissions.

For the simulations in this study, the model was brought to initial state (for Dec. 31) with respect to soil moisture, litter inputs, soil C/N pool sizes and turnover times using monthly climate, together with remote sensing drivers from the CASA-Biosphere version (Potter, 1999), in a 100-year initialization simulation run. Carbon entering the ecosystem yearly as net primary production (NPP; defined as net fixation of CO_2 by vegetation) and annual litterfall return of C and N to the soil for mineralization was estimated on a pixel-by-pixel basis (Figure 4.4), using the 100-year "spin-up" simulation run to approximate reported carbon and nitrogen content of surface soils. The global model setting for nitrogen content of plant leaf litter are provided in Table 4.1 according to vegetation cover class. Further details on the model algorithms for plant water use, snow dynamics in cold winter areas, and a review of limiting factors on fertilizer ammonia emissions are provided in the sections that follow.

Water balance equations

An empirically based potential evapotranspiration (PET) algorithm in this model is based on a modified formulation of the Priestly and Taylor (1972) method described by Campbell (1977) and Bonan (1989):

$$\mathrm{PET} = a\,(\mathrm{T_a} + b)\,\mathrm{R_S} \qquad (1)$$

where PET is potential evapotranspiration (cal $\mathrm{cm^{-1}}$ $\mathrm{day^{-1}}$), $\mathrm{T_a}$ is mean air temperature ($^{\mathrm{o}}$C), $\mathrm{R_S}$ is mean surface solar radiation (cal $\mathrm{cm^{-1}}$ $\mathrm{day^{-1}}$), and *a* and *b* are empirical constants (set as functions of saturation vapor pressure) derived by Jensen and Haise (1963) and Jensen (1973). Conversion of PET to units of cm $\mathrm{day^{-1}}$ is made by dividing by the latent heat of vaporization.

Estimated evapotranspiration flux (ET) for the stand is calculated by comparing PET to the multi-layer model estimate for soil moisture content. The soil profile is treated as a series of three layers: M_1 *the is surface organic layer,* M_2 *is surface layer rooting zone, and* M_3 *is the mineral subsoil (Figure 4.3). These layers can differ by ecosystem and crop cover type in terms of bulk density, moisture holding capacity, texture, and carbon-nitrogen storage. Where drainage is impeded, water can accumulate upwardly in a ponded layer (*M_0*) above the surface layer. Where drainage is unimpeded, excess water percolates through to lower layers and may eventually leave the system as run-off.*

Water balance in each of the organic and mineral soil layers is modeled as the difference between net inputs of precipitation (PPT), plus, in the case of lower soil layers, addition of volumetric percolation inputs), and outputs of ET, followed by drainage for each profile layer.

Snow melt

Snow dynamics algorithms from the Regional Hydroecological Simulation System (RHESSys) developed by Coughlan and Running (1997) have been added to the NASA-CASA model to improve predictions of snow accumulation rate, and the timing and flow rates of spring snow melt at high altitude sites. These snow algorithms were developed to improve estimates of annual forest snow hydrology for point and regional calculations of annual productivity. Model algorithms depend upon surface air temperature, solar insolation, precipitation inputs, and canopy leaf area to compute snowpack water equivalent, snow thermal content, *albedo, and albation from snow melt and sublimation fluxes. Snow accumulation rates are dependent on estimated night time air temperatures. A heat summation function is used for estimation of snow thermal content to determine when the snowpack is isothermal. The RHESSys snow model has been successfully tested at ten snow telemetry (SNOTEL) stations in the western United States (Coughlan and Running, 1997). Comparisons of simulation results to published snow depletion dates have shown that the snow model accurately predicts the relative ranking and magnitude of depletion for different combinations of land cover, elevation, and aspect.*

Ammonia Emission Controllers

In the NASA-CASA component for N trace gas emission, processes of ammonification and nitrification are lumped into combined mineralization fluxes from litter, microbial and soil organic matter pools to a common mineral N pool. This design is intended to make the model general enough to be driven by organic matter inputs derived from remote sensing observations.

The general conditions that potentially favor soil NH_3 emissions from soils and chemical fertilizers, which have been documented to a limited degree, are represented in the NASA-CASA formulation. Our generic NH_3 emission algorithm is built as a function of fertilizer type (FT) and application method (AP) of the applied nitrogen concentration (N_a; g N m^{-2}). In croplands, a correction is made to soil N pool inputs by removing harvested biomass sources from the computation of N available for possible NH_3 emission loss. In this analysis of native soil emissions and land cover types, the FT and AP terms can be ignored, and N_a is estimated as the monthly mineralization rate of soil nitrogen, presumably first into ammonium forms.

The available mineral N substrate for NH_3 emissions is potentially modified by scalars (multipliers ranging from 0-1) for soil surface temperature (T_s ^oC), pH-dependent response (Figure 4.5) and a constant term (*c*), and soil moisture content (M_s). Equation 2 is derived from reports by Denmead et al. (1982) and the National Research Council *Subcommittee on Ammonia* (1979).

$$A = N_{a(FT,\ AP)}\ k_A\ \{1/[1 + 10^{(0.09018\ +\ 2729.92/(273.16+T_s)\ -\ \mathrm{pH}\ c\ )}]\}\ (1-M_s) \qquad (2)$$

The NH_3 emissions Equation 2 includes a scalar term for a maximum rate of volatilization (k_A), which was set at value of 0.25 (Van der Weerden and Jarvis. 1997; Ryden and McNeill 1984), pending the availability of more specific measurements from California native soils.

Soil pH effects

As a first approximation, high NH_3 volatilization can be strongly affected by relatively high soil pH (7-9) levels, as represented in Figure 4.5. However, under special circumstances observed (so far) mainly in cropped areas, volatilization losses can occur from acid as well as from alkaline soils. This is due to elevated pH and NH_4^+ concentrations at wet "microsites" where, for instance, surface-applied urea ($CO[NH_2]_2$) particles may dissolve and hydrolyze (Fenn and Richards, 1986). Microsite formation of ammonium carbonate (NH_4^+ HCO_3^-) by the soil microbial enzyme urease can promote high NH_3 volatilization losses, well after urea is incorporated into the soil organic matter. Therefore, in the absence of more definitive observational information on the magnitude of soil pH in controlling NH_3 volatilization fluxes from native soils in California, we have estimated statewide NH_3 emissions both with a moderate pH effect (version A; $c = 1.3$; Figure 4.5) and with minimal pH effect (version B; $c = 10$). The value of $c = 1.3$ in Equation 2 for version A is fairly consistent with soil pH effects observed in our recent field measurements of NH_3 volatilization losses from fertilized agricultural soils in California's Central Valley (Chapter 2), whereby the most rapid increases in NH_3 volatilization losses were detected between soil pH levels of 7 and 8. This modeling approach will result in a fairly wide range of potential NH_3 volatilization rates, which can nonetheless begin to put rational boundaries on the native soil source of NH_3 emissions for the state. Verification of the actual form of the soil pH effect represented in Figure 4.5 will depend on analysis of new measurements of NH_3 volatilization rates under carefully selected field conditions that are designed to control for native soil pH effects on gas emission fluxes.

Moisture effects

Soil wetting patterns can strongly influence NH_3 losses. Generally, moist soils emit less NH_3 than drier soils, owing to lower gas diffusivity in wetter soils. To account for an effect of limited diffusion of NH_3 gas through relatively moist soil layers in our model, a scalar term (M_s) is defined below as a function of percent volumetric soil moisture content (Θ; m m^{-1}) and its soil texture-dependence. In this context, the M_S scalar is intended to represent the damping influence of elevated soil moisture conditions on NH_3 gas movement through the soil.

$$M_s = (1 + a) / (1 + a\,\Theta^{b}) \qquad (3)$$

where a and b are soil texture-dependent empirical coefficients (defined as in Saxton et al., 1986). According to this equation, heavy clay soils will retain moisture longer than sandy soils, thereby reducing emissions of NH_3 in clays under any given conditions of water supply.

It is worth mentioning, however, that under certain nitrogen application conditions, even moist soils have been shown to emit high amounts of applied fertilizer NH_3 than drier soils (Denmead et al., 1978; McInnes et al., 1986; Burch and Fox, 1989; Al-Kanani, 1991). As already cited, hydrolysis of urea is promoted under conditions of elevated soil moisture, which can then enhance evaporation losses as NH_3 and CO_2. Volatilization rates are typically diminished when, for example, urea can be transported rapidly to deeper soil layers following heavy irrigation (Fenn and Miyamoto, 1981). Field studies suggest that merely delaying urea application for a few hours after irrigation to avoid accumulation at wet soil surfaces may be a practical way to reduce NH_3 volatilization in humid areas (Priebe and Blackmer, 1989). High temperatures and strong winds may interact with humidity and soil moisture to promote higher volatilization losses. However, in the winter, natural snow cover and cold temperatures can decrease airborne soil dust and possibly the evolution of NH_3 from soils (Munger, 1982).

Statewide Ammonia Emission Estimates from Native Soils

Based on our NASA-CASA model inventory estimate, statewide emissions of NH_3 from native soil N sources could range from 12 to 57 x 10^6 kg N-NH_3 annually (Table 4.2). The low end of this range is computed with Equation 2 version A, using the moderate pH effect on soil emissions of NH_3 (Figure 4.5), while the high end estimate is derived from the model version B operating with minimal soil pH effect . Using version A for Equation 2, the model predicts that cropland and semi-agricultural soils generate 60% of the statewide NH_3 emission total (Figure 4.6), whereas version B predicts that these same areas generate 33% of statewide

NH_3 emissions from soils (Figure 4.7). This difference derives from the pattern of relatively large coverage by high pH soils (6.5-8) in the large agricultural counties like Fresno, Kern, Kings, and Imperial, which in version A elevates the importance of predicted NH_3 emissions in croplands, while severely depressing emissions in areas of evergreen needleleaf forest and other woodlands with relatively lower soil pH.

The majority of model results reported subsequently in this study will be based upon the high end estimate from version B, which would appear to be a more conservative approach (particularly in a state with such large cropland areas), and is justified until the time when enough flux measurements are collected to determine the actual magnitude of soil pH effects on NH_3 emissions. As indicated above, the single most important land cover type in terms of contributions to the statewide emission inventory for emissions of NH_3 is evergreen needleleaf forest (36%), followed by cropland and semi-agricultural lands (Figure 4.7). Croplands make up one-third of the total native soil N sources for NH_3 emissions annually. This results from the high nitrogen levels in the soils of these cropland areas that are periodically fertilized for production purposes. Nitrogen that remains in the surface soils and dead root systems each year can mineralize, and potentially on the alkaline soil areas (Figure 4.2), volatilize under optimal conditions of moisture and temperature to generate notable emissions of NH_3 gas.

Other native areas that contribute substantially (22%) to the statewide emission inventory for emissions of NH_3 are soils of woodlands, and wooded grassland ecosystems (Figure 4.7), mainly on the basis of their large area coverage of the state's natural areas. The combination of productive vegetation communities growing on even slightly alkaline soils (pH > 5.5) results in the largest annual emissions of NH_3 from native soil N sources outside the cropland and semi-agricultural land areas.

On the basis of Equation 2 version B estimates of NH_3 emissions from native soil sources, there appear to be several areas in the state with notably high annual NH_3 fluxes (> 0.4 g N m^{-2} yr^{-1}). Within the major valley cropland areas of the state, these include locations in the general vicinity of the geographic coordinates and cities listed in Table 4.3. The model also predicts that there are several areas of high annual NH_3 fluxes that are classified with a land cover of evergreen needleleaf forest, wooded grassland, or annual grassland (Figure 4.1). All of these locations listed in Table 4.3 are associated with relatively high soil pH input values of 6 or greater.

Model estimates of NH_3 emissions from native soil sources are listed by county in Table 4.4. Our model estimates suggest that Mendocino, San Luis Obispo, and Shasta counties, in addition to San Joaquin Valley counties like Fresno and Kern, are among the largest contributors of soil NH_3 fluxes as single-county fractions of the statewide total (in 10^6 kg yr^{-1}), but this mainly due to extensive area coverage, including 40-50% cropland soils in Fresno and Kern counties. On a per m^2 basis, Sacramento Valley counties, including Yuba and Yolo, as well as Lake, Santa Barbara, and Sonoma counties are estimated to emit among the highest annual flux rates (g N m^{-2} yr^{-1}) of NH_3 from native soil sources in the state. This mainly due to the comparatively productive soils of these county areas (Figure 4.4) and the high predicted rates of mineral nitrogen cycling on an annual basis.

When viewed in more detail for several selected areas in the state (i.e., those with notably high annual fluxes; Table 4.3), seasonal flux patterns for NH_3 emissions from native soils appear to be influenced in the model by a combination of surface air temperature and moisture patterns (Figure 4.8). Throughout the state, air temperature and precipitation patterns show a reverse seasonal relationship: rainfall is highest from November to March, whereas surface temperatures reach a maximum in July or

August. In response, the NASA-CASA model generally predicts that spring (March-May) is the season with the lowest predicted NH_3 emissions, since native soils are predicted to remain relatively cool and moist until the summer months. Peak estimated emissions of soil NH_3 come in mid-summer to early fall (July – October), when native soils are predicted to become relatively warm and dry. A pulse of mineralized nitrogen for NH_3 volatilization is frequently added to the soil in October when foliage is shed from vegetation and this organic matter begins to decompose with wetting from early season rainfall.

These predicted seasonal patterns for NH_3 soil emissions for contiguous 8-km zones covering the entire state are shown in Figure 4.9. The model predicts that October is the peak month overall for NH_3 emissions from native soils in California. When totaled for the entire region, native soil sources of NH_3 predicted for Central Valley counties are consistently high from July through January. Zones of consistently high seasonal emissions (July to January) are predicted in the Sacramento Valley between 40^o N and 38^o 15’ N, in the San Joaquin and Salinas Valleys between 37^o 30’ N and 36^o 15’ N, and in the Central Coast Valleys between 36^o N and 35^o N latitude. This seasonal pattern in predicted soil NH_3 emission is fairly consistent with observed seasonality in $PM_{2.5}$ levels for the San Joaquin Valley Air Basin.

Table 4.1. Foliar nitrogen concentration setting in the CASA Model for vegetation types in California (Source: Potter, 1999).

Vegetation	Description	Leaf C:N	N Content
Class			(% dry weight)
2	Evergreen Needleleaf Forest	100	0.50
5	Mixed Forest	75	0.67
6	Woodlands/Wooded Grasslands	70	0.71
7	Grassland	55	0.91
8	Bare Soil	30	1.67
10	Cropland	30	1.67
11	Deciduous Broadleaf Forest	65	0.77
13	Open Shrubland	35	1.43

Table 4.2. Estimated emissions of N-NH_3 from native soils in California using the NASA-CASA model (Equation 2).

		Version A	Version B		
Vegetation	Description	NH_3-N Emission	NH_3-N Emission	Area total	Area total
Class		10^6 kg yr^{-1}	10^6 kg yr^{-1}	(ha)	(percent)
2	Evergreen Needleleaf Forest	0.81	20.26	12,435,200	31
5	Mixed Forest	0.02	0.54	262,400	1
6	Woodlands/Wooded Grasslands	1.64	12.78	6,656,000	17
7	Grassland	0.92	2.66	1,952,000	5
8	Bare Soil	0.07	0.07	710,400	2
10	Cropland/Semi-Agriculture	7.25	18.64	8,505,600	21
11	Deciduous Broadleaf Forest	0.03	0.12	96,000	0
13	Open Shrubland and Desert	1.32	1.96	9,491,200	24
	Total Non-Cropland	**4.81**	**38.39**	**31,603,200**	**79**
	Total Cropland	**7.25**	**18.64**	**8,505,600**	**21**
	GrandTotal	**12.07**	**57.03**	**40,108,800**	**100**

Note: Cropland includes semi-agricultural lands, such as residential lawns, golf courses, parks, and marginal/fallow lands, together with the actively cultivated areas.

Table 4.3. Locations of elevated NH_3 emissions from native soils in California, predicted by the NASA-CASA model (Equation 2 version B).

Vegetation	Deg N	Min	Deg W	Min	Nearest Place Name	County
10	40	2	122	15	Tehama	Tehama
10	39	47	122	4	Orland	Glenn
10	38	59	121	18	Applegate	Placer
10	38	20	122	55	Occidental	Sonoma
10	38	25	121	54	Vacaville	Solano
10	38	17	121	5	Camanche	San Joaquin
10	37	29	121	2	Turlock	Stanislaus
10	37	19	120	2	Mariposa	Mariposa
10	36	11	119	5	Lindsay	Tulare
10	34	50	120	21	SantaMaria	Santa Barbara
10	34	17	119	3	SantaPaula	Ventura
10	33	20	117	24	Fallbrook	San Diego
10	32	51	115	23	BrawleyEast	Imperial
2	40	59	121	59	Wynton	Shasta
2	39	26	123	1	LakePillsbury	Lake
6	35	43	118	47	Delano	Kern
6	34	49	120	5	Cuyama	Santa Barbara
6	34	41	120	19	LosAlamos	Santa Barbara
6	34	28	119	11	Topatopa	Ventura

Key to Land Cover Classes

2	Evergreen Needleleaf Forest
5	Mixed Forest
6	Woodlands/Wooded Grasslands
7	Grassland
8	Bare Soil
10	Cropland
11	Deciduous Broadleaf Forest
13	Open Shrubland

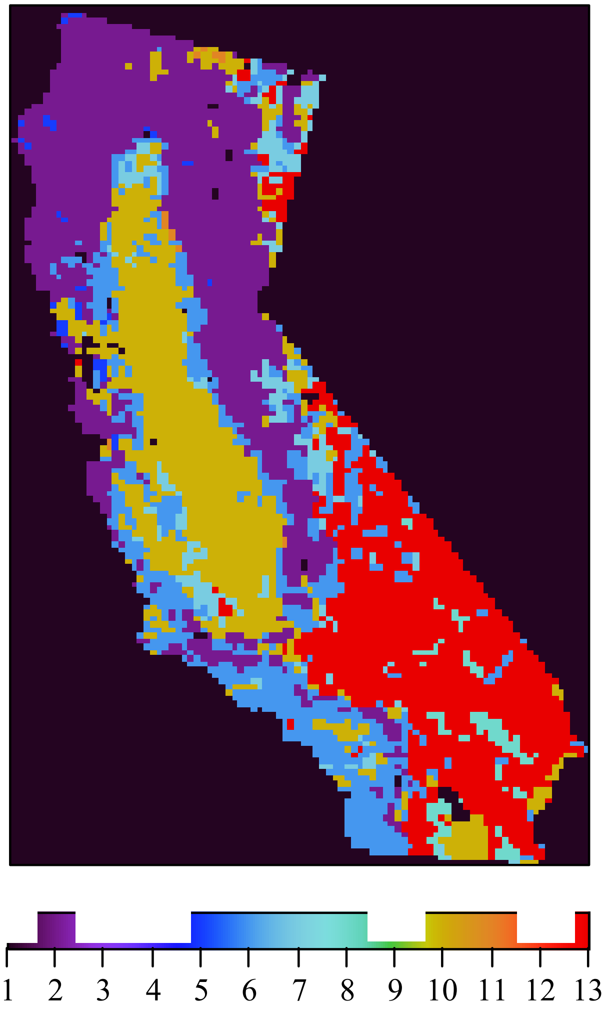
Table 4.4. Estimated emissions of N-NH_3 from native soils for counties of California using the NASA-CASA model (Equation 2 version B).

County		NH_3-N Emission			
		Total	Average area	Average pH	Percent Cropland
Number	Name	10^6 kg yr^{-1}	g m^{-2} yr^{-1}		
1	Alameda	0.20	0.11	5.97	36
3	Alpine	0.14	0.07	6.04	0
5	Amador	0.42	0.28	5.97	13
7	Butte	1.02	0.23	6.36	28
9	Calaveras	0.87	0.29	5.93	2
11	Colusa	0.67	0.22	6.98	58
13	Contra Costa	0.38	0.18	6.24	58
15	Del Norte	0.55	0.21	5.76	0
17	El Dorado	1.21	0.27	5.69	1
19	Fresno	2.12	0.14	6.83	48
21	Glenn	0.78	0.23	6.41	65
23	Humboldt	1.37	0.14	5.50	0
25	Imperial	1.44	0.12	7.49	28
27	Inyo	0.38	0.01	7.79	1
29	Kern	2.20	0.10	7.43	39
31	Kings	0.72	0.20	7.87	91
33	Lake	1.10	0.32	5.84	0
35	Lassen	1.25	0.10	6.69	8
37	Los Angeles	1.40	0.14	6.58	8
39	Madera	0.83	0.16	6.39	51
41	Marin	0.31	0.22	5.25	27
43	Mariposa	0.99	0.25	6.01	21
45	Mendocino	2.53	0.28	5.79	0
47	Merced	1.20	0.24	7.18	97
49	Modoc	1.34	0.13	6.48	16
51	Mono	0.40	0.05	6.48	24
53	Monterey	1.50	0.18	6.65	38
55	Napa	0.51	0.26	6.00	10
57	Nevada	0.63	0.26	6.06	3
59	Orange	0.47	0.21	6.03	0
61	Placer	0.94	0.24	5.63	20
63	Plumas	0.85	0.12	6.03	3
65	Riverside	1.18	0.06	7.36	12
67	Sacramento	0.89	0.33	6.37	98
69	San Benito	0.57	0.16	6.90	47
71	San Bernardino	1.06	0.02	7.84	3
73	San Diego	1.11	0.10	6.49	5
75	San Francisco	0.01	0.06	5.95	50
77	San Joaquin	0.80	0.23	6.72	96
79	San Luis Obispo	2.25	0.26	6.97	28
81	San Mateo	0.15	0.13	5.19	11
83	Santa Barbara	1.99	0.30	6.00	17
85	Santa Clara	0.35	0.10	6.48	17
87	Santa Cruz	0.14	0.13	6.09	0
89	Shasta	2.50	0.25	6.05	8

93	Siskiyou	1.77	0.11	6.19	11
95	Solano	0.56	0.24	6.23	86
97	Sonoma	1.21	0.30	5.93	25
99	Stanislaus	0.91	0.22	6.85	89
101	Sutter	0.34	0.23	7.00	96
103	Tehama	1.72	0.22	6.22	25
105	Trinity	1.18	0.14	6.06	0
107	Tulare	1.63	0.13	6.44	35
109	Tuolumne	0.79	0.14	5.99	3
111	Ventura	1.17	0.24	6.92	8
113	Yolo	0.79	0.29	6.76	83
115	Yuba	0.65	0.39	6.21	31

Figure 4.1. Satellite-based map of major land cover classes in California map at 8-km grid cell resolution.

Key to Land Cover Classes



2	Evergreen Needleleaf Forest
5	Mixed Forest
6	Woodlands/Wooded Grasslands
7	Grassland
8	Bare Soil
10	Cropland
11	Deciduous Broadleaf Forest
13	Open Shrubland

Figure 4.2. STATSGO map of soil pH in California at 8-km grid cell resolution

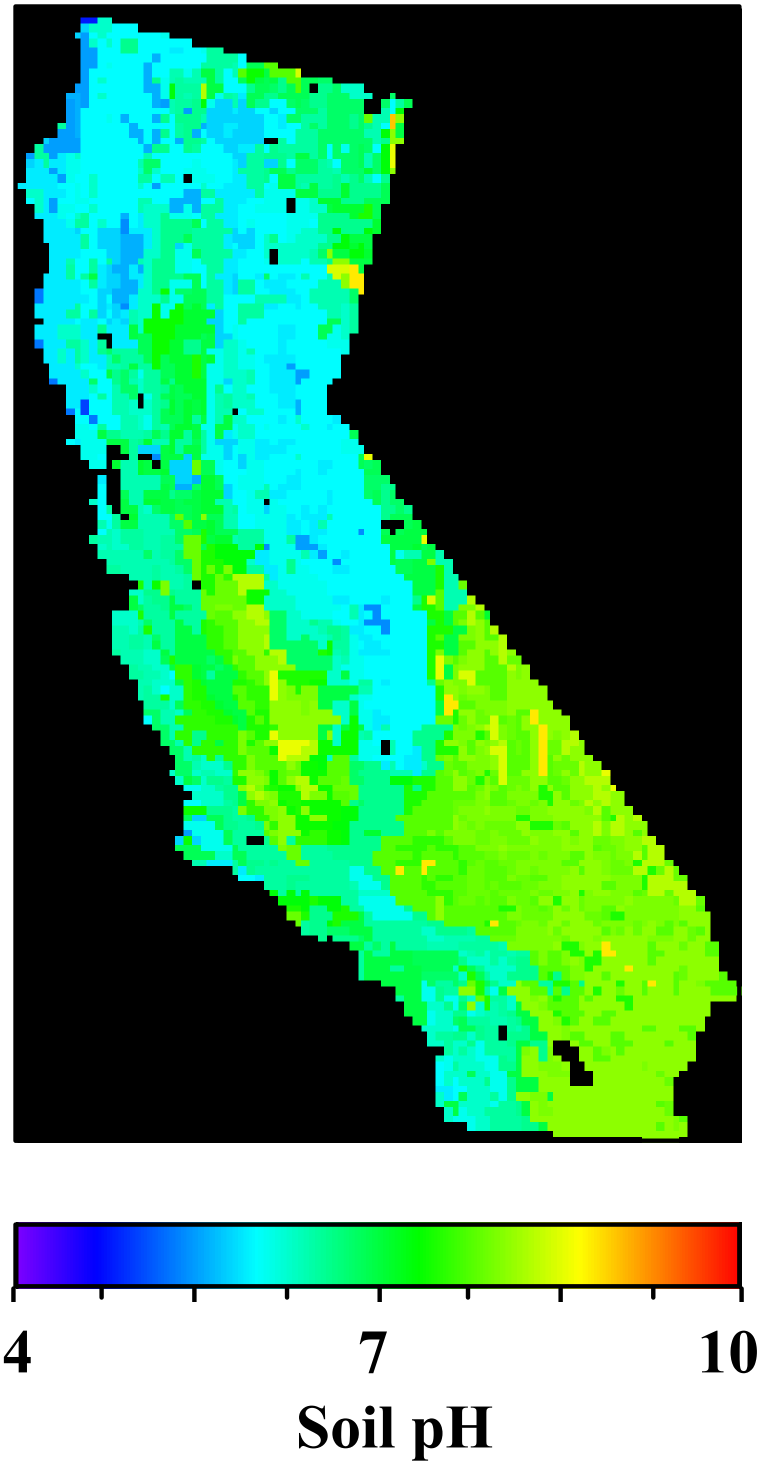


Figure 4.3. NASA-CASA model framework for predicting ammonia emissions from soils.

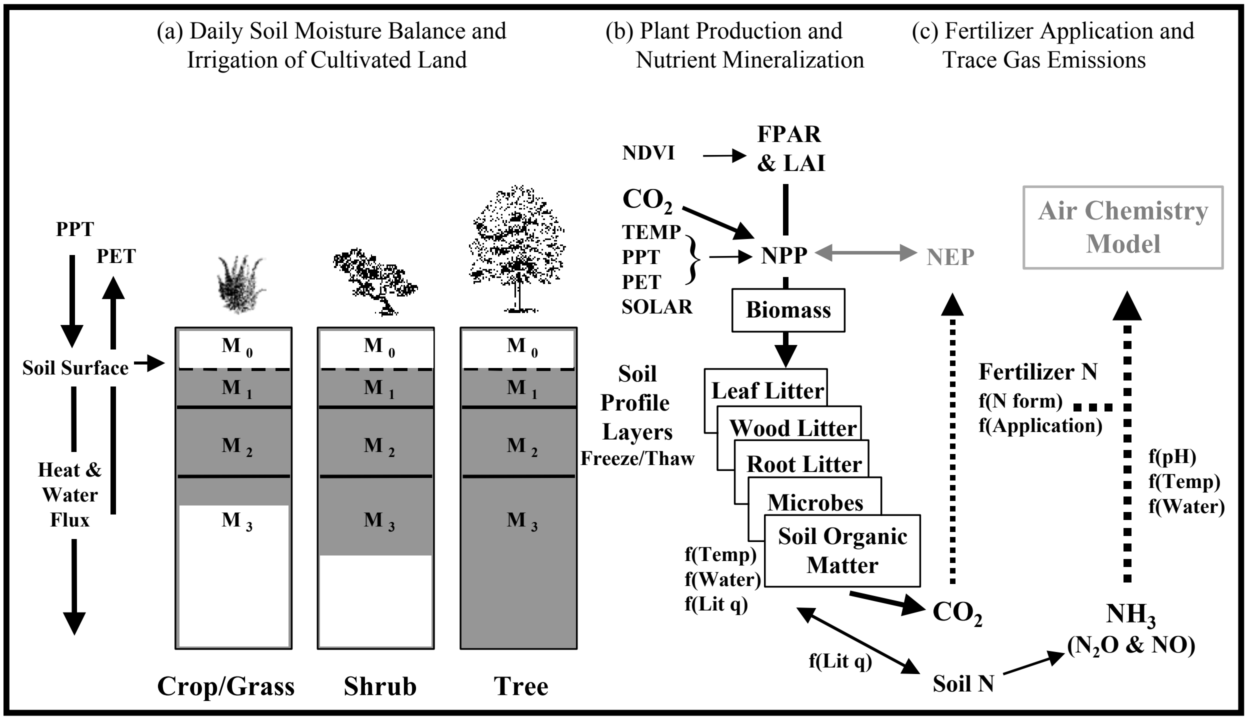


Figure 4.4. Statewide NASA-CASA estimates of annual net primary production (NPP) and soil nitrogen mineralization at 8-km grid cell resolution.

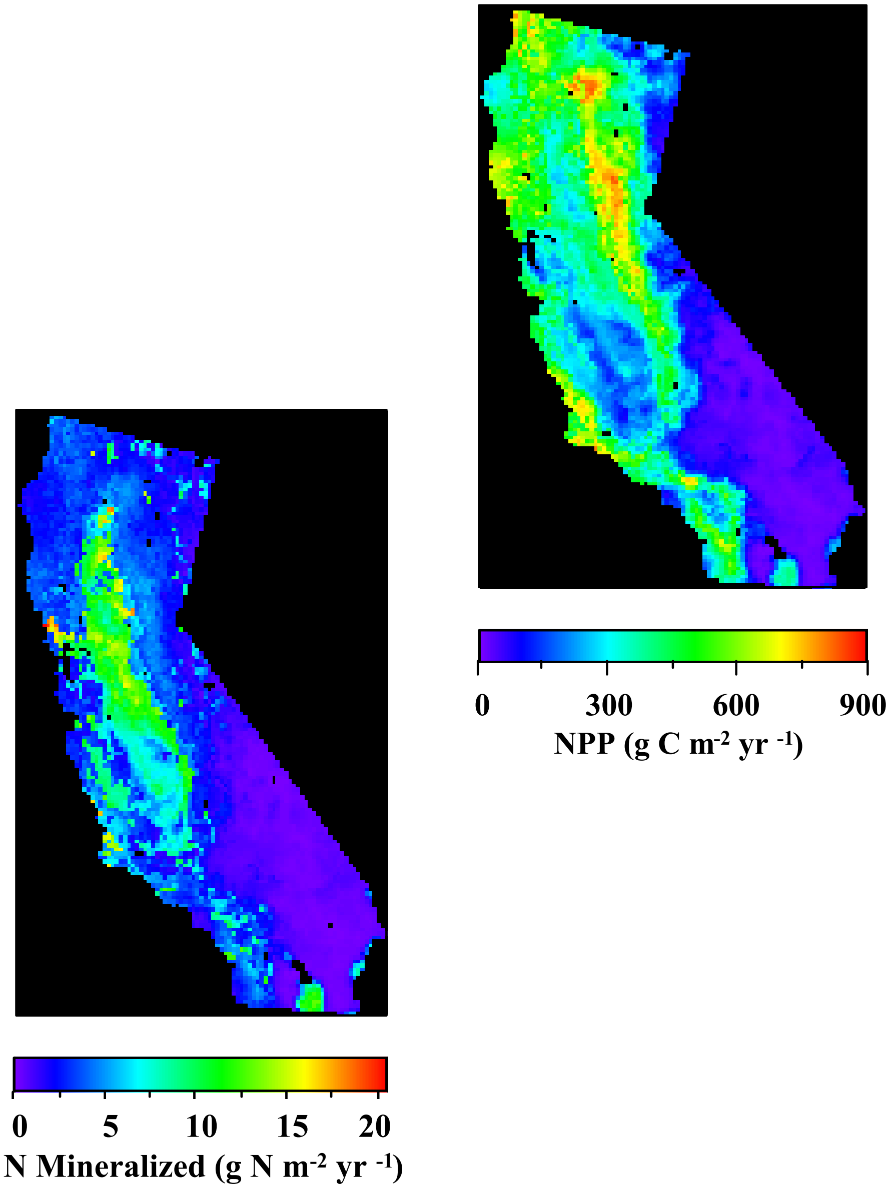


Figure 4.5. Temperature-dependent scalar for the potential effect of soil pH on volatilization of ammonia. Constant value (*c*) in Equation 2 equal to 1.3. Dotted line (30° C), Dashed line (20° C), Solid line (10° C). After Denmead et al. (1982).

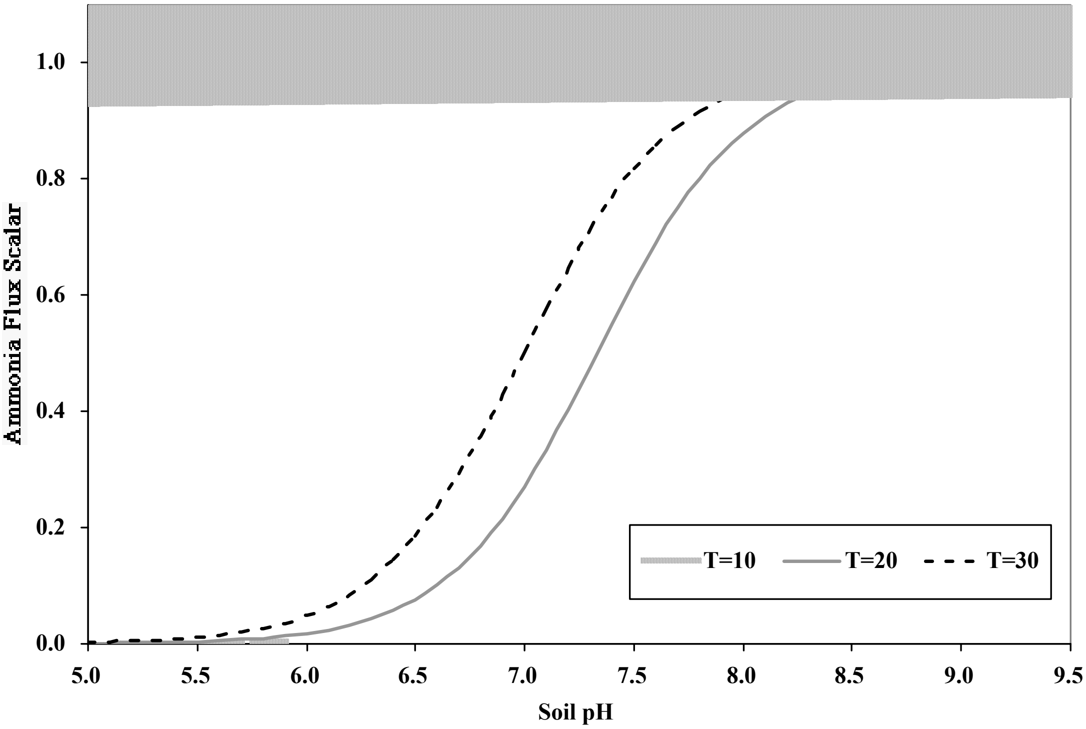
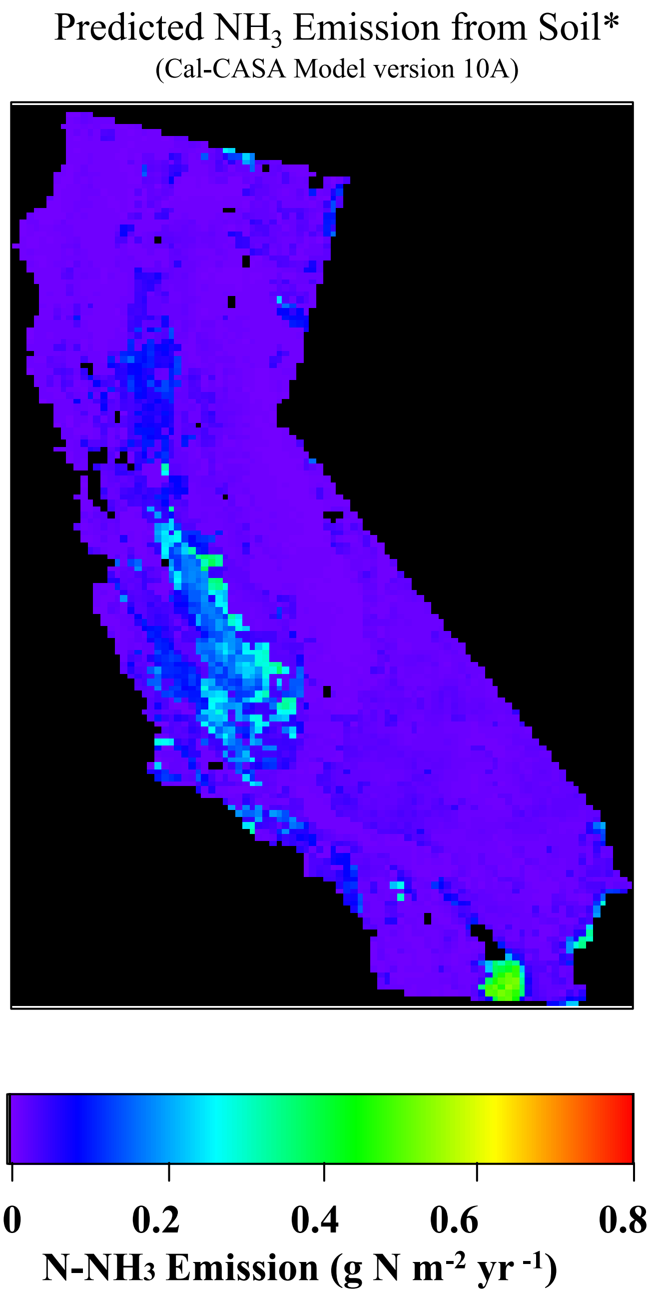
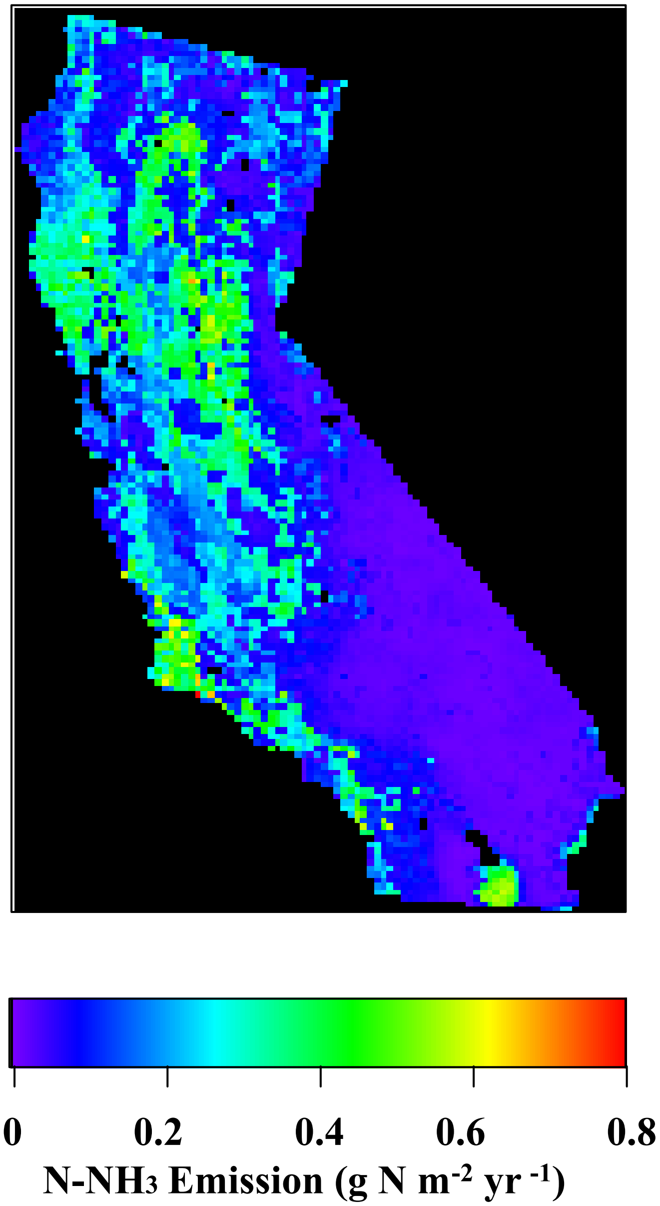


Figure 4.6. NASA-CASA model results (Equation 2; Version A) for statewide ammonia emissions from native soils.



*** Native soils, no direct emissions from fertilizer amendments**
(Moderate soil pH effect)

Figure 4.7. NASA-CASA model results (Equation 2; Version B) for statewide ammonia emissions from native soils.

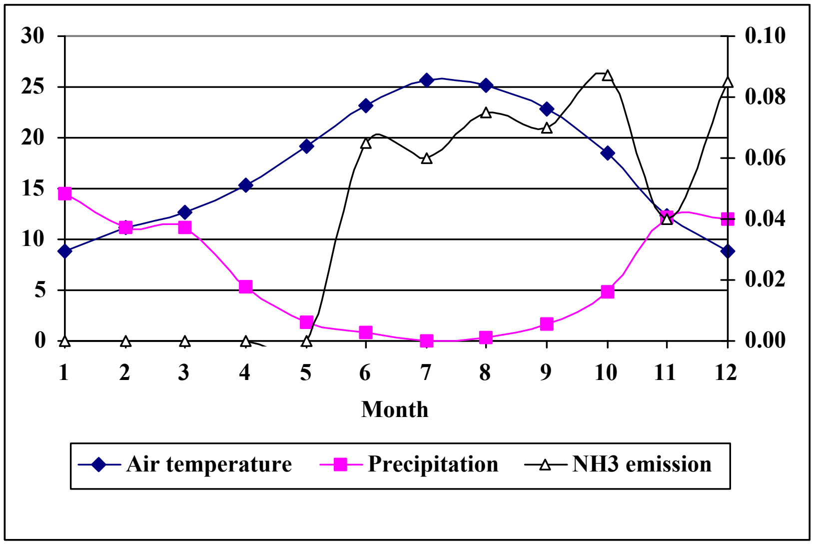


Predicted NH_3 Emission from Soil*

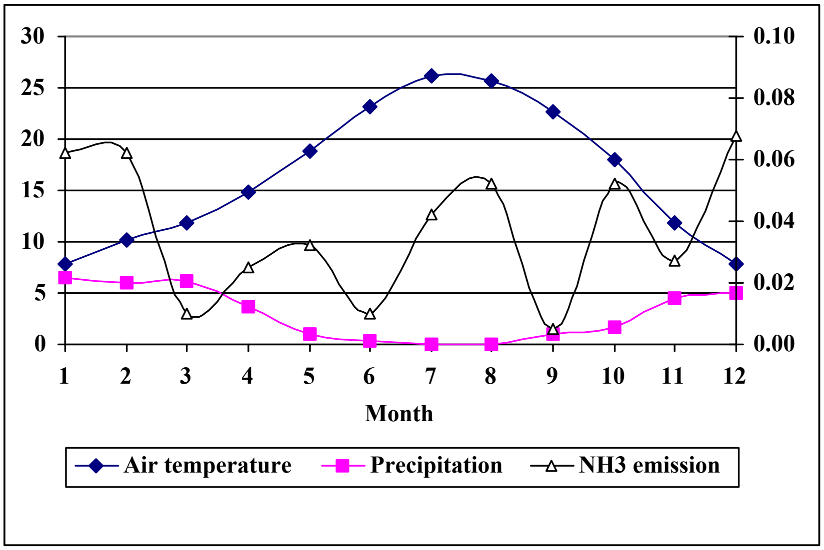
(Cal-CASA Model version 10B)

*** Native soils, no direct emissions from fertilizer amendments**
(Minumal soil pH effect)

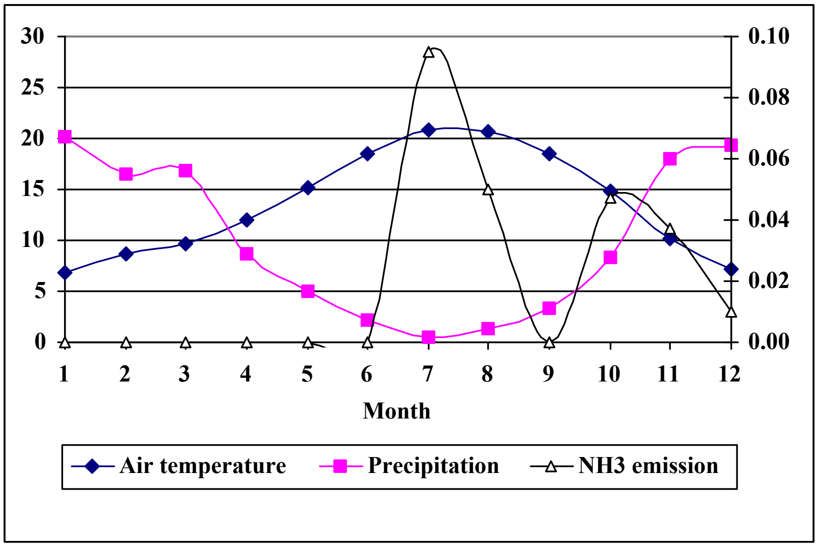
Figure 4.8. NASA-CASA model results (Equation 2 version B) for seasonal NH_3 emission rates (g N m^{-2} mo^{-1}) from native soil sources at four selected locations from Table 4.3. Cropland soils: a. Orland, Glenn County, b. Lindsay, Tulare County; Coniferous forest soil: c. Wynton, Shasta County; Wooded grassland soil: Cuyama, Santa Barbara County. Temperatures in degrees Celsius, precipitation in cm per month.



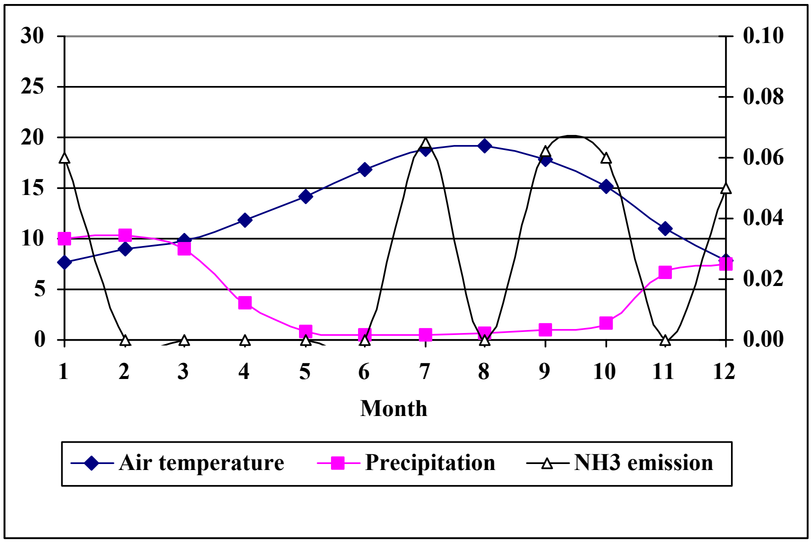
a. Orland cropland soil



b. Lindsay cropland soil

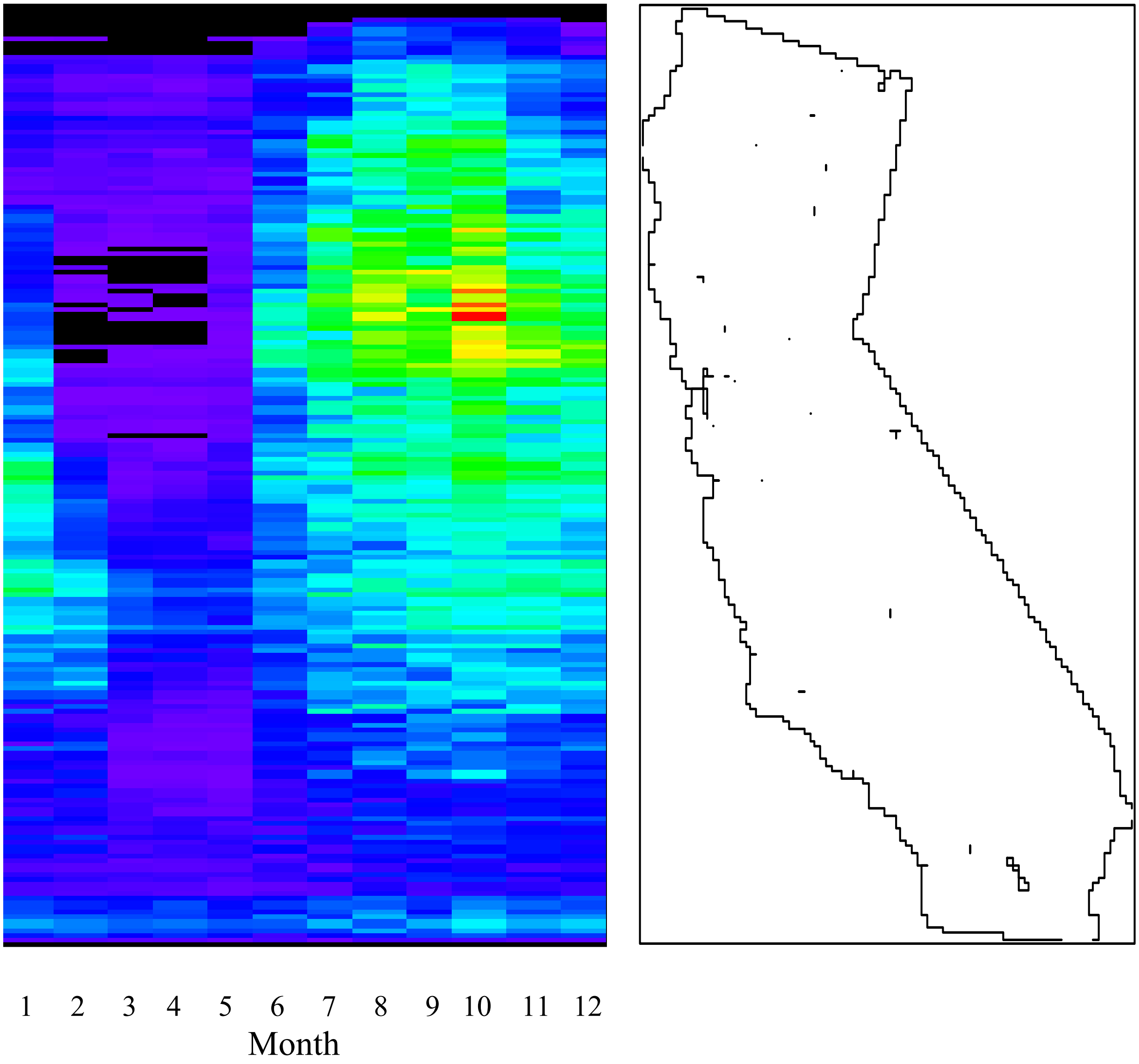


c. Wynton coniferous forest soil



d. Cuyama wooded grassland soil

Figure 4.9. NASA-CASA model results (Equation 2 version B) for total seasonal NH_3 emission rates from native soil sources. Emission fluxes are summed across 8-km latitude zones for each month.



<u>*Key to flux levels:*</u>

CHAPTER 5.

CONCLUSIONS AND RECOMMENDATIONS

Primary Investigators: Christopher Potter (NASA Ames), Charles Krauter (CSUF), Steven Klooster (CSUMB)

Major Conclusions

The mass balance micrometeorological field sampling methodology used for the project successfully detected and quantified volatile NH_3 emissions resulting from a fertilizer application under typical Central Valley farming practices.

Emission flux totals of NH_3 for fertilized sites in the Central Valley show a high level of consistency of emissions factor estimates, regardless of the crop types and fertilizer amounts.

Total measured NH_3 losses for the fertilizer application tests performed ranged from less than 0.1 to 0.7 g N-NH_3 m^{-2} (equal to 0.9 to 6.2 lbs. N-NH_3 emitted per acre). The estimated NH_3 emission factor values for the sites analyzed to date range from 0.05% to 6% of total applied N fertilizer with an average at about 3.6% of applied nitrogen.

Field flux measurements imply that the single most important factor affecting the NH_3 emission rates from cropped sources in the Central Valley is the amount of chemical fertilizer applied per day. Field flux measurements suggest that other significant limiting factors of NH_3 emission rates from chemical fertilizer sources include soil pH and the method of N fertilizer application.

When the fertilizer ammonia emission factors developed through this research are used to calculate statewide ammonia emissions for fertilizer application, the average fertilizer NH_3 emission factor for California is 2.4% of the total applied N fertilizer. Emission factor estimates of higher than 2.5% of applied fertilizer were estimated for the counties of Imperial, Merced, Kern, Kings, and Sutter, chiefly because of the low proportion (< 30%) of soils with pH below 7.

Statewide emissions of NH_3 directly from chemical fertilizer applications are computed to total nearly 12 x 10^6 kg N- NH_3 annually. The leading counties for annual emissions of NH_3 directly from chemical fertilizer sources are shown to be Fresno, Imperial, Kern, Kings, and Tulare. The San Joaquin Valley area accounts for just over one-half of the state's total annual emissions of NH_3 directly from chemical fertilizer sources.

On the basis of DWR crop types, it appears that the generalized categories of field crops and truck crops each account for about one-third of the state's total annual emissions of NH_3 directly from chemical fertilizer sources. Grain, pasture grass, and rice crop categories also contribute large fractions of the state's total annual emissions of NH_3 directly from chemical fertilizer sources.

Statewide emissions of NH_3 from native soil N sources could range from 12-57 x 10^6 kg N- NH_3 annually, depending on the importance of soil pH on emission rates. The most important land cover type in terms of contributions to this statewide emission inventory is cropland and semi-agricultural lands, which make up one-third to one-half of the total native soil N sources for NH_3 emissions annually.

The model predicts that October is the peak month overall for NH_3 emissions from native soils in California. When totaled for the entire region, native soil sources of NH_3 predicted for Central Valley counties are highest from July through January. This seasonal pattern in predicted soil NH_3 emission is fairly consistent with observed seasonality in $PM_{2.5}$ levels for the San Joaquin Valley Air Basin.

Other native soil areas that contribute substantially to the statewide emission inventory for emissions of NH_3 are the evergreen needleleaf forests, woodland, and wooded grassland ecosystems, mainly on the basis of their large area coverage of the state's natural areas.

The combination of productive vegetation communities growing on (even slightly) alkaline soils results in the largest annual emissions of NH_3 from native soil N sources.

This work has significantly advanced the state of the science for ammonia emission inventories. The spatial extrapolation approach and the predictive modeling presented are extensible and flexible enough to allow inclusion of new data of all types as they becomes available. Nevertheless, this report marks the first instance in which ARB is able to spatially allocate NH_3 emissions statewide at the DWR crop-farm level (for fertilizers) and by vegetation classes (for native soils).

Recommendations for Future Emission Inventory Development

Additional sampling of NH_3 emissions in cropped systems should be carried out with experimental manipulations on the primary emission regulators (method of fertilizer application and soil pH) to determine the importance of soil texture, temperature, and moisture management on NH_3 emission factors.

A statewide sampling strategy for emissions of NH_3 from native soils should be developed (guided by the NASA-CASA model results to date) using a number of different NH_3 emission measurement methods, including towers and small soil chambers.

Areas of prime interest for further sampling the emission rates of NH_3 from native soil sources would be located on relatively high pH soils with productive growth of grasses and/or deciduous tree species.

Several important upgrades could now be made in the current NASA-CASA GIS-based modeling approach for the native soils sources of NH_3, including:

(1) modify the GIS-based modeling approach to a 1-km (AVHRR satellite) spatial resolution for the entire state,
(2) use more detailed vegetation class maps as model input parameters,
(3) complete an extensive California-specific literature search of plant litter and soil N inputs to the total ecosystem N mineralization cycle,
(4) add canopy NH_3 uptake algorithms, which could begin to address the processes of foliar (re)absorption of locally emitted (soil) NH_3.

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Appendix A

Summary of Electronic Data Products Provided

- DWR California Crop Map – Consolidated statewide map of DWR county crop polygons assembled with coverages spanning the years 1993 to 1998.

- GIS-based Ammonia Emissions from Fertilizer Applications and Native Soils of California – Program scripted using ESRI ArcView® software to (re)compute and visualize ammonia emission inventory results in this report. Includes database tables and selected state maps for nitrogen fertilizer application rates, fertilizer application scheduling, fertilizer NH_3 emission factors, monthly climate (precipitation and air temperature), soil water index, soil surface temperature, soil pH, and nitrogen mineralization rates.

  Note: This tool was not required as part of the original contract with ARB, but was provided to ARB staff and others to offer the capability to more fully examine, analyze, and utilize the results provided in this report for future emission estimates and linkages to atmospheric models.

- Spreadsheet files that provide complete documentation of measurement data sets collected at field sites, and the resulting NH_3 emission calculations for each site.

Appendix B

Table of Conversion Factors for Metric to English Units

Length
1 mile = 1.609 kilometers; 1 kilometer = 0.621 miles
1 yard = 0.914 meters; 1 meter = 1.094 yards
1 inch = 2.54 centimeters; 1 centimeter = 0.394 inches

Area
1 square mile = 2.59 square kilometers; 1 square kilometer = 0.386 square miles
1 acre = 0.00405 square kilometers; 1 square kilometer = 247.1 acres
1 acre = 0.405 hectares; 1 hectare = 2.471 acres

Volume
1 acre-inch = 102.8 cubic meters; 1 cubic meter = 0.00973 acre-inches
1 quart = 0.946 liters; 1 liter = 1.057 quarts
1 bushel = 0.352 hectoliters; 1 hectoliter = 2.838 bushels

Weight
1 pound = 0.454 kilograms; 1 kilogram = 2.205 pounds
1 pound = 0.00454 quintals; 1 quintal = 220.5 pounds
1 ton = 0.9072 metric tons; 1 metric ton = 1.102 tons

Yield or rate
1 pound/acre = 1.121 kilograms/hectare; 1 kilogram/hectare = 0.892 pounds/acre
1 ton/acre = 2.242 tons/hectare; 1 ton/hectare = 0.446 tons/acre
1 bushel/acre = 1.121 quintals/hectare; 1 quintal/hectare = 0.892 bushels/acre
1 bushel/acre (60#) = 0.6726 quintals/hectare; 1 quintal/hectare = 1.487 bushels/acre (60#)
1 bushel/acre (56#) = 0.6278 quintals/hectare; 1 quintal/hectare = 1.597 bushels/acre (56#)

Temperature
To convert Fahrenheit (F) to Celsius (C): 0.555 x (F - 32); to convert Celsius to Fahrenheit: 1.8 x (C + 32)